CHEMISTRY

2nd EDITION

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1

An Introduction to Learning Chemistry

One of the most important objectives of this text is to help you to become an efficient learner. We therefore begin by discussing some of the practical aspects of learning chemistry. Learning is not easy; in fact, it is an interesting process. In chemistry you will learn about a fundamental law of nature that tells us that things tend to become more disordered. Learning is essentially the reverse of this tendency toward disorder. Understanding the structure of molecules, remembering how to name inorganic compounds, and learning about how atmospheric nitrogen is incorporated into our bodies are processes that bring order to many observations and much information. It takes time and hard work to accomplish this.

1.1 LEARNING LEVELS

As you proceed through the study of chemistry you will find that there are three levels of understanding that you must attain. First, you must learn the *language of chemistry*; that is, the meaning of words such as allotropes, density, and element, as well as slightly more difficult aspects of the language of chemistry, such as naming compounds, knowing the difference between a Brønsted-Lowry acid and a Lewis acid, and so on.

Second, you must learn the concepts or models that constitute the heart of chemistry; for example, the Lewis electron dot model for the explanation of bonding, or the ideal gas model that explains the behavior of gases, or the laws of thermodynamics. You will notice that we have used several words here that seem to be synonymous with concept—model and law. Actually, these are somewhat different than "concept." A **law** is a precisely enunciated description of how some aspect of nature operates. Laws are usually formulated after many observations have been made and are frequently expressed mathematically; for example, the ideal gas law is usually expressed with the equation $PV = nRT$. A **model**, on the other hand, is an attempt to explain or rationalize observations or laws. The word **concept** is a generic word that means law, model, or even, in some cases, a definition.

Finally, you must be able to understand definitions and concepts in sufficient depth to be able to apply them to a new situation. For example, after you have learned about the Lewis electron-dot model, you will know that you need to place eight electrons around each atom (except hydrogen) in a molecule that does not contain an element below the second period.* You should then be able to extend your knowledge to molecules such as

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* The word "period" refers to a horizontal row of elements on the periodic table. This table or chart is one of the best tools of the chemist because it organizes much information about the many elements and allows you to make predictions based on the relative positions of elements in the table. The table can be found in Appendix 8.

the oxalate ion, $C_2O_4^{2-}$, and write more than one acceptable electron-dot formula for this ion. You should also be able to explain what the model tells you about molecular parameters such as bond length.

1.2 LEARNING MODES

There are several ways in which people learn concepts and solve problems. Most of us use these methods all the time; we just are not aware that we are using different ways of learning.

Visualization

The ability to visualize a process or idea is invaluable, and in our opinion, it is one of the most useful tools for learning. Here is an example of how you might think about the problem of converting from cubic centimeters to cubic inches (as, for example, if someone asks you for the displacement of your automobile engine in cubic inches, but you only know it in cm^3). Suppose the problem is this—convert from 1600 cm^3 to in^3. First, you need to know how inches and centimeters are related and presumably you will remember that there are 2.54 cm in one inch. This is a fact that we remember; that is, we have memorized it, and we use a ruler often enough that we are constantly reminded that a centimeter is smaller than an inch. Thus, if we can remember the number 2.54, we should know that there are 2.54 cm per inch, not 2.54 inches per centimeter. The latter would mean that a centimeter is longer than an inch! Notice that we have already visualized part of the problem; indeed, this picture that we have of a ruler allows us to remember the relationship between an inch and a centimeter.

Next, we have to determine how many cm^3 there are in a cubic inch. For this we form the mental picture (we may even draw it as shown below) of a block that is one inch on each side. That block has a volume of 1 in^3. If we remember that each side must be 2.54 cm long, then we should be able to figure out that 1 in^3 = $(2.54\ cm)^3$. Because $(2.54)^3 = 16.4$, there are 16.4 cubic centimeters in 1 cubic inch.

$$(2.54)^3 = 16.4,$$

In the last part of the problem, we visualize a volume of 1600 cm^3, alongside of which we place a cube that has a volume of one cubic inch or 16.4 cubic centimeters (see Figure 1.1).

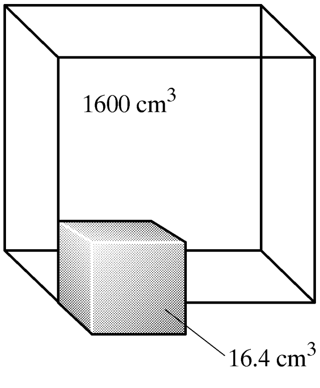


Figure 1.1 Visualizing a Problem

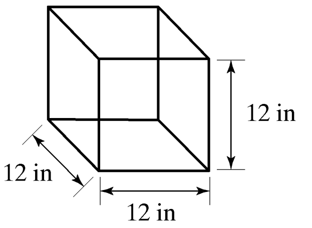
Now we can see that basically the problem is—how many of the small cubes will fit inside the big cube? The answer to this is 1600/16.4 = 97.6. Notice that when we carry out this division with the units attached, we divide cm^3 by cm^3/in^3 with a result of in^3. Thus, the answer to our problem is that there are 97.6 in^3 in 1600 cm^3.

Problem 1.1

Use exactly the same procedure to determine how many cubic feet there are in 3456 cubic inches.

Solution:

Start by visualizing a cubic foot. (See Figure 1.2)



$$1\ \text{ft}^3 = (12)^3\ \text{in}^3 = 1728\ \text{in}^3$$

Figure 1.2 Visualizing a Cubic Foot

Since a cubic foot is 12 inches on each side it must have a volume of 12 × 12 × 12 = 1728 in^3. 1728 in^3 is less than 3456 in^3 and therefore we know that there must be more than 1 ft^3 in 3456 in^3. In fact, there are

$$\frac{3456\ \text{in}^3}{1728\ \text{in}^3/\text{ft}^3} = 2.000\ \text{ft}^3$$

Reasoning by Analogy

The term "analogy" means that if two or more things are alike in some respect, then they will probably be alike in another respect. Thus, when we reason by analogy in chemistry we usually take information about a set of compounds, atoms, etc., and use it to determine something about another member of that set. In some ways the process is similar to extrapolation or interpolation, except that these terms are usually applied to quantitative procedures.

If we know that the formula of perchloric acid is $HClO_4$, then we can be pretty certain that perbromic acid is the bromine analog of perchloric acid and has the formula $HBrO_4$. This analogy is based on the fact that chlorine and bromine are in the same group* on the periodic chart and thus have something in common (their acids are isostructural;† that is, they have the same structure). We can therefore extrapolate to the structure $HBrO_4$. We could not do this with elements in different groups. For example, the fact that phosphoric acid is H_3PO_4 does not allow us to predict that chloric acid is H_3ClO_4 or, even $HClO_4$ because phosphorus and chlorine are in different groups.

Another common use of reasoning by analogy is the prediction of a property based on the way that property varies within a group. For example, if we know that the sizes of atoms increase down the group, we can safely predict that Ra (radium is the heaviest member of group II) will be the largest atom in Group II.

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* The word "group" refers to a vertical column of elements on the periodic chart. For example, the elements Li, Na, K, Rb, Cs, and Fr are all in Group IA. Elements in the same group usually have somewhat similar properties.

† The prefix "iso" means same. Isostructural compounds have the same structure; isoelectronic ions have the same number of electrons.

Problem 1.2

Group VI contains the elements oxygen, sulfur, selenium, and tellurium. H_2SO_4 is sulfuric acid. H_2SeO_4 is selenic acid. What is the name of H_2TeO_4?

Solution:

telluric acid

Memorization and Association

Memorization is essential to all areas of learning. The key element for all memorization is repetition. Of course, memorization is greatly facilitated by knowing some underlying principle. For example, if you are trying to memorize the names of the oxyacids, it is certainly helpful to know (memorize) that the root of the name comes from the name of the central element. $HClO_3$ is chloric acid, H_3PO_4 is phosphoric acid, and so on. When there is no underlying principle, it is helpful to try to find a pattern or use association. For example, the common cations that form ammonia complexes all lie near one another on the periodic chart (Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}). If you are having trouble remembering Avogadro's number, the numbers 2 and 3 may allow you to remember 6.02×10^{23}, six being 2×3. Or, you may be able to use a mnemonic, a device to help you remember. A common mnemonic for remembering the colors of the visible spectrum (red, orange, yellow, green, blue, violet) is the "name" ROY G. BV.

No matter what method you choose to use for your memorization—and remember that some things lend themselves to the use of mnemonics or association, whereas other things simply require lots of repetition—we strongly urge the use of the 3x5″ card system. If you want to memorize the common names of the simple carboxylic acids, put the structure of three or four acids and their names on one 3x5″ card. Or, you may prefer to put the formulas on one side and the names on the other side. That way you can read either the name or the formula and see if you know the other. The most important thing is to carry these cards with you and to pull them out of your pocket or backpack as often as possible. Each time repeat the material out loud, and then put the card away and see if you can remember the material. It is often helpful to use as many of your senses as possible; after you have said the material, write it out. Test yourself again after a day by drawing the structures of all of the acids and then see if you know the names (write them down). If you are 100% correct, review the material after another couple of days. If not, go through the procedure again. The more often you review the longer you will retain the information

Problem 1.3

Carboxylic acids have the generic formula RCO_2H. The simplest acids have the following common names:

Formic acid	HCO_2H
Acetic acid	CH_3CO_2H
Propionic acid	$CH_3CH_2CO_2H$
Butyric acid	$CH_3CH_2CH_2CO_2H$

Memorize these names and the structures of the acids.

Solution:

You might try a mnemonic like Form Acid Prop Buttons, meaning make buttons that you can use as props to remember the acids. Notice that the more closely the mnemonic mimics the names you are trying to remember, the easier your job will be.

Algebraic Reasoning

Some areas of chemistry use a good bit of math, including calculus, differential equations and statistics, whereas other areas use only very simple math. Most areas of chemistry require the use of algebra, and you must be able to manipulate simple equations. For example, you will need to be able to solve explicitly for V in the equation $PV = nRT$, or for x in the equation $2x = 14(2 - x)$; you will need to know how to solve a quadratic equation of the form $ax^2 + bx + c = 0$. If you find that you are uncomfortable with what appears in the sentence above, you will need to dig out your high school algebra book and do some serious reviewing.

Proportion. One of the most simple and important mathematical relationships is proportion. If the number of automobile accidents were proportional to the IQ of the driver, this would mean that: a) the higher the IQ of the driver, the greater the number of accidents, and b) that if driver A has twice the IQ of driver B, driver A will have twice as many accidents. We can symbolize this with the relationship

$$\text{accidents} \propto \text{IQ}$$

where the $\propto$ symbol is the sign for "proportional to". Notice that even though this allows us to predict how the number of accidents will be affected by a change in the IQ of the driver, it does not allow us to determine the actual number of accidents a driver with a certain IQ would have. In order to do this we need to know the proportionality constant. That is, we need to convert the proportionality into an equation. If we knew that a person with an IQ of 100 has 2 accidents per year (obviously, we are assuming that data for a single person are representative of a whole group of individuals, an assumption that in real life is rarely correct), we could write the equation

$$\text{accidents} = 0.02\ (\text{IQ})$$

The factor 0.02 is called the proportionality constant. Notice, again, that no matter what the proportionality constant, if we double the IQ the number of accidents will double. This equation allows us to calculate the number of accidents for a driver with any IQ simply by making the appropriate substitution. Someone with an IQ of 200 will have 4 accidents per year.

Problem 1.4

For most gases, the volume of the gas is proportional to the absolute temperature when the pressure of the gas is kept constant. For a 2.0-g sample of hydrogen gas maintained at a pressure of 1.0 atm, the volume is 22.4 L when the absolute temperature is 273 K. Determine the proportionality constant.

Solution:

This may be a good point at which to review the different temperature scales. Of the two commonly used in science, the Celsius or centigrade scale is a relative scale. It is based on the normal freezing and boiling temperatures of water, which are assigned values of 0 and 100, respectively. Each degree is therefore one-hundredth of this difference in temperature. Although the Fahrenheit system is not usually used in scientific measurements, it is useful to be able to convert from one scale to the other. In the Fahrenheit system the freezing and boiling points of water are 32 and 212 degrees, respectively, and the difference is therefore 180 degrees. Thus, a Celsius degree is larger than a Fahrenheit degree by a factor of 180/100 or 9/5. The relationship between the two scales can be expressed as

$$\mathrm{F} = \frac{9}{5}\mathrm{C} + 32$$

Continued on next page

Problem 1.4 *Continued*

Solution: *Continued*

The other temperature scale of common use in science, the Kelvin scale, is an absolute system. The lowest temperature attainable is assigned a value of 0 and the size of the unit on the Kelvin scale is the same as that of the Celsius scale. The freezing point of water is 273 on the Kelvin scale. Thus,

$$\mathrm{K} = \mathrm{C} + 273$$

Because the volume is directly proportional to the absolute temperature we can write

$$V = kT$$

Under the conditions specified, $V = 22.4$ L and $T = 273$ K. Therefore,

$$\begin{aligned} k &= 22.4\ \mathrm{L}/273\ \mathrm{K} \\ &= 0.0821\ \mathrm{L/K} \end{aligned}$$

If the pressure of the gas were maintained at some other value, say 2.0 atm, then the proportionality constant would be different.

We might have determined that the number of accidents was proportional to the IQ squared; that is, that

$$\text{accidents} = k(\mathrm{IQ})^2$$

In this case, if you double the IQ, the number of accidents goes up four-fold. In fact, the number of accidents could be proportional to any function of IQ, even something like the cosine of IQ. Usually, however, when x is proportional to y, it means that

$$x = ky$$

We can use proportionality to solve problems even if the proportionality constant is not known. For example, if we know that the volume (V) of a gas and its absolute temperature (T) are proportional, we can determine the volume of a gas at 400 K if it has a volume of 1.0 L at 100 K. First, we know that the volume of the gas at 400 K must be greater than the volume at 100 K. Second, the fact that V and T are proportional means that if we double the temperature the volume will double, or in this case the temperature increases by a factor of 4 and therefore the volume will go up by a factor of 4.

This is often expressed by the relationship

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

In words, we say V_1 is to V_2 as T_1 is to T_2. If T increases four-fold, V will increase four-fold. If we solve this relationship explicitly for V_2, which is the new volume—the volume at 400 K—we get

$$V_2 = V_1 \times \frac{T_2}{T_1}$$

or

$$\begin{aligned} V_2 &= 1.0\ \mathrm{L} \times \frac{400\ \mathrm{K}}{100\ \mathrm{K}} \\ &= 4.0\ \mathrm{L} \end{aligned}$$

Sometimes, two variables are inversely proportional; as one increases, the other decreases. For a gas, volume and pressure are variables that are inversely proportional. If the temperature is constant (all other variables must always be kept constant in order to use simple proportional relationships), then

$$V \propto \frac{1}{P}$$

or

$$V = k\,\frac{1}{P}$$

Thus, if we have a certain volume of gas and we double the pressure, the volume will go down by a factor of two. If we have a certain volume of gas and we decrease the pressure by a factor of 10, the volume will go up by a factor of ten. Thus,

$$\frac{V_1}{V_2} = \frac{P_2}{P_1}$$

Hence, if we know that at a certain temperature a gas has an initial volume of 1.0 L at a pressure of 1 atm and we then increase the pressure to 4 atm, the volume will decrease by a factor of 4:

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \\ &= 1.0\ \text{L} \times \frac{1\ \text{atm}}{4\ \text{atm}} = 0.25\ \text{L} \end{aligned}$$

1.3 THE MECHANICS OF LEARNING

Now that we have talked about the ways in which we learn, we are ready to formulate a practical plan to implement these methods. We must stress at the beginning that probably nothing is more important than hard, consistent work. Notice that there are two adjectives before work in the preceding sentence—hard and consistent. What we mean by hard work is a sufficient amount of concentrated effort to master the material. The second adjective, consistent, is equally important. You should make an effort to study each of your subjects each day, except, perhaps, Saturday or Sunday. Some days you will have papers to write or exams to study for and more than the usual amount of time will be spent on those assignments. But even during those times that you have papers to write or exams to study for, you should try to put in at least a half hour on each subject. It is this consistent, every day effort that will eventually pay off in higher grades. In a recent survey of first-year students at the end of their second semester, they said that the most important advice that they would give to a new student was, "Study every day, not just right before exams."

Reading

The most common way of learning is by reading. This is true not just in college, but when you are in graduate or professional school or on the job. After you get a job, how are you going to learn how to operate a new computer system, or learn about a new area of chemistry? Sure, there will sometimes be seminars or "short-courses" devoted to various topics, but usually you will be on your own, stuck with a computer manual, the original literature, a reference book, or information on a computer network. In other words, you will have to learn by reading.

Active Reading. Reading a book to learn is quite different from reading a book for pleasure. We all have read mysteries or romances; they are great entertainment, but for the most part there is little thought involved in reading them. We can be passive, in the same way that we are passive observers when we watch television. Reading a chemistry book in order to learn a concept involves active learning. Here is an example of a passage taken from this text.

> "In some compounds the atoms are bound together in discrete units called **molecules**. For compounds of this type, it is important to know not only the ratio of the different atoms present but also the actual number of atoms in each molecule. This information is given by the molecular formula. For example, the molecular formula for carbon tetrachloride (CCl_4) tells us not only that the compound consists of carbon atoms and chlorine atoms in a ratio of 1:4, but also that each molecule of the compound is an aggregate of one carbon atom and four chlorine atoms. For carbon tetrachloride, the empirical formula and the molecular formula are identical, but for many other compounds this is not the case. Both acetylene and benzene have the empirical formula CH, indicating that both compounds consist of carbon and hydrogen in an atomic ratio of 1:1. But the molecular formula for acetylene is C_2H_2 and that for benzene is C_6H_6, which indicate two different compounds, each with its own specific set of properties."

Let us consider this passage sentence by sentence. In the first sentence we are given the definition of a molecule. In fact, the authors obviously considered this important because they put the word "molecules" in bold face type. At this point in our reading we should write down our own version of what a molecule is, perhaps something like

molecule: atoms bound together in discrete units

We should also be thinking, how are the atoms bound together; that is, what holds them together? What is a discrete unit?

In the second sentence we encounter the word "ratio." Do you really know what that word means? If not, look it up in a dictionary. At this point you should also start to think of your own example of a compound to which you can apply this paragraph. You almost surely know that water is a liquid and therefore it is most likely a molecular compound (do you know the definition of compound?). You also know that the formula for water is H_2O. Now, apply the second sentence to water. The formula H_2O seems to imply that there is a 2:1 ratio of hydrogen atoms to oxygen atoms and perhaps also that in a molecule of water there are two hydrogen atoms and one oxygen atom.

The third sentence tells us that the molecular formula provides information about the number of each atom in one molecule of the compound. So again, we write:

**molecular formula: gives number of each different type
of atom in one molecule of compound**

The fourth sentence assists us by giving an example. In this case the example is carbon tetrachloride. Here we should again be certain that we understand all of the words, like "aggregate," and apply the idea, once more, to our own example, H_2O.

The fifth sentence implies that the empirical formula and the molecular formula may not be the same. Here we could have a real problem. Do you remember what empirical formula means? Actually, the authors discussed empirical formula in the preceding section, so if you do not clearly understand the meaning of empirical formula you should return to this section and review it.

The last two sentences of this passage are designed to explain the difference between empirical and molecular formula. The authors are being helpful in giving examples of the concepts they are discussing. You should again apply your water example to these two sentences. What is the empirical formula of water? [H_2O]. What is the molecular formula of water? [H_2O]. In this case the empirical and molecular formulas are the same.

Now, can you think of some compound for which the empirical and molecular formulas are different? Even though your repertoire of compounds is limited at this stage, you may remember from high school that the formula of glucose (one of the sugars) is $C_6H_{12}O_6$. Is this an empirical or molecular formula? An examination of the formula tells you that the simplest ratio of the atoms in glucose is 1:2:1 (divide the subscripts 6, 12, and 6 by 6). Therefore the empirical formula of glucose is CH_2O. Thus, $C_6H_{12}O_6$ must be a molecular formula.

This is the kind of active, engaged reading of every paragraph that will be required if you intend to really understand and apply the material that you read. It is also the technique that you should apply to studying your notes or a class discussion.

Notes. When you have finished reading a section of a chapter, or in some cases, the entire chapter, it is helpful to go back and make notes about the main point in each paragraph. For example, for the passage above, your notation might be "empirical formula gives simplest ratio of atoms of elements in compound; molecular formula gives number of atoms of each different element in molecule." Some students also find it useful to outline each chapter.

Outlining the Chapter. We suggest that you take notes about each topic and, then at the end of each chapter, produce an outline of each chapter. The outline should be in proper outline style. For example:

Chapter 2. Compounds
    I. Types of Compounds
        A. Ionic
        B. Covalent
    II. Type of formulas for compounds
        A. Empirical
            1. Calculation of empirical formula from percent composition
            2. Calculation of percent composition
            3. Formula weight
        B. Molecular
            1. Calculation of molecular formula from empirical formula and molecular weight
            2. Molecular weight
        C. Structural Formula

Notice that outline style draws your attention automatically to the most fundamental distinctions in the chapter (I, II, III, . . .), and to the topics that are important to understanding these distinctions (A, B, C, . . .).

Taking Notes and Studying Them

Most first-year college students are accustomed to the typical high school situation where the teacher goes over the material fairly slowly and, perhaps, covers the same material several times. Some students have picked up the attitude that it is better to listen carefully to the lecture and "understand" it than to try to write down everything that was said. Even if you were to sit in class today and understand all of the material, would you remember that material two days from now, two weeks from now, at the end of the semester? Almost certainly not! On the other hand, the good student is not just an automaton, a perfect recorder of all that is said. The good student will be listening to the voice of the instructor, trying to understand the concepts, and will write down as much of what the instructor says and writes as possible. The good student will realize that it is not sufficient to record only what the instructor writes on the board.

The first time you attend class and try to be both a listener and a recorder of everything that is said and written on the board you will come away convinced that we are wrong. If you have never played the piano and were asked to play a Beethoven sonata you would react in a similar fashion. Why then would you expect to be able to take good notes the first time you try it? Getting to be a good note-taker, and that includes understanding the material in class as well, takes practice. Fortunately, it does not take as much practice as learning to play a piece of classical music!

It is not sufficient to only take good notes, you must also study those notes. Because your memory of the class will decrease rapidly with time, you should start to study your notes as soon after class as possible. For example, it you have a free period immediately after class, go to some quiet place, get out your notes and read them. As you read them, do the same things we suggested when you read your text. Make certain that you understand all of the words, redo examples that were done in class, and make notes in the margins of your notebook on the meaning of each section.

On your second reading of your notes, be sure that you can apply the concepts to a new problem. Your instructor may help with this by suggesting problems that you can try while you are studying your notes. She may say, for example, "Here is a good problem that you can use to test your understanding of this material." Be certain that you do these problems and that you know whether you have done them correctly. If the instructor does not provide this kind of help, you can usually make up your own problems. These problems (as in the sugar example given above under Reading) can be simple analogies to examples given in your notes.

Producing Your Own Examples

A very helpful principle can be used to produce analogous examples of molecules. It is called the **Isoelectronic Principle**. It is based on the simple fact that if two molecules have the same number of electrons in their valence shells, they will probably have similar structures and bonding. Thus, if we want to find a molecule that is structurally analogous to SO_2, we look for one that has the same number of electrons in the valence shells of the atoms (in this case a total of 18 electrons). Probably the first example we would think of would be O_3, because we know that oxygen and sulfur are in the same Group of the periodic table and therefore must have the same number of valence electrons. Hence, we replace sulfur with oxygen and change SO_2 to O_3. We can create other isoelectronic species by moving to the left or right on the periodic chart. That is, if we change sulfur to nitrogen, we will have one less electron (nitrogen is in Group V, sulfur is in Group VI). We must compensate for that by adding an electron, thereby making the NO_2^- ion.

Problem 1.5

Use the isoelectronic principle to produce species (neutral molecules or ions) that are isoelectronic with

a. CO_3^{2-}

b. ClO_3^-

c. N_3^-

Solution:

We always think first about changing the central atom. In the case of the carbonate ion, CO_3^{2-}, if we change C to N we will have one more electron (because N has one more electron than C). We will therefore need to reduce the charge on the ion by 1 so that the total number of electrons remains the same. Thus, NO_3^- is isoelectronic with CO_3^{-2}. Using the same reasoning, we can change C to B, but will then have to add an electron to get the borate ion, BO_3^{3-}.

For ClO_3^-, go to the left on the periodic chart to find SO_3^{2-} and PO_3^{3-}. For N_3^-, we could have $CN_2^{\ 2-}$. We could also change both the central atom and the terminal atoms to get CO_2 and NO_2^+

In summary, we suggest that you do two things with your notes. First, after reading through them, rewrite them (you may want to keep a separate notebook for these notes) using outline style. This should force you to clarify points you may have missed and it will also force you to figure out what the main points of the lecture were. You should constantly ask, what is the main point here, how does this relate to the preceding material? Second, be certain that you take every idea and work on it until you can apply it to a new problem. Be aggressive with the ideas, nudge them, twist them, hound them until you have wrestled them to the mat. If you are reading about the VSEPR model ask, what is the basis of this model, what do you apply this model to, what does this model tell me about Nature?

Learning the Concepts

For every model or concept, formulate a set of rules that you can use to apply the model. For the VSEPR model the rules might look like this

1. Write the structural formula for the species.
2. Write the electron-dot formula for the species.
3. Determine how many sigma bonds surround the central atom.
4. Determine how many nonbonded electron pairs are on the central atom.
5. Add the number of sigma bonds and the number of nonbonded pairs. Call this sum n.
6. Determine the geometry required to position n electron pairs around the central atom in order to minimize the repulsions between the n pairs.
7. Place the terminal atoms on the electron pairs. Remember that nonbonded pairs should be placed as far apart as possible. (In a trigonal bipyramid these pairs are placed on the equatorial positions.)
8. Describe the geometry of the atoms of the species (not the geometry of the electron pairs). Use proper terminology, such as linear, bent, trigonal planar, pyramidal, tetrahedral, and so on.

Then apply those rules to as many examples as possible. You will find that there are numerous Methodology examples in the text, most of which are followed by a Problem designed to test your understanding of the preceding example. Most chapters also contain Check Points that are designed to make sure that you have achieved some minimal competency with the material before you proceed. If you do not obtain the correct answer to the Check Point questions, you should not continue with the chapter. Instead, you should go back through the preceding parts of the chapter and redo all of the examples and problems.

The end-of-chapter problems are designed to give you practice with the material in the chapter. The more of these problems that you do (without looking at the solutions), the better your understanding of the concepts in the chapter.

Problem-Solving

Problems may be mathematical or quantitative (what is the molecular weight of a gas with a density of 1.23 g/L at standard temperature and pressure?). Or, problems may be qualitative (what is the structure of a compound that has a molecular weight of 58 and is a ketone?). In either case you must develop a rational, logical, step-by-step approach to the problem. Always begin by asking: What do we know and what must we find? In the quantitative example above we know the density at standard temperature and pressure and we must determine molecular weight. Next ask, what principle or concept is involved in solving this problem? In the example above it is the ideal gas law, which is expressed quantitatively as $PV = nRT$.

From here, the approach to solving the problem may vary. For example, in the gas density problem one person might prefer an "algebraic" approach where n, the number of moles, is expressed as g/M (grams of sample divided by the molecular weight) and then solve for M ($\mathrm{M} = \mathrm{g}RT/PV$). Another person might solve the same problem by remembering, or determining from the ideal gas law, that 1 mole of an ideal gas occupies 22.4 L at STP and that therefore one liter at STP is 1/22.4 mol. Thus, 1.23 g of this compound is 1/22.4 mol and therefore 1 mole is

$$\frac{1.23}{x} = \frac{\frac{1}{22.4}}{1}$$

or

$$x = 27.5 \text{ g/mol}$$

Thus, after the question—what principle is involved?—there can be any number of equally valid approaches to the solution of the problem. What works for one person may not work for another. Notice, however, that the second approach involves more visualization than the first approach. The first is mostly mathematical manipulation; the second makes you think about the volume occupied by a mole of a gas at STP and how the number of moles in 1.23 g relates to molecular weight.

In general, then, the generic formula for problem solving is

What is known ⟶ concept ⟶ an approach ⟶ solution

We should add to this formula the important notion that every solution should be checked. First, it should be checked to see if the solution makes sense. If the answer to the problem above came out to be 1200, is this a reasonable number? Actually there are many molecules with high molecular weights. Polymers have molecular weights that range from 10^3 to 10^6. However, as you learn more chemistry you will realize that all substances that are gases at room temperature and pressure have low molecular weights, generally below 100 (you will eventually learn the reason for this).

Second, you should be certain that your answer has the correct units. If the answer comes out to be 0.037 mol/g, you should first recognize that no compound can have a molecular weight less than the atomic weight (1) of the lightest element (H). You should also know that the units for molecular weight cannot be mole per g. The definition of molecular weight* is the weight in grams of one mole of a compound.

Probably the most important advice that we can give on the subject of problem-solving is: Don't give up! Some students decide to consult the solution to the problem almost immediately and assume that reading the solution will help them to learn the concept that is at the core of the problem. In our experience this is rarely effective.

Try to resist looking at the answer until you are reasonably sure you have the correct answer (does it make sense? are the units correct?). If you find that you cannot do the problem, start over and ask: what is the concept that is central to this problem, what are the relationships between the variables in the concept? Go back to your notes and text and reread the section that involves this concept and redo the examples given there. Then try the problem again. You will learn more by working on a small number of problems and thinking about them carefully than by trying unsuccessfully to do a large number of problems.

Methodology 1.1

A block of gold has a mass of 100 g. Gold has a density of 17 g/cm^3. What is the volume of this block?

1. First, list what we know.

   A sample of gold weighs 100 g and has a density of 17 g/cm^3.

2. Next, show what quantities we start with and what we want to find.

   We start with mass and want to find volume.

---

* Actually, molecular weight, like atomic weight, need not have units. A molecular weight of 80 tells you that one molecule is twice as heavy as a molecule of a compound with a molecular weight of 40. When the molecular weight is expressed in grams it also represents the weight of a certain number of molecules—6×10^{23}, or one mole of molecules.

3. What allows us to convert the starting variable to the final variable?

The density, which is mass divided by volume.

4. Now visualize the problem.

The diagram in Figure 1.3 shows a block of gold weighing 100 g. Inside that is a block that is 1 cm^3 and weighs 17 g. The problem then becomes how many of the small blocks (that is, how many cm^3) will fit inside the 100-g block

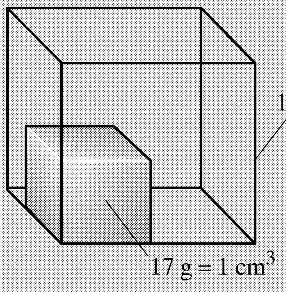


Figure 1.3 Visualizing a Problem

5. Finally, do the math that will result in an answer of cm^3.

$$\begin{aligned} V &= 100\ g/(17\ g/cm^3) \\ &= 5.9\ cm^3 \end{aligned}$$

We could also attack the problem as a plug-in algebraic problem:

$$d = m/V, \quad \text{solve for } V$$

$$V = m/d$$

$$\begin{aligned} V &= 100\ g/(17\ g/cm^3) \\ &= 5.9\ cm^3 \end{aligned}$$

Problem 1.6

A nickel is about 1.5 mm thick and weighs about 2.5 g. How many nickels will there be in a stack 1 ft high?

Solution:

We are told the thickness of a nickel (1.5 mm) and want to determine how many will stack one on top of the other to produce a stack 1 ft high. So we start with thickness and must finish with a number. If we convert the height of the stack into mm, then we can see that we can divide that number by the thickness of the nickel in order to obtain the number of nickels in the stack.

To convert from feet to mm we need to know that 1 ft = 12 in, that 1 in = 2.54 cm, and that 1 cm = 10 mm. Thus,

$$1\ \text{ft} \times \frac{12\ \text{in}}{1\ \text{ft}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{10\ \text{mm}}{1\ \text{cm}} = 305\ \text{mm}$$

in 1 ft there are 305 mm.

Now we divide 305 mm by 1.5 mm/nickel to obtain

$$\frac{305\ \text{mm}}{1.5\ \text{mm/nickel}} = 203\ \text{nickels}$$

A commonly used technique for problem solving is the factor-label or dimensional analysis method. The emphasis in this approach is in setting up the answer so that the units cancel to give the units required for the answer. For example, if you are required to determine the relationship between miles and kilometers—that is, how many kilometers are there in one mile—you would set up the problem as

$$1 \text{ mi} \times \frac{5280 \text{ ft}}{\text{mi}} \times \frac{12 \text{ in}}{\text{ft}} \times \frac{2.54 \text{ cm}}{\text{in}} \times \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{1 \text{ km}}{1000 \text{ m}} = 1.61 \text{ km}$$

At each stage, we use a relationship such as there are 12 inches in one foot. Although many students prefer this method, we urge you not to rely upon simple mechanical cancellation of units, but rather to think the problem through in steps. For example, in the second step, conversion of feet to inches, ask yourself "if there are 12 inches in one foot, how many inches will there be in 5280 ft?" Clearly, the answer to this question requires multiplication of 5280 by 12. In a sense you have visualized a foot, seen 12 inches, and then imagined lining up 5280 of those feet. If you approach this step purely from the standpoint of unit cancellation you merely ask, "how do I get the units to work out to inches?"

Problem 1.7

A train has an average speed of 80 mph. How many minutes does it take to go a distance of 240 km?

Solution:

We can either convert 80 miles to km or 240 km to miles. Because there are 1.61 km per mile, 80 miles will be

$$80 \text{ mi} \times 1.61 \frac{\text{km}}{\text{mi}} = 129 \text{ km}$$

If the train travels 129 km in one hour, how many hours will it take it to travel 240 km?

$$\frac{240 \text{ km}}{129 \text{ km/hr}} = 1.86 \text{ hr}$$

Finally, one hour is 60 minutes, so 1.86 hr is 1.86 × 60 = 112 minutes

Review

After you have finished a section of material, such as one chapter, by successfully solving the problems you should spend some quiet time thinking over the material in the chapter. You can do this before you fall asleep at night (a good time to provide for maximum retention) or while you are taking a walk.

What do you do when you are thinking through the material? First ask, what were the main topics covered in the chapter (or during the lecture)? Was it bonding? If so, what model of bonding was being covered? What aspects of the model were covered? Do you understand the model? Do you know how it was developed and how it is applied? Can you formulate a set of directions that will allow you to apply the model to a new situation?

This type of review accomplishes three objectives: a) it focuses your attention on the forest *and* the trees, b) you find out if you know the material well enough to "see" it in your mind without recourse to your notes or textbook, and c) it provides another opportunity for the kind of repetition that results in longer retention of the information. If you do this several times a week, you will be just about ready for the exam. Obviously, the exam requires a more thorough review. You will also want to redo selected problems from the problem sets.

1.4 MODELS, THEORIES, AND HYPOTHESES

As you study chemistry you should constantly be aware of its underlying structure; that is, the way our present understanding of matter developed and is changing. You certainly already know that we call some things **facts**; for example, the color of a copper sulfate solution is blue. When enough observations of copper solutions have been made, a **generalization** is proposed: solutions containing the Cu^{2+} ion are blue. These generalizations always have exceptions (cupric chromate is red-brown). However, sometimes generalizations with very few exceptions are elevated to the status of rules. The rule that nitrate salts are soluble is true for probably 98% of those salts.

When a generalization can not be shown to have an exception, it is called a **law**. Laws are formulated only after a tremendous amount of experimental work has been done. The law of conservation of mass was thought to be without exception for almost a century. Einstein showed that actually most chemical reactions do involve a very small gain or loss of mass (this mass is converted to energy). However, for all practical chemical purposes, this law is still valid. Some laws, like the ideal gas law, are known to have exceptions, but because they are so useful and are obeyed under certain circumstances, they maintain the title of law.

After a rule or law has been stated, it is human nature to try to make sense of the rule or law. Why are most solutions that contain the Cu^{2+} ion blue, whereas most solutions that contain the Zn^{2+} ion are colorless? Attempts to understand nature frequently involve a guess of the type, "I wonder if the reason is . . ." For example, since Zn^{2+} contains more electrons than Cu^{2+}, we might make the guess that color is related to the number of electrons. This guess, or **hypothesis** can be tested. We can determine the color of ions that have fewer and greater numbers of electrons than copper and zinc. When we find that Ca^{2+} is colorless, as is Sn^{2+}, we suspect that our simple hypothesis is not correct. In trying to disprove our hypothesis we have noticed, however, that the ions of all of the main group elements are colorless, whereas many of the ions of the transition elements are colored. Thus, we could modify our original hypothesis. Transition elements have *d*-electrons in their valence shells, while main group elements have only *s* and *p* electrons in their valence shells. Therefore, a reasonable hypothesis might be that color is related to the number of *d*-electrons.

We continue this process of formulating and rejecting hypotheses until we find one that can withstand every test to which it is subjected. In other words, for the moment, at least, it cannot be disproved. The hypothesis is then elevated to the highest rank in the scientific process—**theory** or **model**. Although the two words, theory and model, are very similar in meaning, we prefer to use the word "model" because it imparts two important aspects of this stage of the scientific process. First, models are temporary. They represent our best attempt at explaining a series of rules and/or laws, but models will probably be changed in the future. Second, models are based on our own knowledge, previous experiences, our limited abilities to perceive, and so on. Hence, they are anthropomorphic; they are humans' best attempt to explain nature; they are not absolute.

To illustrate this whole process, sometimes called the scientific method, let us follow the thoughts and actions of a scientist who happens upon the box pictured in Figure 1.4.

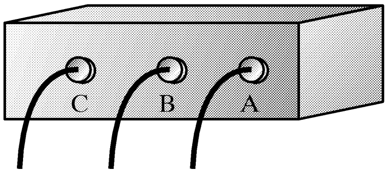


Figure 1.4 A Curious Box

The box is apparently constructed from some heavy metal and has three rather stiff ropes protruding from holes labeled A, B, and C. His curiosity aroused, our scientist attempts to open the box to discover its purpose and inner workings. He soon discovers, however, that he lacks the necessary tools and must content himself with observations made from outside the box.

An initial tug on rope A produces a movement of rope A, but no apparent movement of ropes B and C. This observation triggers the thought that the box may contain three unconnected, independent ropes. This mental visualization is our scientist's first hypothesis of the nature of the interior of the box.

Now, he reasons, if this hypothesis is correct, each rope should move to its limit without affecting (moving) any of the other ropes. Thus, in order to test his hypothesis, he pulls rope A a distance of 6 feet and is surprised to find that rope B has moved out a short distance. This distance he measures as 4 inches. He now pulls rope B a distance of 1 foot and observes an advance of 18 feet for rope A. He repeats these experiments a large number of times using various distances, and finds that rope A always moves 18 times as far as rope B. Throughout these experiments, rope C has not moved.

Since the relationship between the distances moved by ropes A and B does not depend upon how far either rope is pulled—that is, the relationship is a general one—this relationship can be expressed as a mathematical law. If x represents the distance traversed by rope A, and y the distance traversed by rope B, the law becomes

$$x = 18y$$

Apparently the movement of rope B during the initial pull of rope A went unnoticed because of the high 1:18 distance ratio. In any case, the first hypothesis must now be modified. Ropes A and B are not unrelated, although rope C still appears to be independent of the other two.

Because of the specific interdependency of ropes A and B, the scientist now proposes the model pictured below in Figure 1.5. In this model, rope A is wound around a drum attached to an axle; rope B is wound around the axle itself. The circumference of the drum is greater than the circumference of the axle (in fact, 18 times as great), and rope A is therefore played out at a greater rate than rope B. Rope C remains unattached and independent.

While this model of the interior certainly accounts for all of the observations, our scientist is not quite satisfied. He tests his new model by pulling rope C and observing ropes A and B (there is no effect). The experiments possible with these ropes are now almost exhausted, and the model appears to be satisfactory.

Let us now review the investigation of the box. Two models were proposed: The first, based on only one observation, did not explain later experiments and was therefore discarded. The second model, a result of a greater number of observations, provides an explanation for all of the experimental data. This model also permits the formulation of new questions and predictions. For example: Can rope C be withdrawn from the box completely, or is it held inside by a knot at the end? Are the ends of ropes A and B

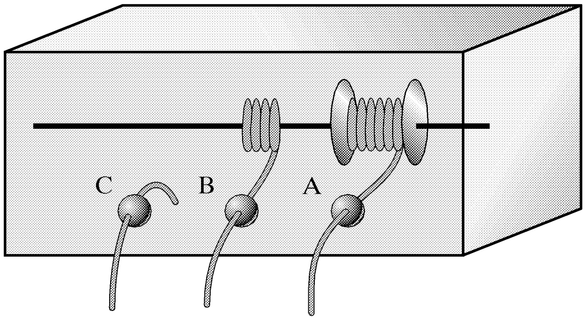


Figure 1.5 A model of the interior of the box.

attached to the drum and the axle? If the model is correct, then when rope A is withdrawn to its limit, rope B may not have reached its limit, and (assuming that the ropes are attached) a further pull on rope B may wind rope A back into the box. These questions suggest additional experiments that might never have been conceived without the help of the model.

While our scientist has spent a considerable amount of energy investigating an almost trivial problem, his approach to the problem contains many of the same features discussed above: experimental observation that leads to the formulation of a law, hypotheses that lead to a model or theory, and the subsequent use of the model to design new experiments. Each hypothesis leads to a model, which may be discarded after additional experiments are performed. If the experiments are all consistent with the model, the model is retained until contradictory evidence is obtained.

Because of the central role of models, it is important to recognize some of their characteristics. First, the scientist usually draws on his own experiences in fashioning a theory. In our example, it might be suggested that the ropes are controlled by elves residing in the box, but our scientist has never seen an elf, nor does he believe in the existence of such creatures. On the other hand, he has seen mechanical devices such as winches that employ ropes on drums, and he has seen a spool of thread. As we shall see later in this text, many models designed to account for the behavior of matter so small that it has never been seen are based on the behavior of macroscopic bodies, such as billiard balls, which lie within the realm of everyone's experience.

Some models are mathematical and abstract in nature. For example, the mathematical nature of the contemporary model of the electron makes many of its features difficult to visualize. Indeed, some scientists feel that the most significant scientific discoveries occur within the realm of mathematics.

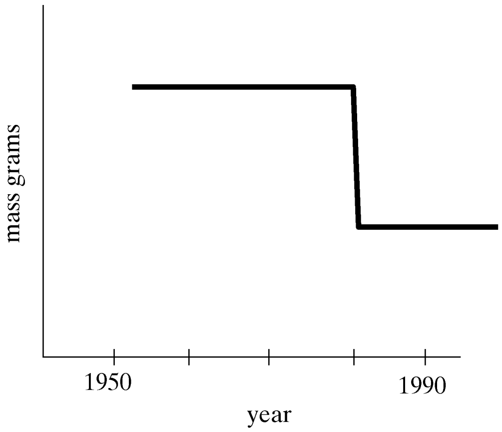
It is also important to realize that a given set of experiments and observations can usually be explained by more than one model. Our scientist could have developed a model based on gears rather than drums, and in fact there are a number of alternate models that will satisfactorily account for the behavior of the ropes. As data and observations accumulate, one of a set of equally good models may become more satisfactory than the rest, or the choice of model may be based on considerations of simplicity or symmetry or usefulness.

Finally, the fact that models may not, and very likely do not, correspond to reality cannot be overemphasized. Since the box cannot be opened, the scientist will probably never know if the box really does contain a drum and axle. When the model is intended as a picture or visualization of matter at the submicroscopic, molecular level, the problem is even more acute. Atoms cannot possibly be either billiard balls or mathematical abstractions, nor is it likely that atoms behave like billiard balls. And yet, the billiard ball model of atoms is at the heart of the determination of the structure of the nucleic acids DNA and RNA, the revelation of the genetic code, and all of its biological implications. Thus, while the correspondence between the model and reality may not be very high, the benefits of the model—the development of new experiments, the discovery of new laws of nature, and so forth—may be very great indeed.

Although the discussion on the next page might lead you to believe that science in general, and chemistry in particular, is very orderly and proceeds nicely according to its own set of rules, many scientific discoveries have resulted purely from accident. The discovery of Teflon is a good example. In 1938, R. Plunkett, a du Pont chemist, was experimenting with the gas tetrafluoroethylene, which was routinely stored in metal cylinders under pressure. Upon opening the valve of one particular cylinder, Plunkett found that no gas was released. Since the cylinder weighed more than it had when empty and therefore should have contained some tetrafluoroethylene, he proceeded to systematically dismantle the cylinder. Having finally sawed the cylinder in half (a very dangerous procedure because of the possibility of high pressure in the cylinder), Plunkett discovered it was partially filled with a white powder. This was the serendipitous discovery of Teflon. The white powder was later found to consist of long chains of CF_2 groups; Teflon therefore is polymerized tetrafluoroethylene.

Problem 1.8

The following is a plot of the average mass of a penny versus the year it was minted.



Produce several hypotheses that could explain this graph and describe how you would test each hypothesis.

Solution:

One explanation for the drop in weight of the penny around 1982 might be that the penny was made smaller that year. This hypothesis could easily be tested by determining the volumes of pennies minted before and after 1982 (for example, by finding out how much water 20 pennies displace when dropped into a graduated cylinder containing water).

Another hypothesis could be that pennies were much more heavily used from 1982 to the present and that therefore there was more wear on them and their size changed. This hypothesis runs contrary to common sense. Why would pennies suddenly receive more wear, and why wouldn't that wear decrease as the age of the pennies decreases? This hypothesis can be tested in the same way as the first (the pennies could also be examined for signs of wear).

It is also possible that in 1982 the government decided to make pennies out of some other, lighter material. If the determination of volume discussed above shows that the volume of pennies has remained constant, then this is the most likely explanation. It could be tested by analysis of the composition of the penny.

As you proceed through the text we hope that you will also think about the roles that curiosity-driven research and use-driven research have played in your life. The discovery of Teflon is also a good example of the role of these modes of research. Although Plunkett worked for a company whose primary purpose is to make money for its shareholders, his work on tetrafluoroethylene was not directly related to the development of a new profit-producing material. The work was very fundamental, curiosity-driven research. But because of Plunkett's persistence and his recognition of the commercial potentials of this new material, this basic research led to a product that has enhanced our lives and enriched the du Pont shareholders and employees.

CHAPTER SUMMARY

Although learning is an individual experience, most efficient learners develop the discipline necessary to read carefully, to take good notes and study them regularly, to do problems systematically, and, most importantly, to work consistently. This text is designed to help you to develop these skills. Make certain that you read every Methodology example and then try to do the problem without looking at the solution. After you have mastered the Methodology examples and Problems in the chapter, do the end of chapter Problems. Always ask: What principles are involved here? Do I understand this material to the point where I could apply the principle to some similar system?

As you proceed with your study of chemistry, examine the structure of the discipline. For example, be certain that you know the difference between an observation, a generalization, a hypothesis, and a model. Watch, particularly, for the models that allow us to understand matter and to make predictions and to develop new materials and processes.

PROBLEMS

1. The table below lists the prefixes that are used in the metric system to describe the magnitude of a quantity. For example, a microliter is 1×10^{-6} L.
 a. Express the length of a wire that is 1.3×10^{23} cm long in nanometers.
 b. Express the weight of 1.00 ton of iron in kilograms.
 c. Express 1.56×10^{12} kilojoules in gigajoules
 d. Express the length of a 1.8 Å bond (an Angstrom is 1×10^{-8} cm) in picometers.

METRIC SYSTEM PREFIXES

FACTOR	PREFIX	SYMBOL
10^{12}	tetra	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{1}	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

2. How many:
 a. Angstroms are there in 1×10^{-6} meters?
 b. liters are there in 40 gallons (1.0 quarts = 0.9464 L, 4 quarts = 1 gallon)?
 c. meters are there in 1.0 Å?
 d. cubic inches are there in 1 cubic foot?

3. Consider the following mass equivalencies:

1 gram = 5.4 grains
1 gram = 0.035 oz
1 pound = 453.6 g

 a. How many grains are there in an ounce?
 b. How many ounces are there in a pound?
 c. What is the weight of a grain in grams?
 d. What is the weight of a grain in pounds?

4. A train is traveling at a speed of 68 mph. Express its speed in meters per second.

5. What is the area in square meters of an 8 × 11 in sheet of paper?

6. The sun is 93 million miles from the earth. How long does it take light from the sun to reach the earth?

7. What is the volume, in cubic centimeters, of a cube that is 3.25 in on a side.

8. The atomic radius of a helium-4 atom is 50.04 pm. Given the masses of the subatomic particles below, calculate the density of a helium-4 atom in g/m^3. The volume of a sphere is $4\pi r^3/3$.

mass of electron:	9.1095×10^{-28} g
mass of proton:	1.67265×10^{-24} g
mass of neutron:	1.67495×10^{-24} g

9. An average adult has 7.0 lb of blood plasma. If the density of the plasma at 25 °C is 1.02 g/mL how many liters of plasma is this?

10. If water is flowing from a pipe at the rate of 355 mL/minute, how many liters of water are flowing from the pipe per hour?

11. If 500 marbles are packed in a bag and each marble weighs 4.50 g, how many pounds does one bag of marbles weigh?

12. The amount of energy released when a pound of coal is burned is about 3.80×10^3 kcal. How many joules is this? [1 cal = 4.184 J]

13. Mercury has a density of 13.6 g/mL. If 100 g of mercury are placed in a 100-mL volumetric flask, how many mL of water must be added to reach the 100-mL mark?

14. A U.S. dime is 1.0 mm thick and weighs 2.5 g. (a) How many dimes would make a stack one foot high? (b) How many pounds would the stack weigh?

15. Copper atoms have a radius of 128 pm.
 a. How long would a chain of copper atoms be if 2.0 mol of these atoms were arranged in a straight line? (1 mole = 6×10^{23})
 b. Compare this distance to that of the average distance at which Pluto orbits the sun, which is 3.67×10^9 miles. (Hint: 1.000 mi = 1.609 km)
 c. How long would it take light to travel from the first copper atom to the last copper atom in the chain?

16. Calculate the cost per gram of gold if its price is $300 per ounce.

17. A student found what appeared to be a nugget of gold. She measured the density of the nugget by volume displacement, obtaining the following data:

Weight of empty flask: 10.6482 g
Weight of flask + nugget: 12.2345 g
Weight of flask filled with water: 21.6235 g
Weight of flask + nugget + water: 22.8947 g
What is the density?

18. If exactly 1 L of a liquid weighs 1.23 kg, what is its density?

19. Nickel metal has a density of 8.90 g/cm^3. What is the volume of a bar of nickel that weighs exactly 1 lb?

20. One kilocalorie (kcal) is equal to 4.184×10^{10} ergs. How many calories are equivalent to exactly one million ergs?

21. What is the cost of 1 gal of ethyl ether if it sells for \$4.00/lb and has a density of 0.708 g/mL?

22. At what temperature do the Fahrenheit and Celsius scales coincide (that is, have the same numerical value)?

23. A student receives the following grades: Exam 1, 73%; Exam 2, 55%; Exam 3, 80%, Final Exam, 70%. Each exam counts 20% toward the course grade, while the final exam counts 40%. Calculate the student's course grade as a percentage.

24. A zinc-aluminum alloy contains 10% zinc. How many grams of zinc are there in 1.0 ton of the alloy?

25. A compound has the formula $C_6H_4ClNO_2$. What percentage of the total number of atoms in this compound are carbon atoms?

26. A mole is a chemist's way of describing a collection of objects (usually atoms or molecules) which numbers 6.022×10^{23}. Just as a dozen eggs is 12 eggs, a mole of eggs is 6.022×10^{23} eggs.

a. How long would a chain of hydrogen atoms be if one mole of them were arranged in a continuous straight line end to end? The radius of a single hydrogen atom is 0.79 Å.
b. Compare this distance to that of the average distance at which Pluto orbits the sun, which is 3.67×10^9 miles (1 mi = 1.60^9 km).
c. How long would it take for light to travel the above distance in a vacuum? ($c = 3.00 \times 10^8$ m/s).

27. A ream of paper is 500 sheets of paper. For a certain quality paper the average weight of one sheet is 9.22 g.

a. What is the weight expressed in pounds of one ream of paper?
b. An office uses 6.0×10^6 sheets of paper per year. How many reams should it buy?
c. A paper factory produces 10.0 tons of paper a day. How many reams does it produce annually?
d. A ream occupies 0.12 ft^3. How much space is required to store 1.0 ton of paper (express the answer in ft^3)?

28. The occupants of the planet Schaf eat the tiny, amazingly uniform seeds of the Birn tree. Each seed weighs 57 mg. The prodigious appetites of the Schafkins require that they eat several thousand seeds per day and therefore the seeds are packaged in units of 1000. Each of these packages is called a tat.

a. What is the mass of one tat?
b. The average Schafkin eats 15 tats at each of 5 meals per day. What is the weight of a 15 tat meal in grams and in pounds?
c. A tat factory produces 1.68×10^8 tats per week. How many Schafkins will this production feed each week (the Schaf week contains 10 days)?
d. The planet has a population of 3.23×10^9 Schafkins. How many factories must there be in order to feed all of the Schafkins?
e. What is the total weight of Birn seeds consumed by one Schafkin in one week?

29. Any number can be quickly converted to its exponential form by following a simple procedure. First, move the decimal point in the given number so that it falls after the first digit in the number. This manipulation gives us the coefficient. Then we multiply this coefficient by 10 with an exponent equal to the number of places we moved the decimal point from its original position. If we moved the decimal point to the left, the exponent is positive; if we moved it to the right, the exponent is negative. The following examples are illustrations of this procedure:

$$132.45 = 1.3245 \times 10^2$$

two places to the left

$$1278 = 1.287 \times 10^3$$

three places to the left

$$0.0045 = 4.5 \times 10^{-3}$$

three places to the right

$$0.000978 = 9.78 \times 10^{-4}$$

four places to the right

Write the following numbers in exponential notation:

a. 151
b. 0.00151
c. 100.0012
d. 0.00000062

30. When a number is correctly written in exponential notation, the number of digits in the coefficient is the number of significant figures. This number represents the precision with which the number was obtained. For example, the number 1.51×10^2 indicates that the person who obtained the number believes that the number is valid to within ±0.01. In other words, the last digit on the right could be off by ±1. Thus, this number has 3 significant figures. The number 1.000023×10^{-5} has seven significant figures.

Give the number of significant figures in each of the following numbers:

a. 5.5
b. 5.005×10^5
c. 0.0050×10^3
d. 1×10^{-2}

31. When numbers are being multiplied or divided, the result can have no more significant figures than the number with the smallest number of significant figures. For example, $\frac{6.002 \times 10^4}{1.4 \times 10^2} = 4.3 \times 10^2$ (two significant figures).

Give the answer to the following operations using the proper number of signifcant figures:

a. $\frac{100.34}{0.34} =$

b. $\frac{6.78 \times 10^3}{10^5} \times 1.0045 =$

c. $\frac{17.12}{0.25} \times 1.0 \times 10^5 =$

d. $\frac{7.467 \times 10^2}{5.23 \times 10^2} \times \frac{12.3}{0.12} =$

32. Professor Moore teaches a General Chemistry class and expects her students to do two hours of homework for every hour of class time. The average grade on Professor Moore's first exam was 70%. Professor Lester uses a lecture-less approach and expects the students to learn everything they need to know during class. Professor Lester's first exam average was 90%. Can any of the following hypotheses be considered to be unreasonable?

a. The students in Professor Lester's class are smarter.
b. The students in Professor Lester's class know less chemistry because they have spent less time studying chemistry.
c. Professor Lester gives easier exams.
d. The material covered in Professor Lester's class is different from the material covered in Professor Moore's.
e. Professor Lester is a better teacher than Professor Moore.
f. Professor Lester grades easier.
g. Professor Lester's teaching style (lecture-less) provides a more efficient way to learn chemistry.

2 The Atomic Model

Our present-day understanding of the nature of matter, and therefore the birth of modern chemistry, may be dated from the development of John Dalton's atomic theory in the first decade of the nineteenth century. Dalton proposed that: a) matter is composed of extremely small, indivisible particles called atoms, b) a number of different kinds of atoms exist and each kind has its own size, mass, and specific set of properties, c) each different kind of atom corresponds to a different element, and d) compounds are composed of atoms of different elements combined with one another in simple ratios. The basic idea behind this theory, however, was not original with Dalton and in fact preceded him by many centuries.

2.1 ATOMISM

In the fourth and fifth centuries B.C. the Greek philosophers Democritus, Empedocles, Leucippus, and others expressed the belief that matter was composed of extremely small particles. They taught that if you were able to break up a sample of matter into increasingly smaller pieces, you would eventually come to those particles that could not be further subdivided. These indivisible "building blocks" of matter came to be called **atoms**, from the Greek *atomos,* meaning "uncuttable." Aristotle and his followers, on the other hand, maintained that matter was continuous and therefore could be divided endlessly into ever smaller pieces. Thus, two schools of thought regarding the basic nature of matter came into being—the Aristotelian or continuous school and the Democritean or atomistic school—and philosophical debates over the merits of each continued through the following centuries.

The writings of the Arab philosophers of the tenth through the twelfth centuries A.D. indicate a rather wide acceptance of the idea of atomism. The theory was used by a number of scientists, including Robert Boyle and Isaac Newton, in their work in the seventeenth and eighteenth centuries.

For more than 2,000 years, then, the concept of the atom was largely a matter of speculation. An attempt to explain the riddle of the universe, it was based on philosophical thought—often metaphysical and religious in nature—not on the data of experience. Not until scientific experimentation had come into its own—until careful observation of facts gave rise to statements of natural laws—could atomism progress from philosophical speculation to an accepted, useful chemical theory.

2.2 CLASSIFICATION OF MATTER

The classification of matter into certain basic types was crucial to the formulation of a theory of the composition and structure of matter. Many centuries of observations led to the classification scheme still in use today; the scheme was enunciated most clearly by Lavoisier in the 18th century. The different types of matter and the processes used to convert one type to another permeate all of chemistry. It is crucial, therefore, that you understand exactly the meaning of the terms discussed in the following pages.

Substances and Mixtures

All specimens of matter can be categorized as either substances or mixtures. A **substance** is a form of matter that has a definite, invariable composition and a specific set of characteristics by which it can be identified. If a specimen of matter contains two or more substances, it is called a **mixture**. For example, calcium carbonate is a substance; all samples of calcium carbonate have the same composition, no matter what their origin. Furthermore, calcium carbonate has specific characteristics that distinguish it from all other substances. Limestone, on the other hand, is a mixture, since it contains, in addition to calcium carbonate, a number of other substances, including magnesium carbonate, silicon dioxide, and aluminum oxide. Furthermore, the relative amounts of these various substances differ among limestone samples; that is, the composition of limestone is variable.

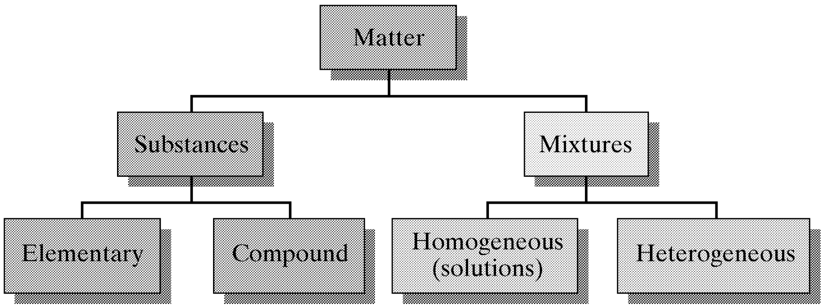
Elementary and Compound Substances

Substances may be classified as either elementary substances or compound substances. During the early development of chemistry (in the seventeenth and eighteenth centuries) these two types of substances were distinguished from each other on a purely empirical basis. If the substance in question could be decomposed or broken down into two or more simpler substances, it was called a **compound substance**. If a substance could not be so decomposed, it was classified as an **elementary substance**. To illustrate, the substance mercuric oxide can be converted easily into two simpler substances, mercury and oxygen, but neither of these can be decomposed by ordinary means to any simpler substances. Therefore, mercuric oxide is classified as a **compound substance** (usually abbreviated to **compound**), and both mercury and oxygen are **elementary substances (elements)**. As we shall see in the following chapter, more precise definitions can be given for these terms.

Homogeneous and Heterogeneous Mixtures

If a mixture is uniform throughout in composition and characteristics, it is **homogeneous**. If this is not the case, then the mixture is **heterogeneous**. Heterogeneous mixtures usually have distinct boundaries between the various substances of which they are composed. Suppose some small pieces of iron are mixed with water (two substances). The result is a mixture, because its composition is variable. Furthermore, it is a **heterogeneous mixture**, because it is not uniform throughout. On the other hand, if salt is mixed with water, the salt dissolves, and the result is a homogeneous mixture—still a mixture because its composition can be varied, but homogeneous because it is uniform throughout. Homogeneous mixtures are commonly called **solutions**.

These basic categories of matter are illustrated schematically below.



The specific characteristics by which a given substance is distinguished from all others are called the **properties** of that substance. Properties such as melting point, color, density, and electrical conductivity, which can be observed without changing the composition of

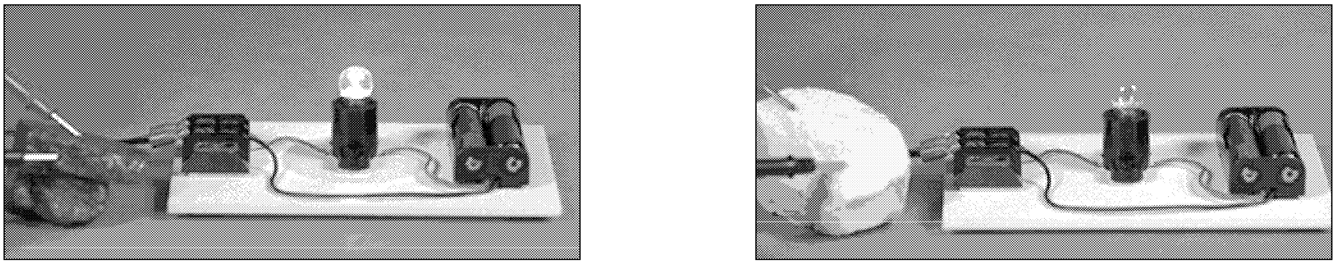


Figure 2.1 A Physical Property of Sulfur and Lead. Sulfur (at the right) does not conduct a current. Lead (at the left) does conduct a current, as shown by the illumination of the bulb as current flows from the batteries through the lead to the bulb.

the substance, are called **physical properties**. The separation of metallic iron from ferric oxide using a bar magnet, takes advantage of the difference in magnetic properties of the two substances. **Chemical properties**, on the other hand, are those that describe the changes in composition that the substance may undergo. Thus, for the elementary substance sulfur, we determine that it is a pale yellow solid with a density of 2.07 g/cm^3, a melting point of 112.8 °C, and a boiling point of 444.6 °C, and that it does not conduct an electric current, are all observations of its **physical properties**. However, the fact that it combines with oxygen to form a different substance (sulfur dioxide) with its own specific set of properties is a statement of a **chemical property**. The electrical characteristics of elemental sulfur and lead are illustrated in Figure 2.1.

States of Matter

Any sample of matter at a given pressure and temperature must exist in one of three physical forms: solid, liquid, or gas. These forms are referred to as the states of matter.

Physical and Chemical Changes

The changes that substances may undergo are classified as either physical or chemical. **Physical changes** are those that do not involve any change in the composition of the substance. They include changes of state (for example, melting and evaporation) and changes in shape or size (such as when a bar of iron is ground to a fine powder). A chemical change in matter is one in which its composition undergoes change; substances are converted into other substances. The combination of sulfur and oxygen to form sulfur dioxide is an example of a chemical change. Chemical changes are commonly referred to as **chemical reactions**.

Systems and Phases

The term **system** is frequently used in science simply to designate the particular body of matter under immediate consideration. It may be the contents of a test tube, the contents of a landlocked sea, or the contents of a living cell. A **phase** is a part of any system that is physically and chemically homogeneous. Thus, we may speak of one-phase systems, two-phase systems, and so forth. A homogeneous mixture is a one-phase system, whereas a heterogeneous mixture is a multiphase system. As an illustration, consider a sealed bottle, half full of water and containing a few pieces of iron. The contents of that bottle are a **three-phase system**, consisting of a solid phase (iron), a liquid phase (water), and a gaseous phase (the air above the water).

Problem 2.1

Classify each of the following as a substance or a mixture. If the matter is a substance, indicate whether it is an element or a compound; if the matter is a mixture, indicate whether it is homogeneous or heterogeneous.

a. air

b. baking soda

c. vinegar

Solution:

a. Air is a homogeneous mixture consisting mostly of the elementary substance nitrogen. A smaller percentage of air is the elementary substance oxygen. Many compound substances, such as carbon dioxide, carbon monoxide, and methane, are present in small quantities.

b. Baking soda is the compound substance sodium hydrogen carbonate (also called sodium bicarbonate).

c. Vinegar is also a homogeneous mixture (uniform in composition throughout) of several compounds, primarily water and acetic acid. The acetic acid gives vinegar its sour taste.

Problem 2.2

Identify each of the following as chemical or physical changes

a. the tearing of paper

b. the rusting of iron

c. the souring of milk

Solution:

a. The tearing of paper is a physical process. Each piece of paper after the tearing has the same chemical composition and the same properties as the whole piece of paper.

b. The rusting of iron is a chemical process. Rust is different in chemical composition from iron—it has a different composition (it is in fact a compound, whereas iron is an elementary substance) and a different set of properties (different melting point, color, conductivity, and so on).

c. The souring of milk is also a chemical process. The fact that sour milk tastes very different from normal milk indicates that a change in composition (and, consequently, properties) has occurred.

Problem 2.3

A 1.00-g sample of a substance is heated in air. When the process is complete, only one substance is found and it weighs 1.24 g. Is the original substance an element or a compound?

Solution:

The original substance could be either an element or a compound. The new substance that is formed after heating could result from the combination of an element with oxygen (or perhaps nitrogen), thereby resulting in a compound that is heavier than the element. On the other hand, the substance could be a compound that could combine with oxygen to produce a new compound that would also be heavier than the original compound.

Problem 2.4

Which of the following experiments would indicate that air is a mixture, not a single substance?

a. Heating a sample of barium in air and finding that only one compound had been produced;

b. Lowering the temperature of a sample of air and finding that liquid condensed at several different temperatures; or

c. Measuring the density of three different samples of air (using the same temperature and pressure) and finding that the densities of each sample were slightly different.

Solution:

a. The fact that only one compound is formed by reaction with barium could be taken as an indication that only one substance is present in air. However, it is entirely possible that barium would only react with one of the constituents of the mixture. In fact, barium will only react with oxygen (not nitrogen) at room temperature. Thus, the observation of only one compound would not prove that air is a single substance, nor would it prove that air is a mixture.

b. The finding that condensation of liquids occurs at several different temperatures indicates that more than one substance is present. In other words, the constituent substances in the mixture have different boiling points.

c. The observation that three different samples of air have different densities must indicate that the gas is a mixture. The density of a gas is a physical property and varies from one substance to another. One liter of carbon dioxide, for example, weighs more than one liter of oxygen. Presumably, the samples were taken at different locations, where the composition of the air differs, perhaps as a result of smog, emissions from factories, etc. If air were a single substance, then all samples should have the same densities (if the densities are measured carefully and correctly).

2.3 SOME LAWS OF MATTER

By the beginning of the nineteenth century, scientific investigation had led to the formulation of several laws dealing with the composition of matter. Three of the most fundamental are the Law of Conservation of Matter, the Law of Constant Proportions, and the Law of Multiple Proportions. Each of these laws is the result of many experiments and observations made over many years and is, in essence, a special type of generalization. (As discussed in Chapter 1, laws are generalizations that have very few, if any, exceptions.)

The Law of Conservation of Matter was first published by Antoine Lavoisier in 1789:

In any chemical reaction, the mass of the system remains constant.

Thus, if substances A and B undergo a chemical reaction, producing substances C and D, then the total mass of A and B consumed is equal to the mass of C and D produced. Another way in which this law is sometimes expressed is **matter is neither created nor destroyed in a chemical reaction**.

In 1799, Proust published **The Law of Constant Proportions** (also called the Law of Constant Composition) which states that:

Different samples of the same pure substance contain elements in the same proportions by weight.

If, for example, we analyzed a number of different samples of pure calcium carbonate taken from a variety of sources, all the samples would be found to contain 40.04% calcium, 12.00% carbon, and 47.96% oxygen. Although this seems like an obvious statement of fact to us, it was an important generalization of much quantitative information from the 17th and 18th centuries.

A third law dealing with the composition of matter, **The Law of Multiple Proportions**, was published by John Dalton in 1805:

When two elements combine to form more than one compound, the weights of one element that combine with the same weight of the other are in the ratio of small whole numbers.

By way of illustration, consider the two different compound substances water and hydrogen peroxide. Each of these substances is composed only of the elements hydrogen and oxygen, but in water the ratio by weight of oxygen to hydrogen is 8 to 1, whereas in hydrogen peroxide it is 16 to 1. Thus, the weights of oxygen that are combined in the two compounds with one part by weight of hydrogen are in the ratio of 8 to 16, or 1 to 2; that is, small whole numbers.

2.4 DALTON'S ATOMIC THEORY

John Dalton's atomic theory was an attempt to understand the fundamental nature of matter. Dalton's thinking was influenced by his knowledge of the three laws of matter and the classification of matter discussed above. His model first appeared in print in 1808 and consisted essentially of the following postulates:

1. Matter is composed of extremely small, indivisible particles called atoms. (It appears that Dalton visualized atoms as tiny, hard spheres.)
2. Different kinds of atoms exist and each kind has its own size, mass, and specific set of properties.
3. Each different kind of atom corresponds to a different element; that is, all atoms of a given element are of the same kind, but atoms of different elements are of different kinds.
4. Compounds are composed of atoms of different elements combined with one another in simple ratios.
5. Chemical reactions involve only the combination, separation, or rearrangement of atoms. Atoms are not created, destroyed, or changed in any way.

Figure 2.2 illustrates the combination of atoms of different elements in a one-to-one ratio to form a compound.

Dalton's model explained the fundamental laws of chemical composition. If atoms have specific masses and if chemical reactions involve only rearrangements of atoms, then matter must adhere to the Law of Conservation of Matter. Furthermore, if compounds are simply combinations of atoms of different elements in fixed ratios, then in every sample of the same compound, the elements must always be present in the same proportions by mass. Finally, the Law of Multiple Proportions is explained by the combination of one atom of one element with one atom of a second element to form a compound, or of one atom of the first with two atoms of the second to form a different compound, and so forth. The laws of composition of matter do not constitute *proof* of the atomic theory, but the atomic theory provides one satisfactory explanation of the laws.

Unsophisticated as it may seem today, John Dalton's atomic theory represented a giant step forward in the development of chemistry. It provided acceptable explanations of observed facts and enabled chemists to make predictions that could then be tested experimentally; it laid the foundation for a system of relative masses of the elements so that chemical reactions could be studied on a quantitative basis; and it paved the way for the multitude of scientific investigations that have led to our present concept of matter and that are still continuing.

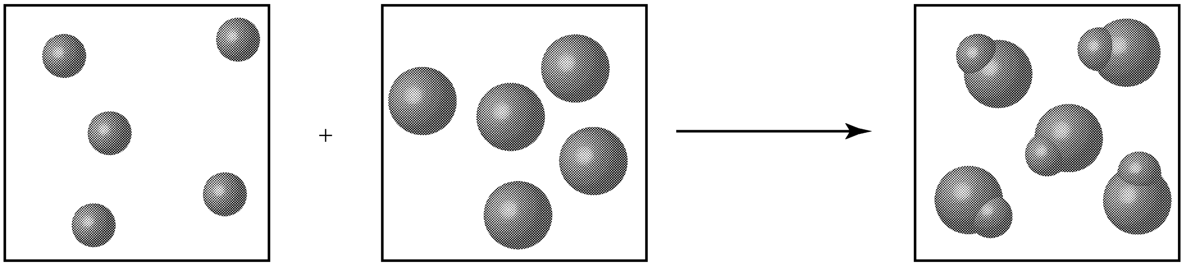
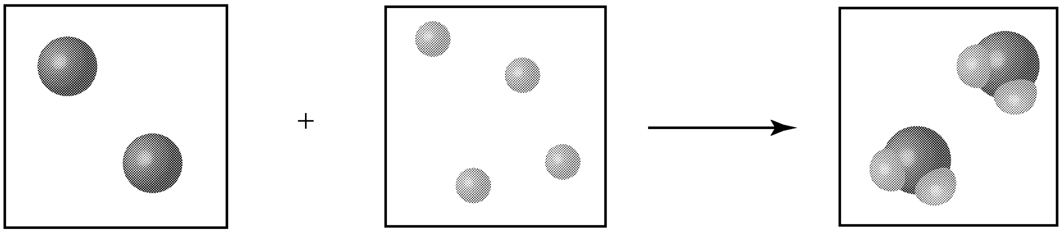


Figure 2.2 Combination of atoms to form compound.

Visualization 2.1

Make a drawing that uses Dalton's model to explain the reaction of one element with another in a one-to-two ratio to form a compound.

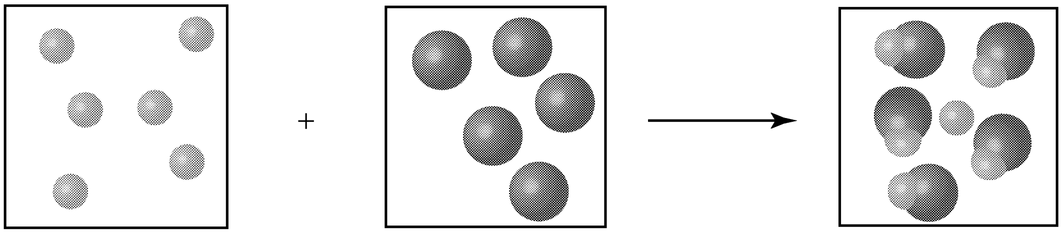


However, any theory is subject to refinement and modification as new observations are made, and Dalton's theory was no exception. While its basic tenets (that matter is made up of atoms, and chemical reactions are simply rearrangements of these atoms) are almost universally accepted today, evidence accumulated since Dalton's day has shown some of the details of his model to be inadequate. In particular, his belief in the indivisibility of atoms has been disproved by experimental evidence accumulated over the years.

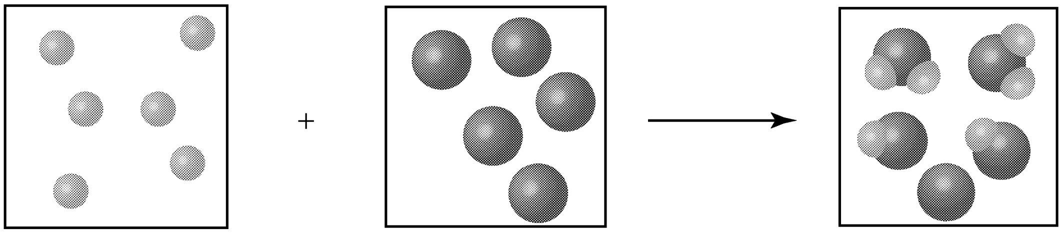
Visualization 2.2

Which of the following depictions of a chemical reaction illustrates the Law of Multiple Proportions according to Dalton's model:

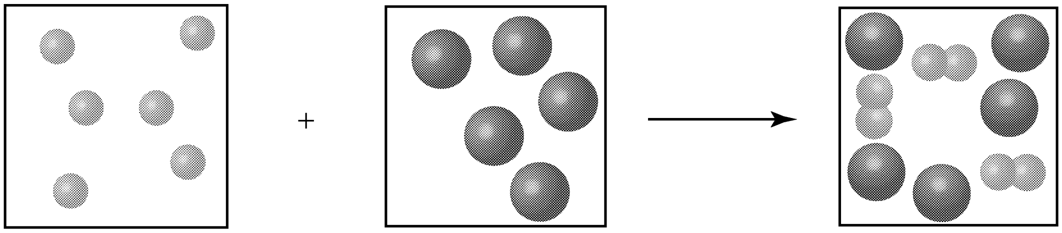
(a)



(b)



(c)



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Visualization 2.2 *Continued*

Solutions:

a. Incorrect, this scheme shows only one type of compound being formed with the atoms in a one-to-one ratio. Notice that one small atom is left over when the reaction is complete.
b. Correct, this scheme shows two types of compounds being formed from the same elements. One of the compounds contains the atoms in a one-to-one ratio, the other contains the atoms in a two-to-one ratio. Notice that one large atom remains when the reaction is complete.
c. Incorrect, this scheme shows no compound being formed. Two small atoms have combined, however, to form what we call a diatomic molecule. The large atoms have not combined in any way.

Problem 2.5

When you are trying to understand a model (or concept), it can be helpful to assume for a moment that some part of the model works differently. For example, if Dalton had postulated that there was only one kind of atom (postulate 2), how would that affect how well the model agrees with observation?

Solution:

If there were only one kind of atom, there could only be one element; that is, there would be no compound substances. However, the atoms could combine with one another in different ways: two atoms could combine to form a diatomic elementary form, three atoms could combine to form a triatomic elementary form, and so on. Each of these different elementary forms would have a different set of properties. Thus, there could be an infinite number of substances, each derived from the combination of some number of the same kind of atom, each with its own set of properties. Presumably each of these substances could be broken down into the simplest form of the element—the monatomic form. In fact, all substances can be broken down into their constituent elements and these elements, in their monatomic forms, are not the same (they have different properties).

2.5 EVIDENCE OF SUBATOMIC PARTICLES

The observations that led to a gradual refinement and extension of the atomic theory are numerous indeed. We present here a brief account of the most significant breakthroughs that are helpful in acquiring an understanding of modern atomic theory.

The Electron

Near the middle of the nineteenth century, a new field of investigation into the structure of matter was opened by the invention of the gas discharge tube, forerunner of the modern television picture tube. Basically, this device consists of a closed glass tube, into the ends of which are sealed two metal plates to serve as electrodes (Figure 2.3). A high voltage (5,000–10,000 volts) is imposed across the electrodes. If the air (or other gas) in the tube is at atmospheric pressure, nothing is observed. However, if most of the air is pumped from the tube, the gas that remains begins to glow and conducts an electric current. At very low pressures the glow fades, although current continues to flow, and the **anode** (the positive electrode) end of the glass tube **fluoresces** (emits light). Rays are emitted at the cathode (the negative electrode) and are directed toward the anode; the fluorescence at the anode end of the tube is caused by rays that pass through holes in the anode and strike the glass. When the rays are allowed to impinge on certain substances (for instance, zinc sulfide), the fluorescence is intensified.

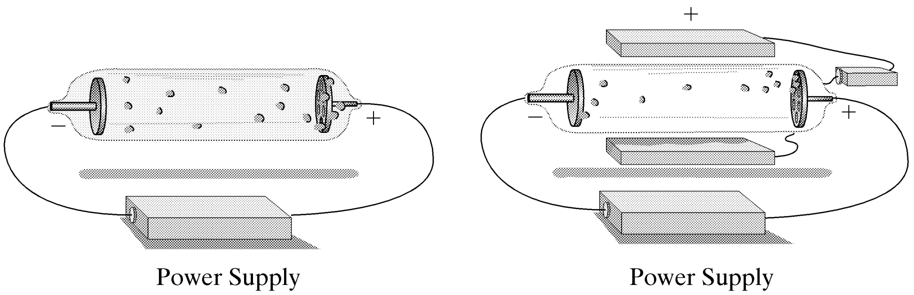

Figure 2.3 The deflection of electrons in the cathode ray tube by an electric field.

These rays, first reported by Julius Plücker in 1859, were shown to be similar to light, in that they cast a shadow. However, unlike light, they could be deflected by a magnet, which suggested that they were electrically charged. They were later given the name **cathode rays**. In 1879 Sir William Crookes reported that cathode rays are bent toward the positive pole of an electric field, indicating that they are negatively charged (Figure 2.3). In another experiment he placed a paddle wheel in the path of the rays and discovered that the wheel turned, from which he concluded that the rays are really streams of particles with definite mass. (Some 20 years later, Joseph J. Thomson showed that the masses are too small to move a paddle wheel and suggested that the motion was caused by the heating effect of the collisions, an explanation that has since been confirmed.)

The accumulated evidence indicated that cathode rays consist of very small, negatively charged particles, called **electrons**, that are emitted from the substance of which the cathode is made. This view became firmly entrenched when, in 1897, J. J. Thomson succeeded in measuring the charge-to-mass ratio of electrons by observing the deflection of cathode rays in electrical and magnetic fields applied at right angles to each other. Thomson's findings showed that this ratio remained constant regardless of the particular gas in the tube or the specific metal of which the cathode was made. This suggested that the electron was a universal particle found in all matter. In a series of experiments extending from 1908 to 1917, for which he won the Nobel Prize in physics, Robert A. Millikan successfully measured the absolute charge of the electron (-1.60×10^{-19} Coulomb (C)) and made it possible to calculate its mass. The electron's mass was determined to be 9.11×10^{-28} g, indicating a particle so light that it weighs approximately 1/1840 as much as the lightest atom, the hydrogen atom.

Here, then, was solid evidence—pieced together from the work of many investigators over a period of a half century—that Dalton's theory of the indivisibility of the atom was incorrect. Cathodes are made from elementary substances (metals), and electrons are emitted from these cathodes. If substances are composed only of atoms, then electrons must be emitted from atoms. Since electrons weigh only 1/1840 as much as even the lightest atom, the atom could no longer stand as the ultimate, indivisible particle.

The Proton

Since matter is electrically neutral and therefore, presumably, so are atoms, it was logical to suggest that the emission of electrons from atoms should leave a positively charged residue. That is, if atoms contain these negative particles, might we not also expect atoms to contain positive particles?*

---

* It is essential that you begin to develop an understanding of some fundamental aspects of charge. First, you should know that a net charge is produced whenever there is an excess of or deficiency of electrons. Objects like a rubber rod can be charged by rubbing them with a material that has a greater or lesser affinity for electrons. Second, the Law of Conservation of Charge, similar to the Law of Conservation of Mass, tells us that the total net charge of an isolated system never changes. Thus, if we manage to produce an excess of electrons (negative charge) at one point in an isolated system, there must be an equal quantity of excess positive charge at some other point. Third, like charges repel each other, whereas opposite charges attract one another. The interaction between charges is one of the most fundamental concepts in chemistry.

Partial evidence for this view was obtained in 1886 using a gas discharge tube in which the cathode was constructed with a number of holes through it. Rays were observed in the end of the tube beyond the cathode (these were called **canal rays**, since they passed through the holes (or canals) in the cathode (Figure 2.4)), and unlike the cathode rays (which are not apparent unless they strike an object that fluoresces, such as glass), canal rays possessed a luminosity of their own. Furthermore, the color of the luminosity varied with the particular gas in the tube.

It was later shown that canal rays are deflected toward the negative pole in an electric field and must therefore be positively charged. Proceeding on the assumption that canal rays were streams of positive particles (and using a technique similar to Thomson's in his studies of the electron), several scientists determined the charge-to-mass ratio of these particles and found that this ratio is not the same for all particles but varies with the particular gas in the tube.

This phenomena is now interpreted as follows: As electrons from the cathode (that is, the cathode rays) travel toward the anode, they collide with atoms of the gas in the tube. These collisions cause electrons to be dislodged from the gas atoms, and the dislodged electrons are attracted toward the positively charged anode. The atoms from which electrons have been removed, called **ions**, are now positively charged and therefore move toward the negatively charged cathode. It is these positive ions that form the canal rays.

The charge-to-mass ratio of any particular ion depends on the mass of the neutral atom, as well as on the number of electrons removed from it. However, when the gas in the tube is hydrogen—the element whose atoms have the lowest mass of all atoms—the charge-to-mass ratio of the ions formed is approximately 1/1840 of the value for an electron. If one assumes that the magnitude of the charge on this positive particle is equal to that of an electron's negative charge, then it can be calculated that the mass of the positive particle obtained when one electron is removed from a hydrogen atom is 1.672×10^{-24} g. This positive particle has been named the **proton**.

The discovery of the proton provided further evidence against the indivisibility of the atom. But it did more than that; it provided scientists with a simple model of atomic structure. A hydrogen atom could now be considered to consist of two parts: a positively charged proton, accounting for essentially all the mass of the atom, and a negatively charged, extremely light electron.

Around the turn of the century, several attempts were made to extend this model of the hydrogen atom to a generalized model that would apply to all atoms. One such model was created by Philip Lenard in 1903. Lenard had observed that cathode rays pass

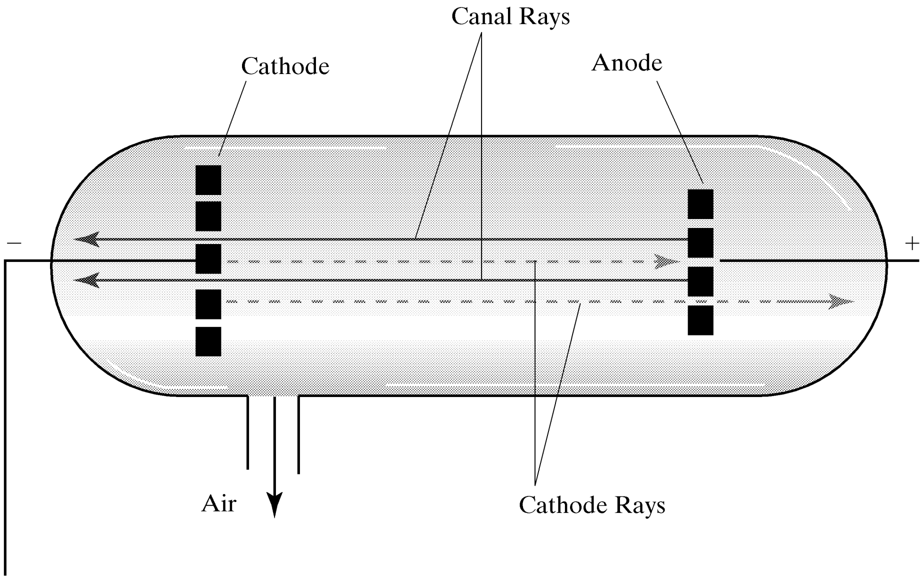

Figure 2.4 Production of canal rays.

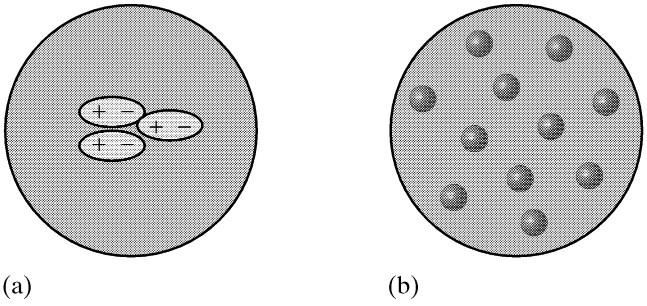

Figure 2.5 Two Models of the Interior of the Atom: (a) The Dynamid model, (b) The Plum-Pudding model.

through a foil of aluminum and was impressed with the apparent "emptiness" of the aluminum atoms. Accordingly, he proposed that atoms are shells, largely empty except for a number of what he called **dynamids** at the center (Figure 2.5a). Each dynamid consisted of a single positive charge and a single negative charge, with the number of dynamids being proportional to the mass of the atom. A second model, elaborated by Thomson in 1904, regarded the atom as consisting of a uniformly positive sphere of matter in which electrons were embedded throughout (Figure 2.5b). This frequently has been referred to as the "raisin muffin" or "plum pudding" model. Neither of these models explained all the facts satisfactorily, but scientific thought had taken a step away from Dalton's structureless atom toward an atom with a describable composition.

Radioactivity

During the same period in which the electron and proton were being characterized, another developing area of investigation—that of **radioactivity**—led to further evidence for the existence of subatomic particles.

In 1896 the French physicist Henri Becquerel made the discovery that compounds containing the element uranium spontaneously emit radiation. This radiation could darken photographic plates, induce conductivity in gases, and pass through objects such as heavy paper or thin metal foil. Marie and Pierre Curie, along with other investigators, later demonstrated that this phenomenon was a property of certain other elements as well.

Immediately following its discovery, radioactivity became an active field of study. One of the most revealing of the early investigations may be described as follows. A narrow beam of radiation was obtained by confining a radioactive substance in a thick lead block with a small hole drilled into the cavity. Since the radiation could not penetrate through lead, this arrangement produced a single directed beam of radiation which could be detected by means of a photographic plate. When the beam was made to pass through an electric field, it was found that some of the radiation was deflected slightly toward the negative electrode, some was deflected through a larger angle toward the positive electrode, and some continued on its course unaffected by the electric field. It was concluded that the radiation emitted by a radioactive element is not homogeneous, but instead consists of three kinds: one positively charged, one negatively charged, and the third without charge (Figure 2.6). These three types of radiation were designated simply by the first three letters of the Greek alphabet: alpha (α), beta (β), and gamma (γ) rays.

Subsequent study of these rays showed that **beta rays** are streams of electrons, identical in all properties to the particles of cathode rays. **Alpha rays** consist of particles with a positive charge equal in magnitude to twice that of a proton and with a mass equal to four times that of a proton. We now recognize that alpha particles are helium ions, that is, helium atoms from which two electrons have been removed. The electrically neutral **gamma rays** are electromagnetic radiation, similar to light but with a very short wavelength.

Here, then, is still further evidence of the existence of particles smaller than atoms, for in radioactivity we see a spontaneous, natural process whereby atoms undergo a self-disintegration to emit particles having masses smaller than the atoms themselves.

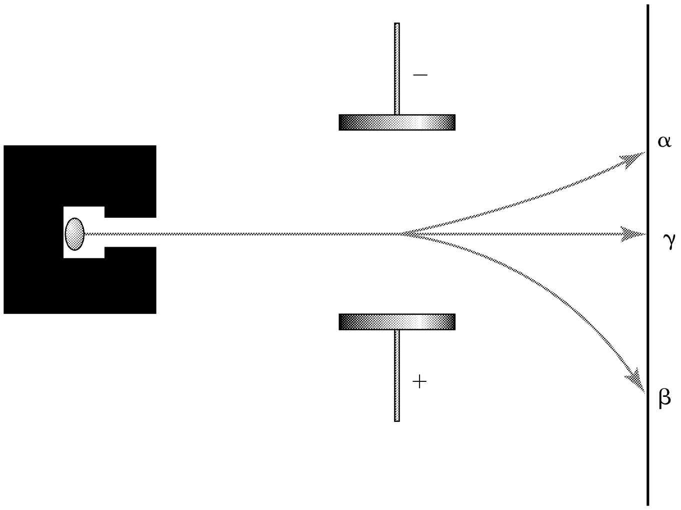

Figure 2.6 Separation of α, β, and γ Rays. Radiation from a radioactive source such as radium contains: (a) alpha particles, which are positively charged and are therefore attracted to the negatively charged plate, (b) beta particles (electrons), which are negatively charged and therefore attracted to a positively charged plate, and (c) gamma rays, which are neutral elctromagnetic radiation.

The Nucleus

As mentioned earlier, there were a number of attempts in the opening years of the twentieth century to devise a model that would represent the arrangement of the positive and negative charges within the atom. The discovery of radioactivity, and particularly of the α-particle, with its ability to penetrate thin sheets of metal, provided a new line of investigation toward the solution of this problem. Although a number of scientists of the period became involved in these "alpha-scattering" experiments, major credit is usually given to Ernest Rutherford, since he joined his own observations to those of others to provide a structural model of the atom that replaced all earlier ones. While not intended to represent any specific experiment, Figure 2.7 illustrates the general nature of these α-particle investigations. As indicated in the figure, a source of α-particles is arranged so that the alpha radiation is directed in a narrow beam onto a screen coated with some material that fluoresces when struck by α-particles (for instance, zinc sulfide). When nothing is placed

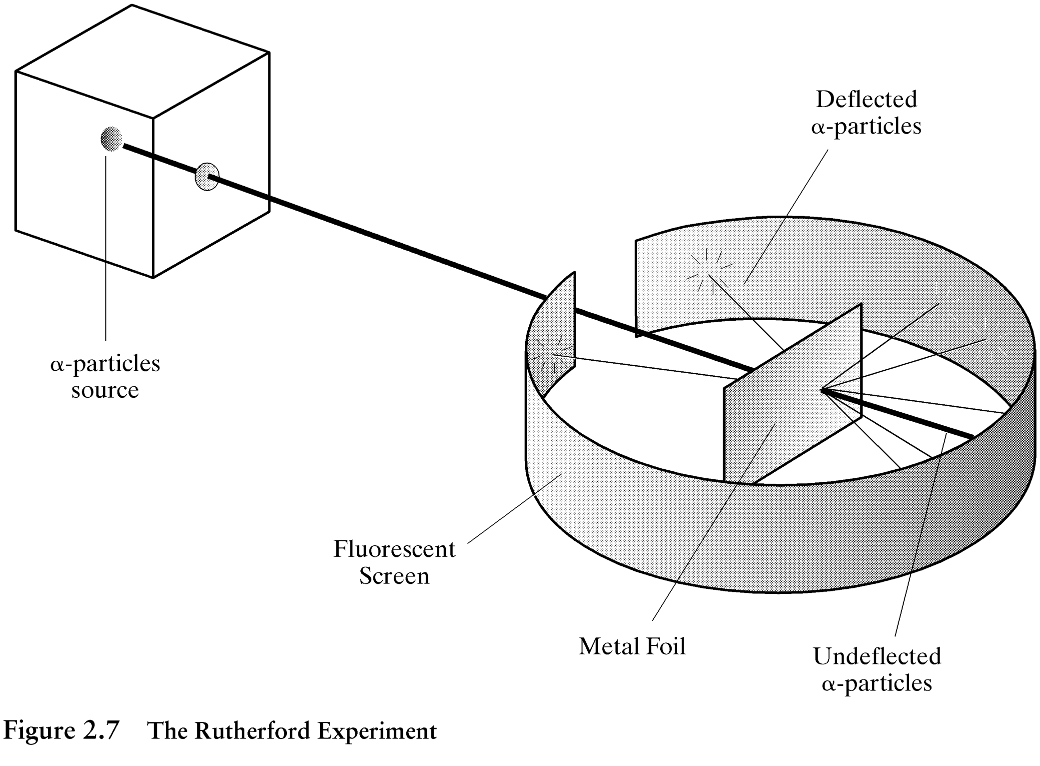

Figure 2.7 The Rutherford Experiment

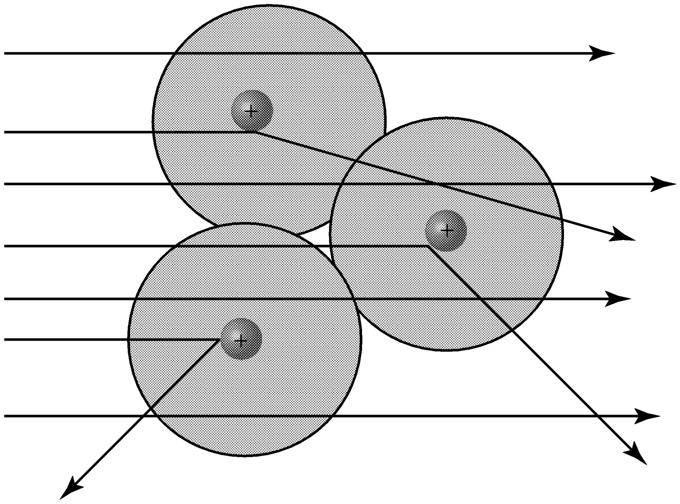

Figure 2.8 Scattering of Alpha Particles

in the path of the beam, the positively charged α-particles continue in a straight line and are observed as a glowing spot on the screen. When a very thin foil of a heavy metal (such as gold or copper) is placed in the path of the beam, most of the α-particles continue on their course, but some are deflected by the atoms in the metal. These deflections, which can be as great as 180°, are detected on the fluorescent screen.

In his interpretation of these results, published in 1911, Rutherford reasoned roughly as follows: Since α-particles bear a positive charge, they will be deflected from their paths by repulsion of other positive charges. However, because the kinetic energy* of an α-particle is very large (the mass, charge, and velocity of α-particles were known), only a particle of considerable mass and high charge within the metal atom could cause deflection through such large angles. If the positive and negative particles (protons and electrons) were distributed uniformly throughout an atom, they would exert little or no influence on the α-particles, which would therefore pass directly through the atom without deflection.

Rutherford therefore postulated that all the positive charge of the atom resides within a particle in the center of the atom. This particle, called the **nucleus**, accounts for essentially all the mass of the atom, but has a very small volume. The electrons are distributed throughout the extranuclear[†] part of the atom.

That this **nuclear model** of the atom explains the observed α-particle scattering is illustrated in Figure 2.8. In order to be deflected, an α-particle must come relatively close to a massive, highly charged nucleus. (The electrons, with their extremely low masses, will have no noticeable effect on the α-particles.) Since the nucleus occupies such a small fraction of the volume of an atom, few α-particles are deflected. The closer the path of an α-particle to a nucleus, the greater is the angle of deflection, with a deflection of 180° representing a "head-on" collision.

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[*] This is our first encounter with energy, another very important concept. Energy is usually defined as the capacity to do work. Since **work** is the product of a force and the distance through which it moves ($w = f \times d$), and force is defined as the product of a mass and its acceleration ($f = m \times a$), then **energy** is the capacity to move matter from one place to another. **Kinetic energy** is the energy a body possesses by virtue of its motion, and the amount it possesses is equal to one-half its mass times its velocity squared ($KE = 1/2\ mv^2$). **Potential energy**, on the other hand, is energy a body possesses because of its position relative to other bodies. Thus, a flowerpot hurtling down from a fifth-floor windowsill has kinetic energy as well as potential energy, but the same flowerpot poised motionless on the edge of the windowsill has potential energy only.

The energy (either kinetic or potential) possessed by the flowerpot is an example of mechanical energy, but energy exists in other forms as well, including heat, light, sound, electrical energy, and chemical energy. Each of these forms of energy may be converted into some other form, and it is through these transformations that energy may be observed. All other forms of energy may be transformed completely into heat, and for this reason energy changes are usually described in terms of heat.

[†] The words **extra**, **intra**, and **inter** are frequently used in chemistry. "Extra" means outside of; "intra" means within; and "inter" means between. For example, extranuclear means outside of the nucleus or beyond the nucleus; intramolecular means within a molecule; intermolecular means between two molecules.

The Neutron

The nuclear atomic model that emerged from the foregoing evidence—a positive nucleus, which could be thought of as an aggregate of protons, and an equal number of extranuclear electrons—had one major shortcoming: It did not account for the **masses** of atoms. A comparison of the hydrogen and helium atoms provides a simple illustration. The hydrogen atom consists of a proton (the hydrogen nucleus) and one electron; its mass, therefore, is essentially the mass of a proton. The second lightest atom, helium, has a nuclear charge twice that of a proton, and therefore the helium nucleus may be thought of as consisting of two protons. In order for the helium atom to be neutral it must have two extranuclear electrons. Two protons plus two electrons would result in a mass twice that of a hydrogen atom; but in fact, the helium atom's mass is approximately four times that of hydrogen.

Some scientists theorized that the nucleus contains more protons than its total charge would indicate, but that some of these protons are neutralized by electrons in the nucleus. Following this view, the mass of the helium atom was explained by assuming that the nucleus consists of four protons and two electrons (in addition to the two extranuclear electrons). Others postulated the existence of yet another kind of subatomic particle to account for the additional mass.

In 1930 the German scientists W. Bothe and H. Becker bombarded the element beryllium with α-particles and observed the emission of a very penetrating radiation. Shortly afterward, James Chadwick (a former student of Rutherford) investigated this radiation and showed that it consists of particles that each have a mass of 1.675×10^{-24} g (almost exactly equal to that of a proton), but no charge. This new particle was named the **neutron**.

Thus, the last essential piece of the puzzle had been put into place, and the nuclear model of the atom became firmly entrenched. In the years since, many additional subatomic particles have been discovered (such as the positron, neutrino, and meson), but these are not essential for an explanation of most of the physical and chemical properties of matter.

2.6 MODERN ATOMIC THEORY

Let us now examine the present concept of the atom—a concept that may indeed be changed drastically in the future but that in our present state of knowledge is the most satisfactory, workable model available to us.

Atoms, the basic building blocks of all matter, are exceedingly small, and have diameters of the order of 100 to 300 pm (1 pm = 10^{-12} m). Their size may be appreciated by the realization that a single grain of sand contains about 10^{18} atoms. (If 300,000,000 planets each had a population equal to that of the earth, their combined population would be approximately 10^{18}.)

Problem 2.6

An aluminum atom has a diameter of about 300 pm. How many of these atoms could be placed side-by-side in a line 1 inch long?

Solution:

We must first convert from inch to meters because the diameter of the atom is given in pm. Since 1 in is 2.54 cm and 1 cm is 0.01 m,

$$1 \text{ in} \times 2.54 \text{ cm/in} \times 0.01 \text{ m/cm} = 0.0254 \text{ m}$$

Thus, we want to know how many atoms with a diameter of 300 pm can be placed on a line 0.0254 m long. We now convert to pm:

$$0.0254 \text{ m/in} \times 10^{12} \text{ pm/m} = 2.54 \times 10^{10} \text{ pm/in}$$

Finally, we must divide 2.54×10^{10} pm by the diameter of one atom in order to get the number of atoms on the line,

$$\frac{2.54 \times 10^{10} \text{ pm}}{300 \text{ pm/atom}} = 8.47 \times 10^{7} \text{ atom}$$

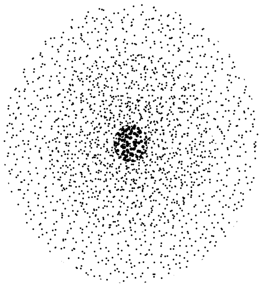


Figure 2.9 The "Electron-Cloud" of the Atom

Each atom consists of one positively charged nucleus and one or more negatively charged electrons. Since an atom is neutral, the nuclear charge is equal to the total charge of the electrons.

The nucleus accounts for only a very small fraction of the volume of an atom. Nuclei have diameters of about 10^{-2} pm. If an atom could be enlarged until its nucleus were the size of a tennis ball, the atom would be a sphere nearly a mile in diameter. The size of an electron is estimated to be in the same range as that of a nucleus, but the electron is extremely light, weighing only about 1/1840 as much as the lightest atomic nucleus. The nucleus, therefore, accounts for essentially all of the mass of the atom.

Electrons may be thought of as particles in rapid motion, but (as we shall see later) with wave-like properties. In effect, they fill the extranuclear part of the atom with a diffuse cloud that may be visualized by comparing it with a multiple-exposure photograph of a moving object, where the density is greatest in the area traversed most frequently by the object. The density of the electron cloud decreases as the distance from the nucleus increases, so that the boundaries of the atom are not sharply defined (see Figure 2.9). The electronic structure of atoms will be dealt with in detail in Chapter 3.

Atomic Number

An atom of the lightest element, hydrogen, has a proton as its nucleus and one electron forming the electron cloud. The sodium atom, with a nuclear charge 11 times as great as that of the hydrogen atom, has 11 protons in its nucleus and, because the atom is electrically neutral, there are 11 extranuclear electrons.

The nuclear charge, equal to the number of protons in the atom, is called the **atomic number**. It is this number—not the atomic mass, as Dalton believed—that distinguishes one element from another. Atoms with the same atomic number are all atoms of the same element; atoms with different atomic numbers are atoms of different elements.

The terms "elementary substance" and "compound substance" may now be given more theoretical definitions based on our atomic model: An **elementary substance** is a substance whose atoms all have the same atomic number, and a **compound substance** contains atoms with different atomic numbers.

Mass Number

All atoms except the hydrogen atom have nuclear masses greater than can be accounted for by the protons alone. Since these mass differences are essentially whole-number multiples of the mass of a neutron, we may consider atomic nuclei to contain, in addition to their protons, some number of neutrons. Taken together, these nuclear particles—protons and neutrons—are referred to as **nucleons**, and the number of nucleons in an atomic nucleus is called the **mass number**. Thus:

$$\text{Mass number} - \text{Atomic number} = \text{Number of neutrons}$$

A particular atom with an atomic number of 17 and a mass number of 35, therefore, contains 17 protons and 18 neutrons in its nucleus, and has 17 extranuclear electrons.

To designate a specific atom and its nuclear contents, the symbol for the element is written with the atomic number as a subscript and the mass number as a superscript, both to the left of the symbol. Table 2.1 illustrates this notation with a few examples.

TABLE 2.1 Some Examples of Atomic Designations

	Protons	Neutrons	Electrons
$^{4}_{2}He$	2	2	2
$^{12}_{6}C$	6	6	6
$^{80}_{35}Br$	35	45	35
$^{127}_{53}I$	53	74	53
$^{227}_{89}Ac$	89	138	89

Isotopes

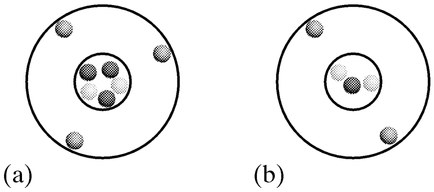
While all atoms of the same element have the same atomic number, they do not necessarily have the same mass number. For example, the element chlorine occurs in nature with atoms of two different masses, one represented by $^{35}_{17}Cl$, the other by $^{37}_{17}Cl$. Note that both atoms have 17 protons and 17 electrons, but one has 18 neutrons, whereas the other has 20. Both are atoms of the same element, and they have the same chemical properties, but they differ slightly in those physical properties that depend on mass. Atoms that have the same atomic number but different mass numbers are called **isotopes**.

As a further example of the occurrence of isotopes, consider the element hydrogen. Most hydrogen atoms have the composition we have indicated above; that is, the nucleus is simply a proton and we can designate the atom as $^{1}_{1}H$. However, about 1 out of every 5,000 hydrogen atoms has a mass twice that of the others. The nucleus of this heavier atom has a neutron as well as a proton, and the atom is therefore designated as $^{2}_{1}H$. This heavier isotope is called deuterium and its nucleus is sometimes referred to as a deuteron.

For a few of the elements only one isotopic form is known, but most elements have several isotopes—as many as 10 in the case of the element tin.

Visualization 2.3

Identify the isotope indicated by the following pictures (protons are indicated by black spheres, neutrons by white spheres, and electrons by grey spheres):


(a) (b)

Solution:

a. ^{5}Li
b. $^{3}H^{-}$. Notice that this atom has one more electron than proton. It is therefore negatively charged.

2.7 ELEMENTS: NAMES AND SYMBOLS

More than 110 different elements are known today (that is, there are atoms with 110 different atomic numbers), but not all of these may be found in nature. Some have been made synthetically in recent years, including a few that may once have occurred in the earth's crust but have disappeared through radioactive disintegration. Some of the elements were discovered and characterized many years before John Dalton; other elements have been synthesized so recently that official names have not yet been established for them.

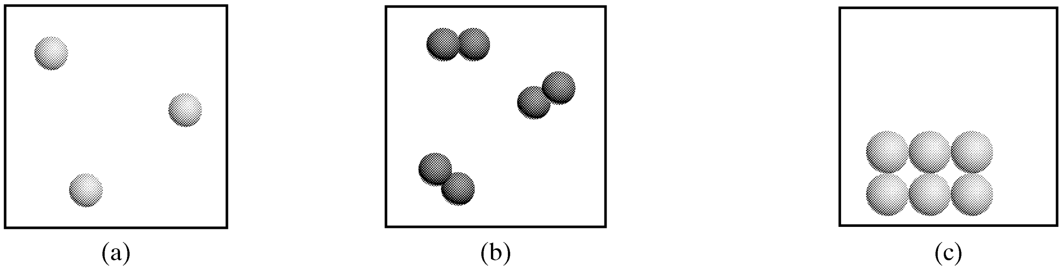
Although the elements may be distinguished from one another by reference to their atomic numbers, each (except for the last several) has been given a name. The origins of the names range widely, from mythological characters (thorium, tantalum, neptunium) to the names of notable scientists (curium, einsteinium, mendelevium). Some elements have been named for an outstanding property, such as bromine (bad odor), phosphorus (light bearer), and argon (lazy one). Nations have been honored (polonium, germanium, americium), as have small villages (magnesium for the ancient town of Magnesia in Asia Minor; strontium for the Scottish village of Strontian).

As a matter of convenience in describing chemical reactions, a system of chemical shorthand has been developed in which each element has been assigned a symbol. This system of symbols, first introduced by the Swedish chemist Jöns Berzelius in 1813, has been extended as new elements were discovered and is now in use by international agreement. The symbols are the initial letters of the names of the elements, and in cases of duplication, an additional letter is taken from the name (for example, C for carbon, Cl for chlorine, Ca for calcium, Cd for cadmium, and so forth). However, not all of the symbols are based on the English name. Some are derived from the Latin name for the element—for example, Hg for mercury (*hydrogyrum*), K for potassium (*kalium*), and Fe for iron (*ferrum*)—and one comes from the German name, W for tungsten (*wolfram*).

For most elements, the symbol has two meanings: it represents an atom of that element (that is, an atom with a specific atomic number), and it represents the elementary substance composed of those atoms. For example, the symbol Cu is used to designate an atom with an atomic number of 29, but it is also used to represent a piece of copper. There are some exceptions to this dual use of the symbol, however. Some elementary substances do not normally exist as collections of separate atoms, but as **molecules**, which are discrete groupings of two or more atoms linked together. In these cases, a numerical subscript is added to the symbol for the element to indicate the number of atoms in each molecule. For example, N is the symbol for the element nitrogen and represents atoms with atomic number 7. But the elementary substance called nitrogen, a colorless, odorless gas, exists in the form of **diatomic** (two-atom) **molecules**. To designate gaseous nitrogen, therefore, we write N_2. Some other common elementary substances in the same category are oxygen (O_2), hydrogen (H_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), iodine (I_2), phosphorus (P_4), and sulfur (S_8).

Visualization 2.4

In the diagrams below light grey is used to indicate chlorine, black is used for oxygen, and gray is used for silver. For each picture, describe the substance depicted as accurately as possible.



Solutions:

In diagram (a) the light grey circles represent chlorine atoms, Cl, which because of their separation are presumably in the gas phase. In diagram (b) two oxygen atoms are attached to each other to form diatomic oxygen, represented with the formula O_2. In diagram (c) atoms of silver are stacked very closely and orderly. Diagram (c) therefore represents solid elementary silver.

2.8 ATOMIC WEIGHTS

With the acceptance of Dalton's postulates that the masses of atoms are different for each element and that chemical reactions are simply rearrangements of atoms, it became apparent that knowledge of atomic masses was of great importance in the investigation of chemical processes. The actual masses of individual atoms are extremely small, however. As indicated earlier in this chapter, the lightest atom weighs only about 1.67×10^{-24} g, and even the heaviest atom known weighs only about 270 times that. Furthermore, chemists are not able to carry out reactions with only a few atoms but must use amounts of substances that contain very large numbers of atoms.

Efforts were made, therefore, to determine the *relative* masses of atoms. To understand the method used, assume that some arbitrary value is assigned to the mass of an atom of element Q, and that the mass of element X that will combine with a given mass of Q is experimentally determined. If one knows the ratio in which atoms of Q and X combine, a value can be assigned to the mass of an atom of X *relative* to the arbitrary mass assigned to Q. These *relative* masses are called **atomic weights**. Since oxygen combines directly with nearly all the other elements, it is not surprising that it was chosen as the reference standard early in the development of atomic weight systems. After a number of attempts to find a suitable reference value, 16 was chosen as the arbitrary mass of an oxygen atom, because this particular value gave approximate whole-number atomic weights for many other elements, and gave hydrogen, the lightest element, an atomic weight of approximately 1. Thus, the atomic weight of an element was established as the mass of an atom of that element relative to the mass of an oxygen atom taken as exactly 16 units. This atomic weight scale served chemists well for more than a century.

The discovery of the existence of isotopes altered the concept of atomic weights somewhat. It was found that all atoms of the same element are *not* identical in mass, and that most natural samples of an element are mixtures of two or more isotopes. In working with substances in the laboratory, one is dealing with enormous numbers of atoms, with the various isotopes present in fixed ratios. An experimentally determined atomic weight, therefore, is really an average of the masses of the various isotopes of the element, weighted according to their relative abundance. Even in the reference standard, oxygen, the assigned value of exactly 16 units did not apply to any single atom, but to a weighted average of the naturally occurring isotopes, ${}^{16}_{8}\mathrm{O}$, ${}^{17}_{8}\mathrm{O}$, and ${}^{18}_{8}\mathrm{O}$.

The realization that atomic weights are really average masses of atoms did not reduce the usefulness of the oxygen-based atomic weight scale, for chemists usually work with elements in their naturally occurring mixtures. However, as interest in nuclear reactions increased, and scientists began to deal with pure isotopes, it became convenient to develop a different atomic weight system based on the assignment of exactly 12 units to the carbon-12 isotope $({}^{12}_{6}\mathrm{C})$. The **atomic mass unit** (abbreviated **amu**) is now defined as a mass equal to 1/12 the mass of the $({}^{12}_{6}\mathrm{C})$ atom. The atomic weights of the elements based on this reference standard are listed in Appendix 8.

Based on the carbon-12 scale, the masses of both the proton and neutron are very nearly 1 amu. More precisely, the mass of the proton is 1.0073 amu, the mass of the neutron is 1.0087 amu, and that of the electron is 0.00055 amu.

Historically, atomic weights were determined by chemical analysis, using a variety of chemical reactions and employing the reasoning described above for the hypothetical elements Q and X. These methods have been largely replaced by techniques that permit the determination of the relative atomic masses and the relative abundances of the various isotopes of an element. The instrument used for these measurements is designed to determine the mass-to-charge ratio of positive ions and is called a mass spectrometer, shown schematically in Figure 2.10.

One type of mass spectrometer consists of a curved, evacuated tube, positioned in a magnetic field. At one end of the tube, the element under investigation is admitted as a gas through a very small opening. Inside the tube the atoms of the sample gas are bombarded by electrons from the "electron gun." (When a metal filament such as tungsten is heated to a very high temperature, atoms of the metal emit electrons. The "electron gun"

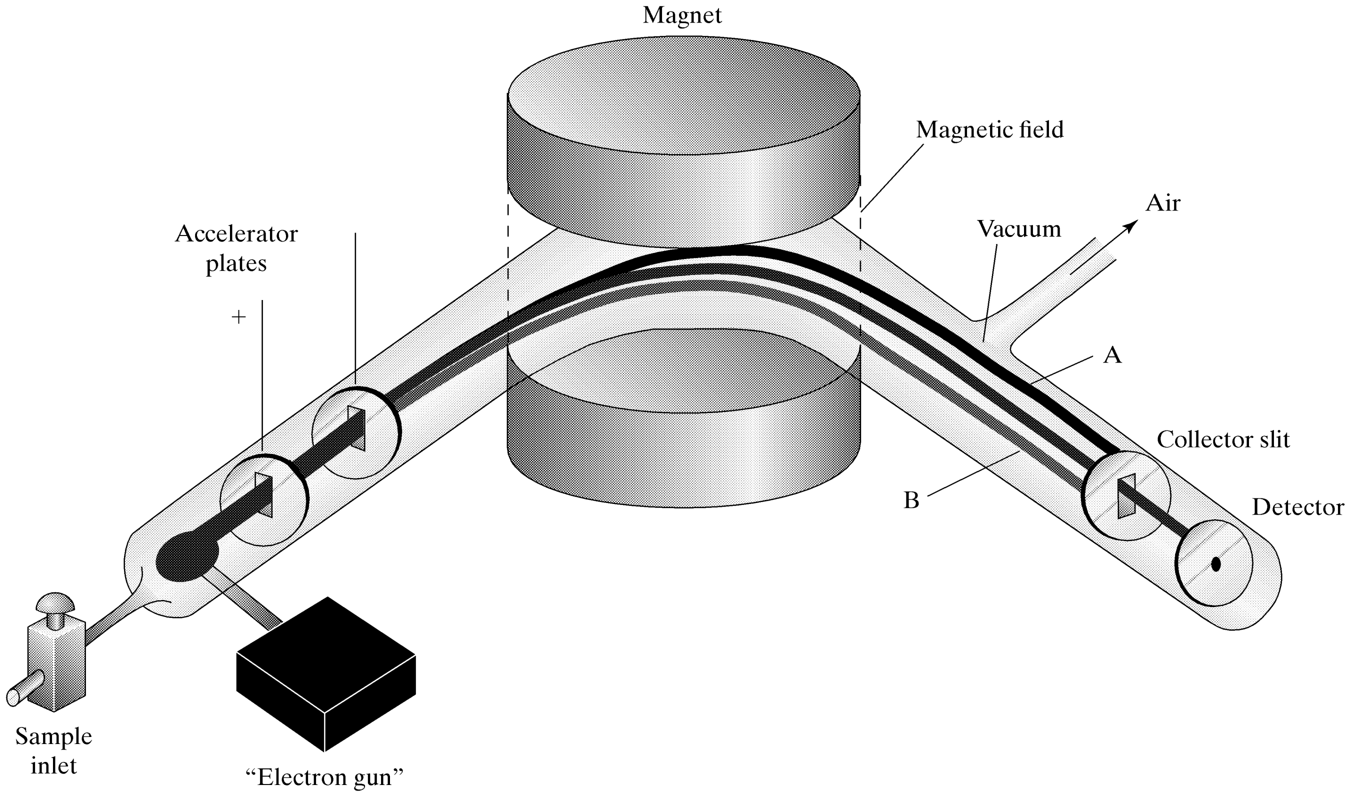


Figure 2.10 A mass spectrometer

accelerates these electrons so that they enter the ionization chamber of the mass spectrometer with very high energy.) Some of the collisions between the bombarding electrons and the atoms of the gas result in the dislodgment of one or more electrons from the atoms, forming positive ions. A strong electrostatic field (500–5,000 volts), produced by two charged accelerator plates, accelerates the positive ions into the magnetic field. The magnetic field causes the ions to be deflected from their straight-line paths.

The extent to which an ion is deflected depends on a number of factors: the strength of the magnetic field (the stronger the field, the greater the deflection); the voltage between the accelerator plates (the greater the voltage, the less the deflection); the mass of the ion (the greater the mass, the less the deflection); and the ion's charge (the greater the charge, the greater the deflection). The magnetic-field strength and the accelerating voltage can, of course, be varied by the operator of the instrument. However, at any given field strength and voltage, the extent of deflection (that is, the path of the ion beam) is determined by the mass-to-charge ratio of the ion. The smaller this ratio, the greater the deflection of the ion from its straight-line path. If we compare ions that have the same charge, then the heavier the ion, the less deflection it will undergo. Thus, if the ion beam passing through the collector slit consists of ${}^{12}_{6}C^+$ ions; beam A represents heavier ions (for example, ${}^{19}_{9}F^+$) and beam B represents lighter ions (for example, ${}^{4}_{2}He^+$).

For a given field strength and a given accelerator voltage, only those ions with a specific mass-to-charge ratio can pass through the collector slit, where they strike the detector. The electrical impulse they produce is amplified and fed into a recorder. By systematically varying *either* the field strength or the voltage, all the different ions present (that is, ions with different mass-to-charge ratios) can be focused one-by-one on the collector slit. The resultant recording, called the mass spectrum* is a series of peaks, each repre-

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* A spectrum is a plot of intensity vs. some variable whose magnitude varies monotonically. For example, a visible spectrum is a plot of the amount of light absorbed by a sample *vs.* the wavelength of the light; that is, the intensity of each peak indicates the amount of light absorbed as the wavelength of the light passing through the sample is changed.

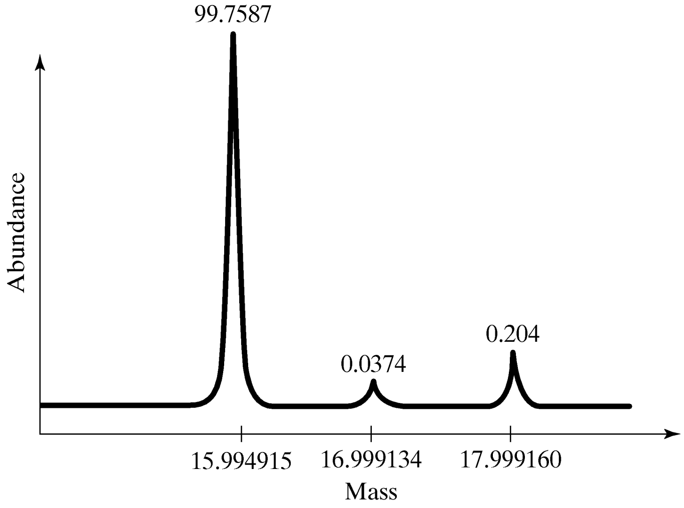

Figure 2.11 The mass spectrum of oxygen.

senting a different mass-to-charge ratio. The position of each peak is a measure of the atomic mass, which can be calculated (relative to the carbon-12 mass) from the known field strength and the acceleration voltage. The height of each peak is a measure of the relative abundance of each different ion (that is, each different isotope).

The mass spectrum of oxygen is shown in Figure 2.11. (Only the peaks for the ions with a single positive charge are shown.)

The spectrum reveals the presence of three isotopes, ^{16}O, ^{17}O, and ^{18}O, with relative abundances of 99.7587, 0.0374, and 0.204, respectively. The isotopic masses are relative to $^{12}C = 12.0000$ amu. From this information, the atomic weight of oxygen can be calculated as follows:

$$\begin{aligned} 0.997587 \times 15.994915 &= 15.9563 \\ 0.000374 \times 16.999134 &= 0.00636 \\ 0.00204 \times 17.999160 &= \underline{0.03670} \\ \text{atomic weight} &= 15.9994 \end{aligned}$$

A modern commercial mass spectrometer and a spectrum displayed on its computer monitor is shown in Figure 2.12.

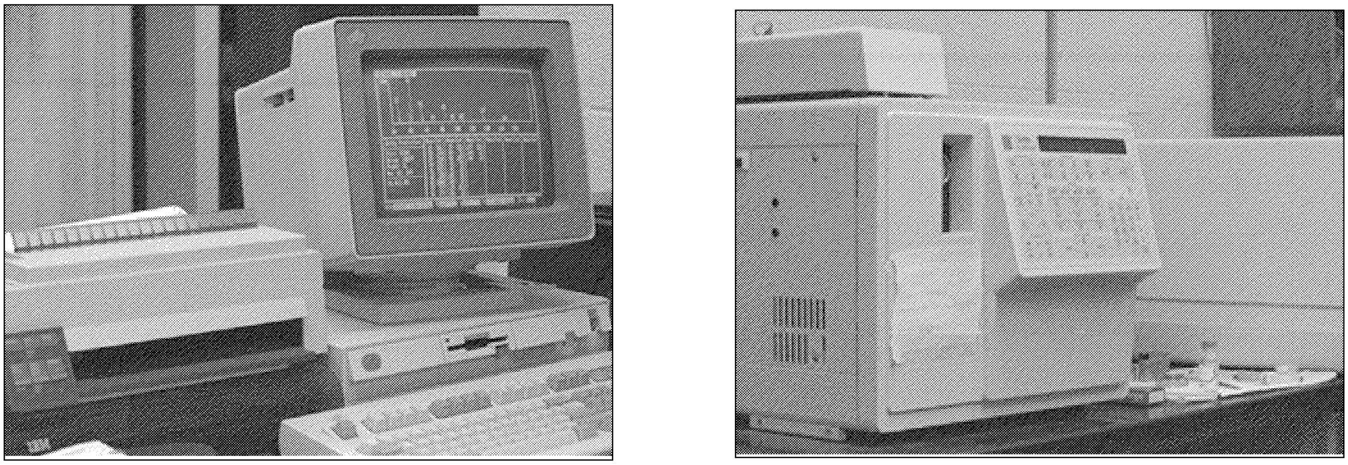

Figure 2.12 A Commercial Mass Spectrometer. Notice that the spectrum is displayed on a computer monitor. The computer also contains a data base of the spectra of tens of thousands of compounds. Many compounds can be identified by computer matching of the experimental spectrum with the spectra in the data base.

Methodology 2.1

Boron has two naturally-occurring isotopes. One of these isotopes is ^{11}B and has an abundance of 80.22% and a mass of 11.009 amu. Calculate the mass of the other isotope.

1. What is the abundance of the other isotope?

Because there are only two isotopes, the other isotope must have an abundance of 19.78%.

2. What does the atomic mass of 10.81 for boron represent?

The mass of the "average" atom of boron.

3. If there are only two isotopes, how is this average obtained?

As the weighted average

$$0.8022(11.009) + 0.1978(x) = 10.81$$

where x is the mass of the other isotope.

Solve for x.

$$\begin{aligned} 8.813 + 0.1978x &= 10.81 \\ x &= 10.00 \end{aligned}$$

4. What isotope has this mass?

Because the mass of the proton and neutron are nearly identical and each is very close to 1.00 amu (and the mass of the electron is much less), the total number of protons and neutrons must be 10. Thus, this isotope is ^{10}B.

2.9 AVOGADRO'S NUMBER AND THE MOLE

Chemists cannot work with individual atoms. They must work with visible amounts of matter containing huge numbers of atoms, and they must weigh substances in grams, not in atomic mass units. It is therefore necessary to be able to relate the masses of single atoms to the masses of bulk samples.

Suppose we have two hypothetical elements, A and B, whose atomic weights are, respectively, 2 and 5; that is, an average atom of B weighs 2.5 times as much as an average atom of A. Now, suppose we take a sample containing 1,000 atoms of A and another sample containing 1,000 atoms of B. It is obvious that the masses of the two samples will be in the same ratio as the masses of the individual atoms: 2 to 5. The sample of 1,000 B atoms will weigh 2.5 times as much as the sample of 1,000 A atoms. This relationship will hold regardless of the number of atoms, as long as there are equal numbers of atoms in the two samples. Looking at this from the other direction, 2 lb of A must contain the same number of atoms as 5 lb of B, or 2 g of A must contain the same number of atoms as 5 g of B. No matter what units they are measured in, if the masses of the samples of the two elements are in the same ratio as the masses of single atoms of the elements, then the two samples will contain the same number of atoms. Because in chemistry mass is usually expressed in grams, we attach special significance to that amount of an element whose mass in grams is numerically equal to its atomic weight. This amount is referred to as a **gram-atomic weight**.

It follows that one gram-atomic weight of any element contains the same number of atoms as one gram-atomic weight of any other element. This number has been determined by several different methods and has been established as 6.022×10^{23} atoms. It is known as **Avogadro's number**, in honor of the nineteenth-century Italian chemist Amadeo Avogadro.

The fundamental significance of Avogadro's number in chemical calculations has led to the designation of an important quantity in chemistry, the **mole** (abbreviated mol), which is defined as **that quantity of matter that contains Avogadro's number of particles**. Thus, 6.022×10^{23} electrons is a mole of electrons, 6.022×10^{23} ions is a mole of ions, and (although the term is not normally used outside of science) 6.022×10^{23} bricks could correctly be called a mole of bricks. The mass of a mole of an element is referred to as its **molar mass**. Thus, since the atomic weight of calcium is 40.08, the molar mass of calcium is 40.08 g and this amount of calcium contains 6.022×10^{23} atoms.

To illustrate the relationship between Avogadro's number and atomic weight, let us determine the weight of 1×10^{18} atoms of fluorine. Because we know that a mole of fluorine weighs 19.0 g and contains 6.02×10^{23} atoms, we need only determine the number of moles* of fluorine represented by 1×10^{18} atoms.

$$\frac{1 \times 10^{18}\ \text{atoms}}{6.02 \times 10^{23}\ \text{atoms/mol}} = 1.7 \times 10^{-6}\ \text{mol}$$

Finally, we multiply the number of moles by the mass of one mole in order to determine the mass.[†]

$$1.7 \times 10^{-6}\ \text{mol} \times 19.0\ \text{g/mol} = 3 \times 10^{-5}\ \text{g}$$

Notice that the mass is given to only one significant figure because the number of atoms was given to only one significant figure (the other two numbers—molar mass and Avogadro's number—are expressed to three significant figures, but we can express the answer to only one significant figure).

Problem 2.7

How many moles of phosphorus are there in 100 g of phosphorus?

Solution:

One mole of phosphorus atoms weighs 30.97 g (the molar mass of phosphorus). Thus, in 100 g there are

$$\frac{100\ \text{g}}{30.97\ \text{g/mol}} = 3.23\ \text{mol}$$

Methodology 2.2

How many atoms are there in 50.0 g of copper?

1. What do we do first?

Establish what is given and what we want to determine. We know that we have 50.0 g of copper and we must find the number of atoms of copper in this amount of copper.

2. What is the relationship between weight of copper and the number of atoms?

The relationship lies in our knowledge that one mole of copper contains 6.022×10^{23} atoms.

3. So, what do we do next?

Find the number of moles of copper. In order to do this we must remember that the molar mass of copper is its atomic weight in grams. The atomic weight of copper is approximately 63.5 (each mole of copper weighs 63.5 g). The number of moles in 50.0 g of copper is therefore

$$\frac{50.0\ \text{g}}{63.5\ \text{g/mol}} = 0.787\ \text{mol}$$

Continued on next page

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* Try to visualize the 1×10^{18} atoms as a small part of Avogadro's number, 6.02×10^{23} atoms. Then ask: What fraction of a mole, or what part of a mole, is this 1×10^{18} atoms?

[†] If you have trouble seeing this, ask yourself, what is the mass of one mole of fluorine (19 g); what is the mass of two moles of fluorine (2×19 g); what is the mass of 1×10^{-6} moles ($1 \times 10^{-6} \times 19$ g).

Methodology 2.2 Continued

4. How do we get from moles to number of atoms?

Because each mole of copper contains Avogadro's number of atoms, to obtain the number of atoms we multiply the number of moles by 6.022×10^{23} atoms/mol.

$$0.787 \text{ mol} \times 6.022 \times 10^{23} \text{ atoms/mol} = 4.74 \times 10^{23} \text{ atoms}$$

Problem 2.8

What is the mass of a single phosphorus atom?

Solution:

One mole of phosphorus atoms weighs approximately 30.97 g. This is the mass of Avogadro's number of phosphorus atoms and therefore the mass of one phosphorus atom must be

$$\frac{30.97 \text{ g/mol}}{6.022 \times 10^{23} \text{ atoms/mol}} = 5.143 \times 10^{-23} \text{ g/atom}$$

✓ Check Point 2.1

What is the mass of 1×10^{20} atoms of phosphorus?

Solution:

$$5 \times 10^{-3} \text{ g}$$

◇ ◇ ◇ ◇ ◇

Problem 2.9

A compound contains 46.6% iron and 53.4% sulfur. What is the ratio of the moles of iron to moles of sulfur?

Solution:

Assume that we have 100 g of the sample. In this sample we will have

$$100 \text{ g} \times 0.466 = 46.6 \text{ g Fe, and}$$
$$100 \text{ g} \times 0.534 = 53.4 \text{ g S}$$

In order to obtain the number of moles of each we must divide by their atomic weights in grams (that is, by their molar mass):

$$\frac{46.6 \text{ g Fe}}{55.85 \text{ g/mol}} = 0.834 \text{ mol Fe}$$

$$\frac{53.4 \text{ g S}}{32.06 \text{ g/mol}} = 1.67 \text{ mol S}$$

The ratio is $\frac{1.67}{0.834} = 2$. The compound contains two moles of sulfur for every mole of iron.

Problem 2.10

If a room containing 300 kg of air is contaminated with one ppm of radon, how many atoms of radon does the room contain?

Solution:

Part per million, like per cent (part per hundred), is generally based upon mass, and is used when small amounts of substances are involved. If the room contained one million grams of air, it would contain one gram of radon. Thus, we must multiply the mass of air by $1/10^6$ or 1×10^{-6}:

$$3 \times 10^5 \text{ g air} \times 1 \times 10^{-6} \frac{\text{g Rn}}{\text{g air}} = 0.3 \text{ g Rn}$$

In order to obtain the number of atoms of Rn we must first determine the number of moles by dividing by the molar mass of Rn (222 g):

$$\frac{0.3 \text{ Rn}}{222 \text{ g/mol}} = 1 \times 10^{-3} \text{ mol Rn}$$

Finally, we obtain atoms by multiplying by Avogadro's number

$$1 \times 10^{-3} \text{ mol} \times 6 \times 10^{23} \text{ atoms/mol} = 6 \times 10^{20} \text{ atoms Rn}$$

CHAPTER SUMMARY

For more than 2,000 years, the idea of atomic matter had been considered, but an acceptable model—in the form of Dalton's atomic theory—did not appear until the beginning of the nineteenth century. Dalton's theory was a response to the need for an explanation of accumulated observations about the nature and behavior of matter. These observations had already resulted in the recognition of three natural laws: the Law of Conservation of Matter, the Law of Constant Proportions, and the Law of Multiple Proportions. While these laws are now only of historical interest, they played an important role in paving the way for Dalton's theory, and you should understand them and their relationship to the atomic theory.

The gradual refinement of the atomic model was largely a result of the discovery of subatomic particles and their relationships to the atom. Some of the high points of this historical development of atomic theory are as follows:

1850–1880:	Cathode ray experiments led to the discovery of the electron
1886–1902:	Canal ray experiments led to the discovery of the proton
1896:	The discovery of radioactivity and the study of this phenomenon led to the recognition of alpha, beta, and gamma rays
1897:	Determination of the charge-to-mass ratio of the electron
1908–1917:	Measurement of the charge of the electron
1911:	Introduction of the concept of the nucleus
1932:	Discovery of the neutron

The historical development of the atomic theory, which was altered and revised to accommodate each new observation, provides a good example of the "scientific method" at work.

To apply modern atomic theory to the study of matter, and thus to comprehend the chapters that follow, you will need a thorough understanding of the concepts of atomic numbers, mass numbers, isotopes, and atomic weights. You will also need to become familiar with the elemental symbols, since they are a part of the language that chemists use to describe matter. Although it is not necessary to know the symbols of all of the elements, you should learn the symbols for some of the more common ones. The following list of 45 elements and their symbols includes most of the elements you will encounter in this text.

Aluminum	Al	Copper	Cu	Oxygen	O
Antimony	Sb	Fluorine	F	Phosphorus	P
Arsenic	As	Gold	Au	Platinum	Pt
Barium	Ba	Helium	He	Potassium	K
Beryllium	Be	Hydrogen	H	Radium	Ra
Bismuth	Bi	Iodine	I	Rubidium	Rb
Boron	B	Iron	Fe	Selenium	Se
Bromine	Br	Lead	Pb	Silicon	Si
Cadmium	Cd	Lithium	Li	Silver	Ag
Calcium	Ca	Magnesium	Mg	Sodium	Na
Carbon	C	Manganese	Mn	Strontium	Sr
Cesium	Cs	Mercury	Hg	Sulfur	S
Chlorine	Cl	Neon	Ne	Tin	Sn
Chromium	Cr	Nickel	Ni	Uranium	U
Cobalt	Co	Nitrogen	N	Zinc	Zn

One final topic you should understand before proceeding to the next chapter is that of the mole and its relationship to atomic weight and to Avogadro's number. Be sure that you are able to perform calculations based on these relationships.

TERMS

A summary of the important concepts and terms introduced in this chapter is provided below:

Electron A subatomic particle with a mass of 9.11×10^{-28} g (about 1/1840 the mass of the lightest atom—the hydrogen atom) and with a negative electrical charge equal to 1.60×10^{-19} coulombs (C). Electrons are distributed throughout the extranuclear part of the atom.

Proton A subatomic particle with a positive charge equal in magnitude to the negative charge of an electron and with a mass of 1.672×10^{-24} g. A proton is the nucleus of a hydrogen atom.

Neutron An uncharged, subatomic particle with a mass approximately equal to the mass of a proton (1.675×10^{-24} g).

Nucleus The positively charged center of an atom, which accounts for essentially all of the atom's mass but only a very small fraction of its volume. The nucleus of the hydrogen atom is a proton; the nuclei of all other atoms may be thought of as consisting of some number of protons and neutrons.

Nucleons The nuclear particles, both the neutrons and protons, in an atomic nucleus.

Atomic number The positive charge of an atomic nucleus expressed as a number of protons. Thus, an atom with an atomic number of 14 may be thought of as containing 14 protons in its nucleus. In a neutral (uncharged) atom, the atomic number is also the number of extranuclear electrons in the atom.

Element The name applied to all atoms with a specific atomic number. Atoms with the same atomic number are all atoms of the same element; atoms with different atomic numbers are atoms of different elements.

Elementary substance A substance in which all the atoms have the same atomic number.

Compound substance A substance that contains atoms with different atomic numbers; that is, a substance that consists of more than one element.

Mass number The total number of nucleons (protons and neutrons) in an atomic nucleus. The mass number of an atom is its atomic number *plus* the number of neutrons in its nucleus.

Isotopes Atoms that have the same atomic number but different mass numbers; that is, atoms that have the same number of protons but different numbers of neutrons. (Note that in keeping with our definition of the term "element," isotopes are atoms of the same element that have different masses.)

Atomic weight The mass of an atom of a given element *relative* to the mass of an atom of the most abundant isotope of carbon, carbon-12, which is arbitrarily assigned a mass of 12 atomic mass units (amu). Because atomic weights are experimentally measured values and because most elements occur naturally as mixtures of two or more isotopes, the atomic weight of an element is an average of the masses of the element's various isotopes weighted according to their relative abundance.

Atomic mass unit A mass equal to exactly 1/12 the mass of a carbon-12 atom.

Mole of an element That quantity of an element whose mass in grams is numerically equal to the atomic weight of the element. It consists of Avogadro's number (6.022×10^{23}) of atoms.

Molar mass The mass of one mole of a substance. For an element it is the atomic weight in grams. The molar mass of iron is 55.85 g and this amount of iron contains 6.022×10^{23} atoms.

PROBLEMS

1. Indicate the difference between the terms in each of the following pairs:
   a. nucleus and nucleon
   b. atomic number and mass number
   c. isotopes and isobars
   d. atomic weight and mass number
   e. alpha particles and beta particles
   f. atomic number and atomic weight

2. When heated a material produces oxygen gas and a residue. Is the substance a mixture of elements, a mixture of compounds, a compound, or an element?

3. A student finds a liquid in the laboratory and proceeds to try to determine whether the liquid is a mixture or a pure substance. The student places 40 mL of the liquid in a distillation flask, heats the liquid and collects the vapors of the liquid as it begins to boil. A total of 30 mL are collected at a boiling point of 98–100 °C and then a total of 10 mL are collected at a boiling point of 100–102 °C. The student then determines both the refractive index and density of the two samples. For the first sample the refractive index is 1.3334 and the density is 0.9988 g/cm3 at 25 °C. For the second sample the refractive index is 1.3337 and the density is 0.9993 g/cm3 at 25 °C. What should the student conclude about the nature of the liquid?

4. Thomson's model of the atom assumed that it was a uniformly positive sphere of matter in which electrons were imbedded throughout. Would an equally acceptable model have been a uniformly negative sphere of matter in which protons were imbedded throughout?

5. When discussing nuclear reactions it is sometimes convenient to think of a neutron as a composite of a proton and an electron.
   a. Does this model make sense on the basis of charge and mass?
   b. Is this model similar to any of the early models of the atom?

6. Indicate the number of protons and the number of neutrons in the nucleus of each of the following elements:

$$^{3}_{1}\mathrm{H} \quad ^{31}_{15}\mathrm{P} \quad ^{34}_{16}\mathrm{S} \quad ^{206}_{82}\mathrm{Pb} \quad ^{99}_{43}\mathrm{Tc} \quad ^{235}_{92}\mathrm{U}$$

7. Name the elements represented by the following symbols:

Li, B, P, Al, Co Se, Au, Cd, Sb, Br, Cu, Mg, Na

8. Give the chemical symbol for each of the following elements: sulfur, potassium, zinc, manganese, uranium, strontium, tin, arsenic, argon, beryllium, nickel, mercury, lead, silicon, iodine, chlorine.

9. When 20 g of one element is heated with 3.2 g of sulfur, 23.2 g of a compound that contains a 1:1 ratio of sulfur atoms to atoms of the other element is formed.
   a. Assign an atomic weight of 1 to sulfur and determine the relative atomic weight of the other element.
   b. Use the atomic weight of sulfur as given on the periodic chart to determine the atomic weight of the other element.
   c. What element was mixed with sulfur?
   d. What is the formula of the compound?

10. A 431 milligram sample of an element reacted with 32 milligram of O_2 to form a compound with the formula M_2O. Calculate the atomic weight of the element.

11. If carbon were assigned an atomic weight of 20, what would be the atomic weight of hydrogen and silicon?

12. If carbon consisted of only one naturally-occuring isotope—^{12}C—what would be the atomic weight of carbon? What would be the atomic weight of lead?

13. The natural abundance of the two stable isotopes of carbon are carbon-12 = 98.89% and carbon-13 = 1.11%. The atomic mass of carbon-13 is 13.003. Calculate the atomic weight of carbon.

14. Chlorine consists of two stable isotopes, whose natural abundances are 75.53% ^{35}Cl and 24.47% ^{37}Cl. If the atomic weight of chlorine is 35.453 and the atomic mass of ${}^{35}Cl$ is 34.96885, calculate the atomic mass of ${}^{37}Cl$.

15. How many atoms are there in
  a. 1.0 g of gold?
  b. 1.0 kg of iron?
  c. 5.0 L of helium with a density of 0.18 g/L?

16. Calculate the mass of a single atom of silicon.

17. What is the mass of 1 million silver atoms?

18. Which weighs more, 0.5 mol of calcium or 0.2 mol of barium?

19. Calculate the number of moles of carbon in a 1.5 carat diamond. (Diamond is pure carbon, and 1 carat weighs 200 mg.)

20. How many moles of zinc are there in 15.5 g of the pure metal?

21. Commercial bronze contains 90% copper and 10% zinc (by weight). What is the atomic ratio of copper to zinc?

22. From the average diameter of a nucleus and that of an atom, calculate the volume of an atom and compare it with that of the nucleus.

23. What percentage of the mass of a hydrogen atom is contributed by the electron?

24. The only natural isotope of fluorine is ${}^{19}_{9}F$, an atom of which weighs 3.154×10^{-23} g. Calculate the atomic weight of fluorine.

25. The mass of an atom of calcium-40 is 6.635×10^{-23} g.
  a. Use this value to calculate the atomic weight of calcium ($1 \text{ amu} = 1.6604 \times 10^{-24}$ g).
  b. Account for any discrepancy between your value and that given in the Periodic Table (Appendix 8).

26. The radius of a copper atom is 0.117 nm. If a mole of copper atoms were lined up in single file, how long would the line be, in kilometers?

27. There is only one natural isotope of helium. What is the mass of a helium atom expressed in (a) atomic mass units and (b) grams?

28. Keeping in mind that the elementary substance oxygen consists of diatomic molecules (O_2), a mole of this substance contains (a) how many atoms and (b) how many molecules?

29. If you could take one kilogram of aluminum and divide it into samples that contained one billion atoms each, how many samples would you have?

30. Multiple-choice questions

1. If an atomic weight scale had been adopted with the mass of a carbon-12 atom assigned the value of 100 amu (instead of 12 amu), the atomic weight of fluorine would be (consult the table of atomic weights)
   (a) 1899.84 (b) 227.98
   (c) 158.32 (d) 18.9984

2. The number of neutrons in an atom of ${}^{127}_{53}I$ is
   (a) 53 (b) 74
   (c) 127 (d) 180

3. The approximate atomic weight of calcium is 40. The weight of Avogadro's number of calcium atoms is about
   (a) 40 amu (b) 40 g
   (c) 2.4×10^{25} g (d) 6.6×10^{-23} g

4. The correct symbol for copper is
   (a) C (c) Cr
   (b) Co (d) Cu

5. The number of electrons in an atom of ${}^{23}_{11}Na$ is
   (a) 11 (c) 23
   (b) 12 (d) 34

6. Which contains the largest number of atoms?
   (a) 1 mol of H_2
   (b) 1 g of diatomic hydrogen gas
   (c) 1 g of hydrogen
   (d) 1 g of fluorine

7. Which is an isotope of sulfur?
   (a) ${}^{16}_{8}X$ (b) ${}^{34}_{16}X$
   (c) ${}^{32}_{15}X$ (d) ${}^{16}_{31}X$

8. Which contains the largest number of atoms?
   (a) 1 lb of copper
   (b) 1 lb of iron
   (c) 1 lb of silver
   (d) all the above contain the same number of atoms

9. Which weighs more?
   (a) 0.20 mol of K (b) 0.30 mol of Na
   (c) 0.40 mol of Li (d) 0.10 mol of C

10. The total number of protons in 3.0 mol of Ba is
   (a) 168 (b) 1.8×10^{24}
   (c) 3 (d) 1.0×10^{26}

3

The Electronic Structure of Atoms

While Rutherford's model remains the basis for our contemporary belief that the atom consists of a nucleus and one or more extranuclear electrons, it leaves many questions about the electronic structure of the atom unanswered. For example, are the electrons fixed in space about the nucleus? If they are stationary, what prevents them from being attracted into the positively charged nucleus? Or are they moving about the nucleus like a miniature solar system?

This last suggestion seemed most likely in the early part of the 20th century, because the rotation of the electron around the nucleus could provide sufficient energy to keep the electron away from the nucleus. There were, however, two serious objections to this proposal. First, according to the laws of physics, such a system of moving charges should continuously radiate light of all frequencies. Second, this radiation would be accompanied by a loss in energy of the charged bodies, and the electron therefore should spiral inward and eventually collide with the nucleus. Under certain conditions atoms do emit light, but this light contains only certain frequencies—by no means all frequencies. Furthermore, at room temperature, most elements emit no light whatsoever and are quite stable.

The facts, therefore, could not be reconciled with the solar system model, and scientists at the beginning of the twentieth century were in a quandary. It remained to Niels Bohr, a Danish physicist, to provide a model that is at least in partial agreement with the experiment.

3.1 THE NATURE OF LIGHT AND EMISSION SPECTRA

Many ideas were vital to the construction of Bohr's model, but he probably drew most heavily upon the work of another physicist, Max Planck, on the nature of light. Up to the middle of the seventeenth century, light was believed to be a stream of particles that entered the eye and caused the sensation of "seeing." In the eighteenth and nineteenth centuries, a number of experiments pointed to a wave nature of light. For example, consider a single light source, such as a light bulb, that is directed at an opaque partition containing two parallel slits. The light emerging from the two slits will form a band pattern that can be viewed on a screen placed behind the partition. This behavior is almost impossible to rationalize with the particle model, but if light is assumed to consist of waves, very much like the waves produced when a pebble is dropped into a still pond, then the band pattern can be rationalized as follows. The source sends out concentric waves, which strike the partition and form a set of identical concentric waves at each slit. At some points on the screen, the crests of waves from slit A meet crests of waves from slit B, or troughs meet troughs, and at these points the waves *reinforce* one another and form a bright band. At other points, crests meet troughs and *cancel* the effects of one another, so that no light is observed at these points.

The **wavelength** of such waves (denoted by the Greek letter *lambda*, λ) can be defined as the distance from crest to crest (Figure 3.1).

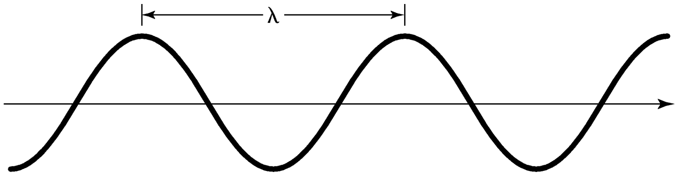


Figure 3.1 The definition of wavelength.

The **frequency** (denoted by the Greek letter *nu*, ν) is the number of crests per second that pass a given point. The maximum height of the wave is called the **amplitude**.

Light was later found to travel at a constant speed of 3.00×10^8 m/s, which means that one concentric wave (using the pebble-in-water analogy) could travel 186,000 miles in one second. The wavelength, frequency, and speed of light (c), are related by the equation

$$\lambda\nu = c$$

For example, if a beam of light has a wavelength of 254 nm, we can calculate the frequency of this light as,

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{2.54 \times 10^{-7}\, m}$$
$$= 1.18 \times 10^{15} \text{ s}^{-1}$$

Notice that since the speed of light is given in units of meters per second, the wavelength must be converted to units of meters; $\lambda = 2.54 \times 10^{-7}\, m$. The motion of a wave from one crest to another is referred to as a **cycle**. Therefore, frequency is often expressed in units of cycles per second, and the result above can be given as 1.18×10^{15} cycles/s. The unit of cycles per second is also called Hertz, abbreviated Hz.

After agreeing that certain properties of light could be explained by the wave theory, scientists began to wonder about what was waving. It is clear that when a pebble is dropped into water, it is the water itself that oscillates up and down; but what about light? Some physicists speculated that a mysterious material, a "luminiferous ether," was the medium for the oscillations. This theory was discarded in 1888, when Heinrich Hertz found that light could be produced from electromagnetic oscillations in a loop of wire. This experiment and others have led scientists to think of light as perpendicularly oscillating electric and magnetic fields.

The term "light" is often used to mean ordinary visible light, the **electromagnetic radiation** that strikes our retinas and allows us to "see." But the term may also be used to refer to any electromagnetic radiation, including high-energy x-rays and low-energy radar waves. The various types of radiation are represented on an **electromagnetic spectrum** in Figure 3.2.

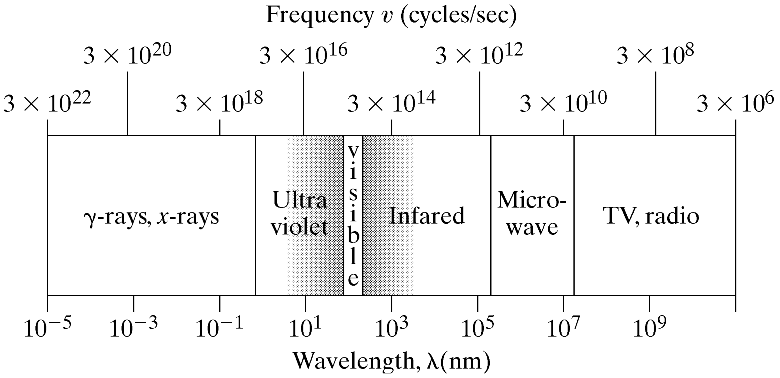


Figure 3.2 The electromagnetic spectrum.

TABLE 3.1 Colors of the Visible Spectrum

COLOR	WAVELENGTH BAND (nm)
Violet	400–450
Blue	450–500
Green	500–570
Yellow	570–590
Orange	590–620
Red	620–750

Those electromagnetic vibrations that can be detected by the human eye, and are therefore part of the visible region of the spectrum, have wavelengths ranging from approximately 400 to 750 nm. Although the human visual apparatus is unable to distinguish between two vibrations that have nearly the same wavelength, it can detect differences between relatively large bands of wavelengths. Each of these bands elicits a somewhat different response from the visual nervous system, and each different response is equated with a different color. The wavelength bands of the visible spectrum corresponding to the six major colors are given in Table 3.1. The divisions between colors are not abrupt, of course, and the wavelengths given are only approximate.

The component vibrations of a given band of electromagnetic radiation can be separated and identified much more accurately by instrumental techniques. For example, ordinary white light-whether sunlight or the light from an incandescent bulb—can be dissected into its component waves by the apparatus shown in Figure 3.3.

Light from an incandescent bulb is passed through a slit in order to produce a narrow beam. This beam is allowed to fall obliquely onto the side of a glass triangular prism. As the light beam passes from the air to the more dense glass, it is **refracted** (bent). But not all the component vibrations that make up the beam are refracted through the same angle, for they do not all have the same frequency; those vibrations with the greatest frequency (shortest wavelength) are refracted most. As the light emerges from the prism into the air, this time entering a less dense medium, more of this unequal bending occurs. As a result, if the light is allowed to fall upon a screen, one sees on the screen not a narrow band of white light but an enlarged, continuous band of light showing a "rainbow" of colors. Through refraction the white light has been separated into its component vibrations, according to the wavelengths of those vibrations as listed in Table 3.1. The components of white light thus displayed on the screen constitute the visible spectrum.

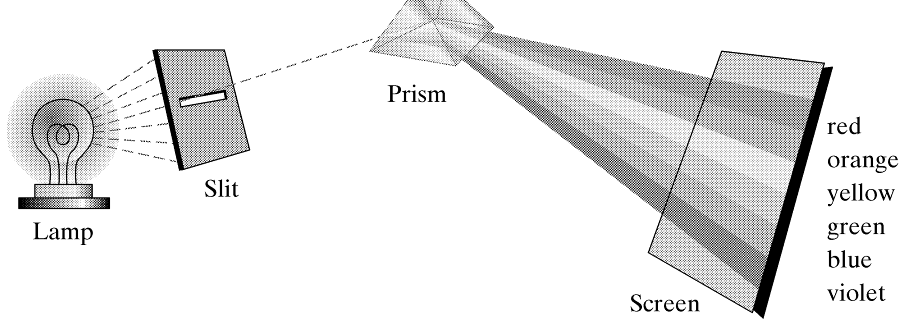
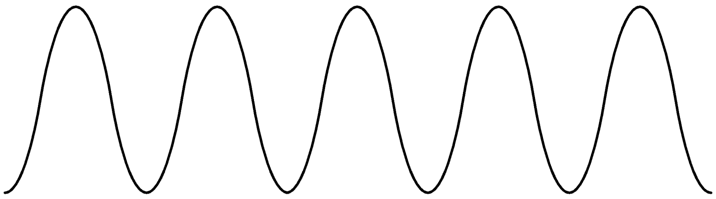


Figure 3.3 The separation of light waves with a prism.

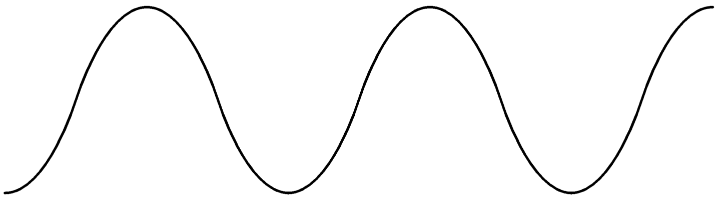
Visualization 3.1

If both of the waves below represent light in the visible region, which is more likely to be red? Which has the higher frequency?

(a)



(b)



Solution:

Wave (a) has the shorter wavelength and therefore the greater frequency. Because of both characteristics it is less likely to represent red light (which has the lowest frequency in the visible region).

The wave theory of light reigned supreme for a number of years, but early in the twentieth century the physicists Max Planck and Albert Einstein found the wave theory unsatisfactory for explaining certain experimental observations. One of these, the **photoelectric effect**, concerned electrons released from the surfaces of certain metals upon exposure to ultraviolet light. That electrons were released was not surprising, since light is an oscillating electric field and must surely interact with the negatively charged electron. The surprising feature of the experiment lay in the relationship between the intensity of light and the velocity of the liberated electrons. The wave theory predicted that when the intensity or amount of light falling on the metal was increased, the electrons would leave the surface with a greater velocity. Experiments showed that an increase in intensity affected only the number of electrons leaving the metal; it was necessary to increase the frequency of the light to increase the velocity of the electrons.

According to Einstein, the photoelectric effect could be explained by assuming that light consists of tiny bundles of electromagnetic radiation. Each bundle of radiation, called a **photon**, has an energy given by an equation derived by Planck:

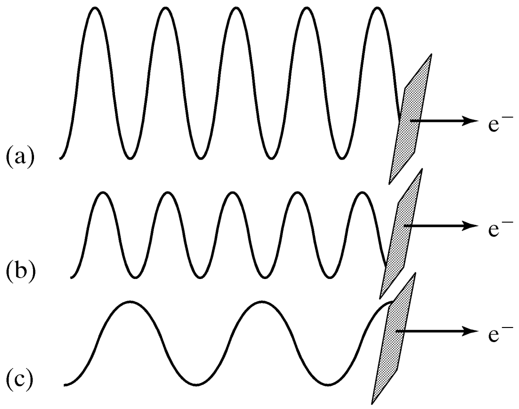
$$E = h\nu$$

where ν is the frequency of light and h is a constant (called **Planck's constant**) with a value of 6.6×10^{-34} J-s. As the number of photons hitting the metal is increased, the number of electrons knocked out increases. Also, as the frequency of the photons increases, their energy and the jolt they impart to the electrons increase.

While the new photon theory was eminently successful in explaining the photoelectric effect and several other phenomena, it was incapable of providing insights to phenomena such as interference bands. The wave and photon models, then, are complementary. Neither adequately explains all phenomena, and each one works when the other does not. Therefore, both models remain in use and both will be necessary until a better model is devised.

Visualization 3.2

The diagram below shows three different waves of electromagnetic radiation, each of which strikes a piece of metal and ejects electrons. According to the wave theory, which wave should produce electrons with the greatest velocity? When the experiment was performed, which wave was found to produce electrons with the lowest velocity?



Solution:

According to the wave theory, the greater the intensity of the light, the greater the interaction with the electrons and therefore the greater the velocity of the ejected electrons. Thus, wave (a) which has the greatest amplitude, and therefore the greatest intensity, would produce electrons with the greatest velocity. Wave (b) has the smallest amplitude and should produce the lowest velocity. The experiment showed, however, that only the frequency of the wave was related to the velocity of the electron. Wave (c), which has the lowest frequency, therefore produced electrons with the lowest velocity.

Another observation that Bohr utilized in the development of his atomic model was that the light emitted from an element to which energy is imparted contains only certain frequencies. For example, if hydrogen gas is exposed to an electrical arc and the emitted light is passed through a prism, only certain frequencies appear in the resulting spectrum. Each line in this spectrum is an image of the narrow slit through which the light has passed and corresponds to light of a different frequency.

Problem 3.1

The light responsible for one of the lines in the visible spectrum of hydrogen has a wavelength of 656 nm. Calculate the frequency and energy of a photon of this light.

Solution:

The frequency can be obtained from the relationship

$$\lambda\nu = c$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{6.56 \times 10^{-7}\ \text{m}} = 4.57 \times 10^{14}\ \text{s}^{-1}$$

The energy is calculated from the Planck equation

$$\begin{aligned} \text{E} &= h\nu = 6.626 \times 10^{-34}\ \text{J-s} \times 4.57 \times 10^{14}\ \text{s}^{-1} \\ &= 3.03 \times 10^{-19}\ \text{J} \end{aligned}$$

Check Point 3.1

Calculate the wavelength (in meters) of a photon of light with an energy of 1×10^{-11} J. Give your answer just to a power of ten; for example, 10^{-8} *m*.

Solution:

$$10^{-14}\, m$$

◇ ◇ ◇ ◇ ◇

Every element has its own unique line spectrum, and it would seem likely, therefore, that these spectra are in some way characteristic of an atom's electronic structure. Hence, any successful model of electronic structure must certainly provide an explanation for the line spectra of the elements.

3.2 THE BOHR MODEL OF THE ATOM

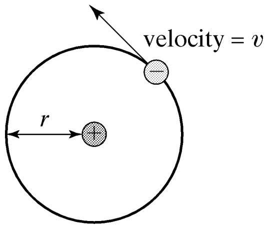


Figure 3.4 An electron moving in a circular orbit according to the Bohr Model.

In 1913, armed with the photon model and a knowledge of line spectra, Niels Bohr proposed the following model of the hydrogen atom. Around the single proton, which is the nucleus of the hydrogen atom, revolves one electron in a circular orbit (see Figure 3.4).

The energy of this simple atom can be easily calculated from the laws of physics. The kinetic energy of the electron due to its circular motion is given by the relationship

$$KE = \frac{1}{2} mv^2$$

where *m* is the mass of the electron and *v* is its linear velocity (the tangential velocity shown above). In addition to its kinetic energy, the atom has potential energy, which results from the attraction of the negatively charged electron for the positively charged proton. Because of the importance of electrostatic interactions in chemistry, we will digress briefly to examine some fundamental laws used to describe these interactions.

Problem 3.2

Calculate the kinetic energy (in joules) of an electron moving at a speed of 1×10^6 m/s.

Solution:

Because we want to express the answer in joules, we must use units of m/sec for velocity and kg for mass. The mass of the electron is 9.11×10^{-28} g and therefore,

$$\text{KE} = \frac{1}{2}\,(9.11 \times 10^{-31}\ \text{kg})(1 \times 10^6\ \text{m/s})^2 = 5 \times 10^{-19}\ \text{J}$$

Notice that the units come out to kg-m^2/s^2 which are the units of energy in joules.

Electrostatic Interactions

It is well known that oppositely charged objects (for example, one atom with an excess of electrons and another atom with a deficiency of electrons) are attracted to each other, while objects with the same charge repel each other (Chapter 2). In the latter part of the eighteenth century, the French physicist August Coulomb put these observations on a quantitative basis with his experiments on the force between oppositely charged bodies.

He found that this force varies directly with the product of the charges on the two bodies and inversely with the square of the distance between the two bodies. Mathematically, this is expressed as

$$F = \frac{kq_1q_2}{r^2} \tag{1}$$

where F is the force between the two bodies, q_1 and q_2 are the charges on the first and second bodies, r is the distance between the bodies, and k is a proportionality constant.

The charge can be expressed in a number of different units. Probably the most fundamental is the **atomic unit** (au), which is the charge on a single proton. The charge on an electron has the same magnitude but a negative sign. The **coulomb** (C) is the SI unit of charge and is equal to 6.2×10^{18} atomic units, and the **electrostatic unit** (esu) is equal to 2.1×10^{9} atomic units.

Another way to express the attraction or repulsion between charges is in terms of their potential energy. As noted in Chapter 2, potential energy is the capacity of a system to do work by virtue of its position; in the SI system of units this is expressed in joules. A motionless boulder perched on the edge of a cliff has the potential to do work because as soon as it is released, it possesses kinetic energy, which enables it to knock over obstacles in its path, for example. Two charges held a fixed distance apart also have potential energy. If these charges have opposite signs and if they were able to move, they would move toward one another, and this motion could produce work. If, on the other hand, the charges are of the same sign, work must be done to prevent them from flying apart. For two charges separated by a distance r, the potential energy, PE, can be obtained by multiplying equation (1) by r (work = force × distance) and is given by the expression

$$PE = \frac{kq_1q_2}{r} \tag{2}$$

When the charge is expressed in coulombs, r must be given in meters and the constant k has the value of $8.99 \times 10^{9} \frac{\text{J-m}}{\text{C}^2}$.

Note carefully two aspects of this equation: First, if the bodies are oppositely charged, the potential energy is negative (because one of the q's is negative). Second, as r becomes larger, PE approaches zero, and when r reaches infinity, PE is zero. Consequently, the potential energy for any given r is the negative of the work necessary to separate the charges to infinity.

Problem 3.3

Calculate the potential energy of a proton and electron held at a separation of 100 pm.

Solution:

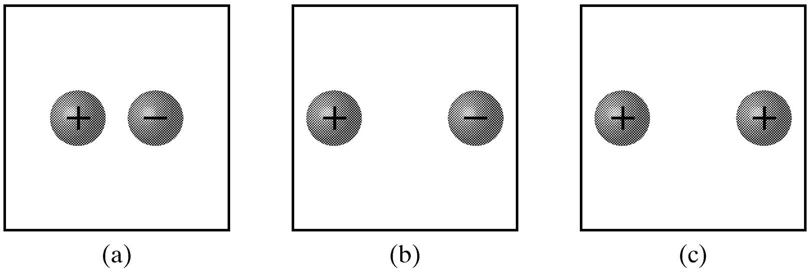
Appendix 1 gives the charge on a proton as 1.60×10^{-19} C. The charge on the electron has the same magnitude but a negative sign (-1.60×10^{-19} C). The distance between the charges is 100×10^{-12} m. These values and the constant $8.99 \times 10^{9} \frac{\text{J-m}}{\text{C}^2}$ are inserted in the equation

$$PE = \frac{kq_1q_2}{r}$$

$$PE = \frac{(8.99 \times 10^{9}\ \text{J-m/C}^2)(1.60 \times 10^{-19}\ \text{C})(-1.60 \times 10^{-19}\ \text{C})}{100 \times 10^{-12}\ \text{m}} = -2.30 \times 10^{-18}\ \text{J}$$

Visualization 3.3

Examine the following three sets of charges:



1. Which set has a positive potential energy?
2. Which set has the most negative potential energy?
3. Which set requires the most work to separate the charges to infinity?

Solution:

1. Set (c) has a positive potential energy because the charges have the same sign.
2. Set (a) has the most negative potential energy because the charges are of opposite sign and their separation is less than that for set (b) (that is, r is smaller for (a))
3. Set (a) will require the most work for separation to infinity. The more negative the potential energy, the more work required for separation.

Let us now return to the Bohr model of the hydrogen atom. Bohr first expressed the *total* energy of this atom as the sum of the kinetic and potential energies:

$$E = \frac{1}{2}mv^2 + \frac{kq_1q_2}{r} \tag{3}$$

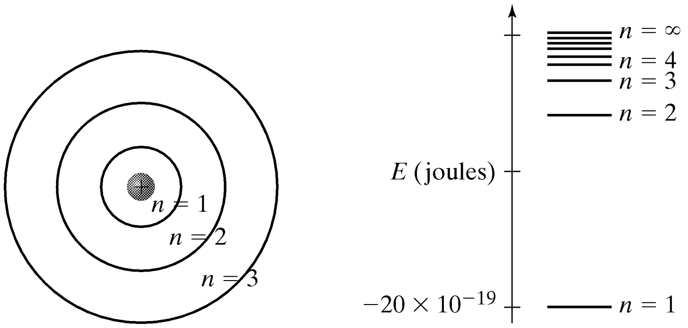
Then Bohr made a major departure from the laws of classical physics. According to classical physics, the angular momentum of an object confined to a circular orbit must remain constant. It can, however, have *any* value. (The angular momentum p of a mass m traveling with a velocity v on a circular orbit is given by the relationship $p = mvr$). Using the ideas of Planck and others, Bohr assumed that the angular momentum of the electron could have only certain values. Specifically, he assumed that it could only be integral multiples of Planck's constant divided by 2π:

$$mvr = n\left(\frac{h}{2\pi}\right) \tag{4}$$

where n is any integer from 1 to infinity. The angular momentum can therefore only have values of $h/2\pi$, $2h/2\pi$, $3h/2\pi$, . . ., and is said to be **quantized** (from the Latin *quantus* meaning "how much"). The integer n is called the **quantum number**. By combining Eq. (4) with Eq. (3) and the relationship for centripetal force taken from classical physics, Bohr was able to obtain an expression for the radius of each orbit in the hydrogen atom:

$$r = \frac{n^2h^2}{4\pi^2kme^2} \tag{5}$$

This equation gives r in terms of only constants (m, h, 4, p, k, e) and the integer n. In other words, the radius of the orbit, like the angular momentum, can have only certain values. This is analogous to a small boy twirling overhead a stone attached to a string who finds that the stone will revolve about him when the string has a length of, say, 1 meter, 4 meters, 9 meters, and so forth, but not when it is 2, 4.5, or 12 meters.



The three orbits closest to the nucleus

Energy levels

Figure 3.5 Some low-energy Bohr orbits.

Finally, Bohr also calculated the energy of the electron as

$$E = -\frac{2\pi^2 kme^4}{n^2h^2} \tag{6}$$

which, after substituting* the numerical values for each constant, is equivalent to

$$E = \frac{-21.7 \times 10^{-19}\,\text{J}}{n^2} \tag{7}$$

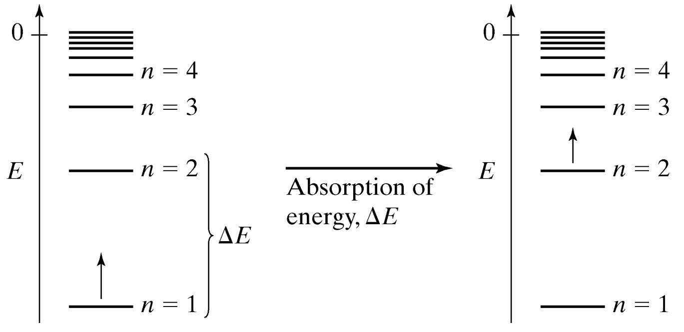
The value of the quantum number n—be it 1, 2, or 3—determines both the radius of the orbit and the energy of the electron: the higher the value of n, the farther the electron is from the nucleus and the higher its energy. Some of the allowed orbits and energies are shown in Figure 3.5.

The energy of the electron in the orbit closest to the nucleus, where $n = 1$, is -21.7×10^{-19} joule. The negative sign indicates that the electron is attracted, rather than repelled, by the nucleus. The spacings between the energy levels decrease as the energy increases (as n becomes larger). When $n = \infty$, the potential energy of the electron is zero, as is the kinetic energy; the atom has for all practical purposes **ionized** (lost its electron).

Note the similarity between the spacings of the energy levels shown above and the spacings in the line spectrum of hydrogen. As the similarity suggests, these energy levels can be used to explain the observed line spectrum. At room temperature the hydrogen electron resides in the low energy orbit $n = 1$, called the **ground energy level**. When the atom is exposed to a source of energy, the electron may obtain just the right amount of energy to produce a jump to a higher energy level. This transition to a higher level, referred to as excitation, is illustrated in Figure 3.6, where the electron is designated by an arrow.

---

* In order to obtain joules we must use coulombs for charge, kilograms for mass, and we must express h in joule-s, and $k = 8.99 \times 10^9 \frac{\text{J-m}}{\text{C}^2}$.



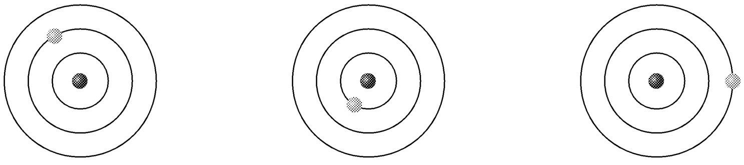
Electron in a higher energy level

Figure 3.6 Excitation of an electron.

Visualization 3.4

Examine the diagrams below and answer the following questions:

1. Which atom is closest to ionization?
2. Which atom has the most potential energy?
3. For which atom does it take the greatest amount of energy to remove the electron?
4. Which atoms are excited?



(a) (b) (c)

Solution:

1. Atom (c) because the electron has the highest energy.
2. Atom (c)
3. Atom (b) because the electron has the lowest energy (the most negative energy).
4. Atom (a) and (c). Atom (b) has the electron in the closest orbit and has the lowest energy.

After the electron has made the transition to a higher energy level, it can then fall back down to a lower level. In doing so, it emits energy in the form of a photon. For example, suppose an electron has been excited to the $n = 4$ level. It may now fall back, or relax, to the $n = 3$, the $n = 2$, or the $n = 1$ level. If it falls back to $n = 3$, as shown in Figure 3.7, its energy decreases from -1.36×10^{-19} to -2.41×10^{-19} J, a change of 1.05×10^{-19} J.

According to the Law of Conservation of Energy, this energy must now appear in another form—as an emitted photon with an energy of 1.05×10^{-19} joule. The frequency of the photon can be calculated from the Planck equation.

$$E = h\nu$$

$$\nu = \frac{E}{h} = \frac{1.05 \times 10^{-19}\,\text{joule}}{6.6 \times 10^{-34}\,\text{joule-s}} = 1.6 \times 10^{14}\,\text{s}^{-1}$$

According to the Bohr model, the origin of the line spectrum for hydrogen is as follows: The electron is excited by an energy source into a level of higher energy. When the electron relaxes, it emits a photon, which registers as a line in the spectrum. When a collection of many hydrogen atoms is excited, some atoms experience excitation to very high energy levels, while others are excited to lower energy levels. When relaxation occurs, the electrons of some atoms will fall back to the next lower level, others to the third lower level, and so on. The many lines in the spectrum, therefore, are a result of numerous electronic transitions.

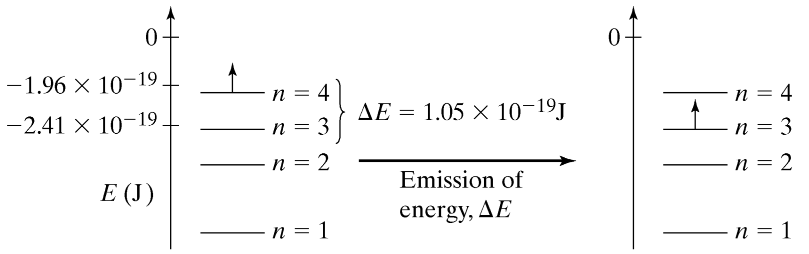
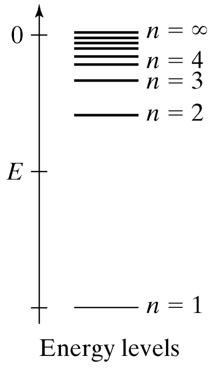


Figure 3.7 Relaxation and emission of energy.

Visualization 3.5

Use the diagram below to determine which requires more energy:

1. Excitation from $n = 1$ to $n = 2$, or
2. Excitation from $n = 2$ to $n = 3$, or
3. Relaxation from $n = 4$ to $n = 1$



Solution:

Relaxation gives off energy, whereas excitation requires energy from an external source. The greatest amount of energy is required to excite the electron from $n = 1$ to $n = 2$.

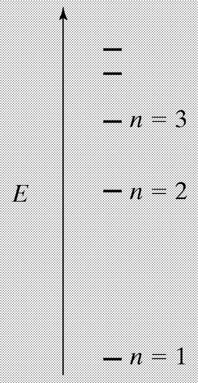
Methodology 3.1

Calculate the wavelength of the photon emitted when an electron in a hydrogen atom relaxes from the $n = 3$ energy level to the $n = 2$ level.

First, be sure that you know the meaning of the word "relax."

In this context, relaxation is the decrease in energy of an atom when an electron drops from one energy level to another.

Make a crude diagram of the energy levels for the hydrogen atom.



How do we go about determining the energy of the $n = 3$ and $n = 2$ levels?

We can determine these from the equation $E = -21.7 \times 10^{-19}/n^2$ J. The energy of the $n = 3$ level is $(-21.7 \times 10^{-19}\ \text{J})/(3)^2$ while that of the $n = 2$ level is $(-21.7 \times 10^{-19}\ \text{J})/(2)^2$.

Continued on next page

Methodology 3.1 Continued

Calculate the difference in energy between the $n = 3$ and $n = 2$ levels.

The difference in energy is

$$\Delta E = \frac{-21.7 \times 10^{-19}\,\mathrm{J}}{(3)^2} - \frac{-21.7 \times 10^{-19}\,\mathrm{J}}{(2)^2} = 3.01 \times 10^{-19}\,\mathrm{J}$$

This amount of energy is given off as a photon. What is the wavelength of that photon?

The wavelength of this photon can be calculated from the Planck equation and the equation $\nu\lambda = c$.

$$E = h\nu = \frac{hc}{\lambda}$$

or:

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\,\mathrm{J\text{-}s} \times 3.00 \times 10^{8}\,\mathrm{m/s}}{3.01 \times 10^{-19}\,\mathrm{J}}$$

$$= 6.60 \times 10^{-7}\ \mathrm{m} = 660\ \mathrm{nm}$$

This value is in good agreement with the wavelength of one of the lines in the visible region of the hydrogen emission spectrum. (See Problem 3.1.) In fact, all of the lines in the visible region of the emission spectrum, referred to as the **Balmer Series**, result from transitions from higher energy levels to the $n = 2$ level.

Bohr was able to account for most of the lines in the spectrum of hydrogen in this way. Indeed, the energy of the ground state of hydrogen as calculated by Eq. (6) is in excellent agreement with the experimentally determined ionization energy of hydrogen (which is, after all, the energy required to remove an electron from the ground state to the $n = \infty$, or zero, energy state). That it explained much of the hydrogen spectrum was clearly a major triumph for the Bohr model, and in 1922 Bohr received the Nobel Prize for his revolutionary idea. The victory was short-lived, however, because it soon became apparent that the model could not explain some of the lines in the hydrogen spectrum, and it was also inadequate for atoms containing more than one electron.

3.3 THE WAVE MODEL OF THE ATOM

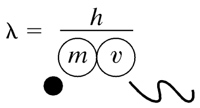
The currently accepted theory of electronic structure, the wave model, began with a suggestion by the French physicist Louis-Victor de Broglie. He proposed that if light, which was traditionally conceived of as a wave motion, could also be interpreted as having the qualities of a particle (the photon), then it is possible that the electron, traditionally treated as a particle, is also endowed with wave properties. This proposal was later verified experimentally by an interference experiment of the type discussed in Sect. 3.1. De Broglie went on to relate the wave properties of the electron to its particle properties with the relationship

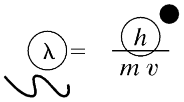
$$\lambda = \frac{h}{mv}$$

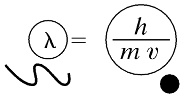
where λ is the wavelength of the wave, m is the mass of the electron, v is its velocity, and h is Planck's constant. An electron moving at a speed of 10^7 cm/s would have an associated wavelength of 7 nm, a very small but detectable wavelength.

Visualization 3.6

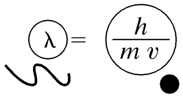
Which of the following sketches summarize the de Broglie relationship between the wave (∿) and particle (●) aspects of an electron?







Solution:



Problem 3.4

Calculate the wavelength of a 100-lb woman moving at a speed of 10 miles per hour.

Solution:

Before we can use the de Broglie equation, we must be certain that we have the mass and velocity in comparable units. If we use Planck's constant in J-s we will need kilograms for mass and m/s for speed.

First, convert 100 lb to grams:

$$100 \text{ lb} \times 454 \text{ g/lb} = 4.54 \times 10^4 \text{ g} = 4.54 \times 10^1 \text{ kg}$$

Next, convert 10 miles to meters:

$$10 \text{ mi} \times 5280 \text{ ft/mi} \times 12 \text{ in/ft} \times 2.54 \text{ cm/in} \times \frac{1 \text{ m}}{100 \text{ cm}} \; 1.6 \times 10^4 \text{ m}$$

Then, convert hours to seconds:

$$1 \text{ hr} \times 3600 \text{ s/hr} = 3600 \text{ s.}$$

The velocity therefore is:

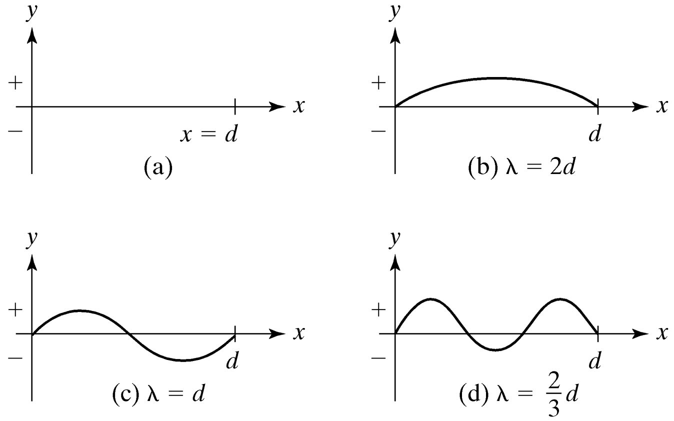
$$\frac{1.6 \times 10^4 \text{ m}}{3600 \text{ sec}} = 4.4 \text{ m/s}$$

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34} \text{ J-s}}{(4.54 \times 10^1 \text{ kg})(4.4 \text{ m/s})} = 3.3 \times 10^{-36} \text{ m}$$

(Notice that because a joule is a *kg*-m^2/s^2 the units cancel to give *m*.)

This, then, was the seed that fell upon the fertile minds of such physicists as Werner Heisenberg, Erwin Schrödinger, and P.A.M. Dirac and blossomed into the vastly important subject of wave mechanics. The discoveries in this field, which have led to our contemporary wave model of the atom, have been quite mathematical and abstract in nature; we will therefore attempt to provide only a qualitative understanding of its principal features.

Let us visualize an electron as something that we must endow with both particle and wave properties, these properties being related by the de Broglie equation. Since an atom



(a)

(b) $\lambda = 2d$

(c) $\lambda = d$

(d) $\lambda = \frac{2}{3}d$

Figure 3.8 Several waves confined to a line that have zero amplitude at the ends of the line.

is a rather complex three-dimensional object, let us first examine a much simpler one-dimensional problem: an electron confined to move along a line, say from $x = 0$ to $x = d$ on the x axis as shown in Figure 3.8. The electron has some of the characteristics of a wave, and we shall assume, therefore, that a wave exists in this region. We will represent the amplitude of the wave by measuring along the y axis in such a way that the vertical center of each oscillation falls on the x axis ($y = 0$). Every trough lies below the x axis (y is negative) and every crest lies above the x axis (y is positive).

Now we must impose a condition on our waves, which we will justify later: At the boundaries of the region, that is, at $x = 0$ and $x = d$, the amplitude of the wave shall be zero ($y = 0$). Even with this boundary condition, there are a number of waves that can occur in the region. For example, the wave shown in (b) above is one-half of a complete oscillation and has a wavelength (distance between crests) of twice the distance from 0 to d, or $2d$. The wave shown in (c) is a complete oscillation and therefore has a wavelength of d. The wave in (d) is one and one-half oscillations and has a wavelength of $\frac{2}{3}d$. For *any* wave occurring in this region, the wavelength can be expressed as

$$\lambda = \frac{2d}{n}$$

where n is an integer from 1 to infinity. For the first wave in the figure, then, $n = 1$; for the second, $n = 2$; and for the third, $n = 3$.

As we have seen in the Bohr model, the energy of the electron is of great importance. Can we now, by treating the electron as a wave, and from our knowledge of how the wave must fit into this region of space, obtain an equation giving the energy of the electron? We have previously found that the energy of electromagnetic radiation is directly proportional to its frequency ($E = h\nu$) and that frequency is inversely proportional to wavelength ($\nu = c/\lambda$). The energy of electromagnetic radiation is therefore also inversely proportional to its wavelength. Thus, the greater the n value for the wave, the smaller the wavelength and the higher the energy.

The energy can be determined more quantitatively by first combining the de Broglie equation and our equation for wavelength.

$$\lambda = \frac{2d}{n} \quad \text{(for waves confined to a line)}$$

$$\lambda = \frac{h}{mv} \quad \text{(de Broglie relation)}$$

Thus,

$$\frac{2d}{n} = \frac{h}{mv}$$

Solving for v, we obtain

$$v = \frac{nh}{2md}$$

Finally, if we treat the electron as a particle with a kinetic energy of $\frac{1}{2}mv^2$ (in the region from $x = 0$ to $x = d$ the electron has *only* kinetic energy), we have

$$E = \frac{1}{2}mv^2$$

$$v = \frac{nh}{2md}$$

Therefore

$$E = \frac{m}{2}\left(\frac{nh}{2md}\right)^2 \quad \text{or} \quad E = \frac{n^2h^2}{8md^2}$$

The energy of the electron is a function of several constants and the integer n. The relative energies and the wave associated with each energy level for $n = 1, 2, 3$, and 4 are shown in Figure 3.9.

It is now apparent that this electron can have only certain energies, which are prescribed by the number n. Hence, the energies are quantized, and n, like the number n in the Bohr equation, is referred to as a **quantum number**. This quantization of energy is a natural consequence of the wave character of the electron *and* the boundary conditions imposed upon these waves.

Now we return to the same question that we encountered in our discussion of light. What is waving? What do these electron waves mean? The best explanation of the physical significance of the wave was provided by the German physicist Max Born: The square of the amplitude of the wave at a given point is proportional to the probability of finding the electron at that point. Figure 3.10 shows the $n = 1$ and $n = 2$ waves and their squared values. Since the square of the amplitude for the $n = 1$ wave is greatest in the center of the region, this is the place where the electron is most likely to be found at any given time.

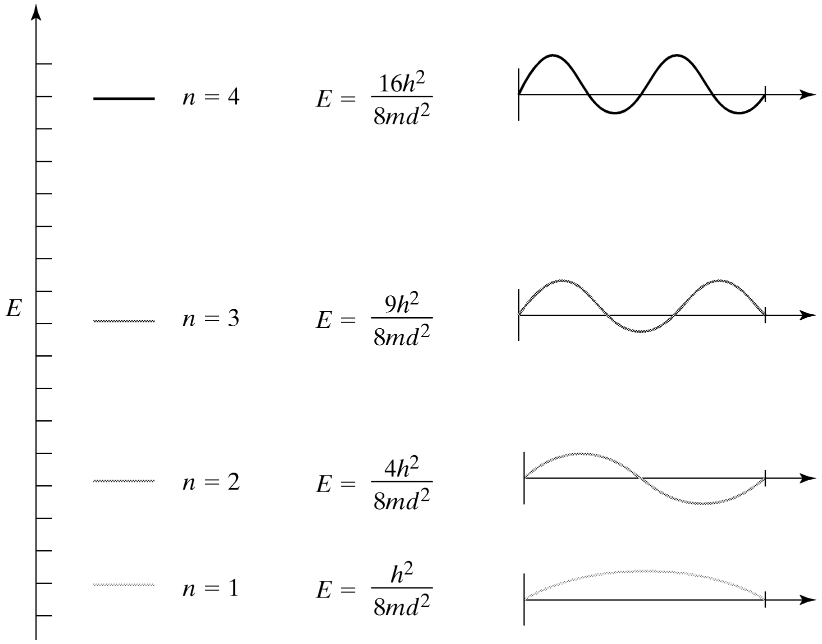


Figure 3.9 The energies of the waves characterized by $n = 1, 2, 3$, and 4.

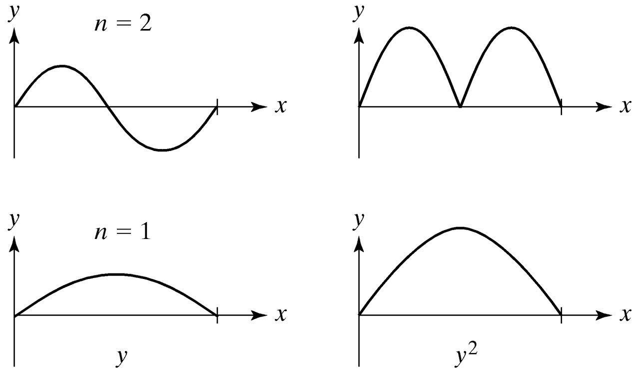


Figure 3.10 Relative location probabilities for an electron confined to a line.

For the $n = 2$ electron, the points of greatest probability lie on either side of the center of the region, and the probability of finding the electron at the very center of the region is zero.

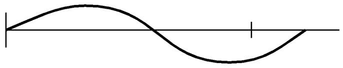
We can now explain our decision to restrict the waves to those with zero amplitudes at the boundaries of the region. If the electron is to be confined between $x = 0$ and $x = d$, it must have zero probability of being on or beyond the boundaries: hence, the amplitude at $x = 0$ and $x = d$ must be zero.

Visualization 3.7

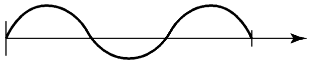
Assume that an electron can be described as a wave confined to a line. In the following diagrams,

1. Which electron has the highest energy?
2. Which electron has the highest probability of being at the center of the line?
3. Which electron can exist outside of the region to which it should be confined?

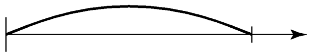
(a)



(b)



(c)



Solution:

1. The wave associated with electron (b) has the shortest wavelength and the highest energy.
2. Electron (c). Electron (b) has equal probabilities of being at one sixth of the line, three sixth of the line, and five sixth of the line.
3. Electron (a) does not obey the boundary conditions imposed upon it. Because the wave does not go to zero at the right boundary, it has a finite probability of being outside of the specified region.

The Heisenberg Uncertainty Principle

Another problem that arises when the position of an electron is examined is known as the **Heisenberg uncertainty principle**:

The position and the velocity of an electron cannot both be known with complete certainty.

If the position of the electron is pinpointed, the velocity becomes very uncertain. If the velocity is accurately known, the position is virtually unknown. In order to observe the position of a moving electron, we must be able to "see" it, which means that we must shine light on it. One of the laws of optics tells us that the smaller the object being observed, the shorter the wavelength of the light needed to observe it. Since an electron is extremely small, we need extremely short-wavelength light to "see" it in some hypothetical microscope. According to the Planck relationship, short-wavelength electromagnetic radiation has very high energy; thus, when the high-energy photon hits the moving electron so that we can observe it, the photon imparts a considerable jolt to the electron, changing its energy.

Let us assume that we note the position of the electron before it is moved by the photon. To determine the velocity of the electron, we would observe its position again after a certain interval of time. But since we have changed the energy, the velocity of the electron is not the same as the first time we observed it. Thus, we can never know the electron's original velocity, because in pinpointing its position we change its velocity. On the other hand, we might decrease the energy of the photon, and consequently increase its wavelength, so that the velocity of the electron would be altered only slightly. However, our "picture" of the electron would then become much less distinct*—the uncertainty in its *position* would increase.

Clearly, the wave-mechanical vision of the electron is a strange one: Sometimes the electron is treated as a particle, at other times as a wave. Its position can be dealt with only in terms of probabilities, and its energy is restricted to certain values. The strangeness of the vision, particularly the apparent wave-particle duality, is probably due in part to the inadequacies of the models, as indicated in our discussion of the nature of light. On the other hand, it is not unreasonable to suppose that the behavior of submicroscopic particles does not parallel the behavior of the macroscopic world.

Application of the Wave Model to Real Atoms

The application of the wave model to the simplest of all atoms, the hydrogen atom, is vastly more complex than the description of an electron oscillating along a line. Since an atom is a three-dimensional object, *three* quantum numbers, rather than one, are required to specify the energy and probability of finding the electron at any given point in space. The three quantum numbers are designated with the letters n, l, and m.

1. The **principal quantum number,** n, can have any integral value from 1 to infinity. For the hydrogen atom, n determines the total energy of the electron, according to an equation identical to that derived by Bohr.

$$E = \frac{2\pi^2 kme^4}{n^2h^2}$$

   It also specifies the most probable separation between the electron and the nucleus. The greater the value of n, the more likely the electron will be farther from the nucleus.

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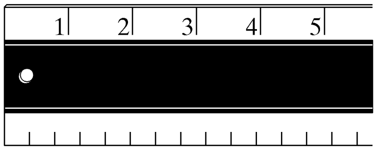
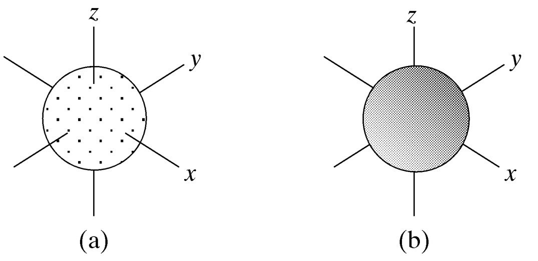
* The relationship of wavelength to the accuracy with which we can identify an object is similar to trying to measure the width of a grain of sand with a ruler that has lines only at the inch positions



In order to determine the width of the grain of sand we would need a micrometer, that is, a device that can measure to a thousandth of a millimeter. The grid of the measuring device is similar to the wavelength of light. The smaller the wavelength, the more accurately a small object can be measured.



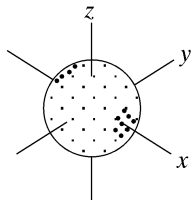
(a) (b)

Figure 3.11 The angular location probability patterns for an $l = 0$ electron.

2. The value of the **angular momentum quantum number**, l, depends upon n and can be any integer from 0 to $n - 1$. If n for a given electron is 1, l can only be zero; if $n = 2$, l can be either 0 or 1. This quantum number describes the angular momentum of the electron and also helps specify how far from the nucleus the electron is likely to be. Most important, however, the value of l determines the relative probability of finding an electron at any point on a hypothetical sphere surrounding the nucleus. (This we will refer to as the *angular* location probability pattern). Suppose, for example, an electron is designated by $l = 0$. The probability of finding this electron at equally spaced points on a sphere surrounding the nucleus is shown in Figure 3.11a, where relative probabilities are indicated by the size of the dots. Since all dots are of equal size, the probabilities are equal. This same information is often conveyed by the more picturesque electron-cloud picture (Figure 3.11b). Note that neither picture offers any information about how far from the nucleus the electron is most likely to be.

Problem 3.5

When $l = 1$ the probabilities of finding the electron at equally spaced points on a sphere are not the same. Draw a picture similar to that in Figure 3.11a that shows the probabilities greater along the x-axis for $l = 1$.



3. The value of the magnetic quantum number, m, depends upon l and can be any integer from $-l$ to $+l$, including zero. If an electron has an l quantum number of 2, its m value could be $-2, -1, 0, +1$, or $+2$. It is known that a moving electrical charge produces a magnetic field. The value of m is related to the magnetic field produced by the electron. When the atom is located in an external magnetic field, m helps to determine the energy of the atom. Probably a more important characteristic, however, is that it determines the spatial orientation of the electron cloud, as we shall see below.

Since the values for the three quantum numbers are interrelated, only certain sets of the three are possible. For example, if $n = 1$, l must be zero and m must be zero; only one set containing a principal quantum number of 1 is possible. Table 3.2 shows that there are four sets of numbers for $n = 2$: $(2, 0, 0)$, $(2, 1, -1)$, $(2, 1, 0)$, and $(2, 1, 1)$. Each set is a unique

TABLE 3.2 Possible Sets of *n*, *l*, and *m* Quantum Numbers for *n* = 1, *n* = 2, and *n* = 3

n	l	m	ORBITAL DESIGNATION
1	0	0	$1s$
2	0	0	$2s$
	1	-1	$2p_x, 2p_y, 2p_x$
		0	
		$+1$	
3	0	0	3s
	1	-1	$3p_x, 3p_y, 3p_z$
		0	
		$+1$	
	2	-2	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
		-1	
		0	
		$+1$	
		$+2$	

description of the energy and location probabilities of an electron. The electron in a hydrogen atom might be characterized by the set $n = 1, l = 0, m = 0$, or by the set $n = 2, l = 1, m = -1$, or by any other set, depending on its state of excitation. Each unique description—that is, each set of n, l, m numbers—is called an **orbital**. To simplify reference to these orbitals, the letters s, p, d, and f are used to designate l values of 0, 1, 2, and 3, respectively, while m values are designated by the subscripts shown in Table 3.2 above. Thus, the $n = 1$, $l = 0, m = 0$ orbital is referred to as a $1s$ orbital; the $n = 2, l = 0, m = 0$ orbital is a $2s$ orbital; the $n = 3, l = 1, m = 0$ orbital is a $3p_y$ orbital; and so forth.

Problem 3.6

Suppose that the relationship between n, l, and m obeyed a different set of rules. These rules are

$$n = 1, 2, 3, \ldots.$$

$$l = 0, \ldots, \mathrm{n}$$

$$m = -l, \ldots 0 \ldots . l$$

Determine the number of orbitals that have a principal quantum number of 1.

Solution:

In this hypothetical set of n, l, m values, l can have integer values from 0 to n. Thus, if $n = 1$, l can be 0 and 1. When $l = 0$, m can only be 0. When $l = 1$, m can be −l, 0, and 1. The following sets are possible $(1, 0, 0), (1, 1, 0), (1, 1, -1), (1, 1, 1)$. Each set describes an orbital and there are therefore four orbitals with $n = 1$.

We can now discuss more specifically how the orbital designation specifies the energy and location of an electron. The location probabilities for the s orbitals have already been given (Figure 3.11). Every s orbital, whether $1s$, $2s$, $3s$, and so forth, has the same angular location probability pattern. However, since the principal quantum number determines how far from the nucleus the electron is likely to be, a $2s$ electron will have a greater probability of being farther from the nucleus than a $1s$ electron. The

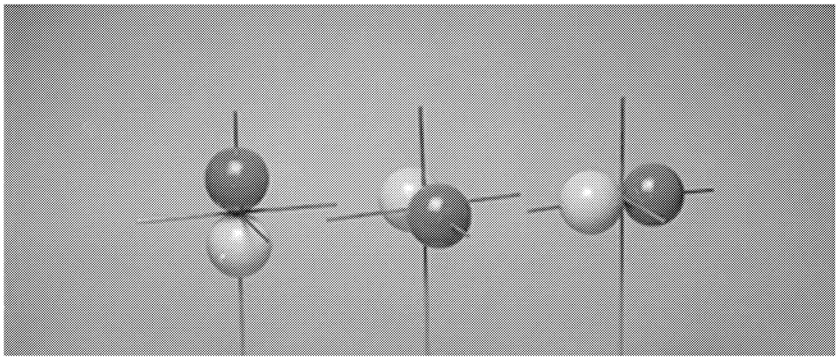


Figure 3.12 The three *p*-orbitals.

angular location probabilities for the three *p* orbitals are shown as electron-cloud models in Figure 3.12.

Notice that the two lobes of each orbital are given different colors. The colors represent the change in sign of the wave that defines each orbital. For example, for a p_x orbital the wave changes sign* as x goes from plus to minus (crosses the z-axis). A change in the m quantum number simply shifts the orientation of the orbital from one axis to another. All *p* orbitals have the same probability patterns, but, as noted above, n determines the distance from the nucleus. The electron-cloud pictures are given for the *d* orbitals in Figure 3.13, but the *f* orbitals are even more complex and are not shown.

In addition to characterizing the electron's location probability, the orbital also specifies the total energy of the electron. The electron energy levels for the hydrogen atom are shown in Figure 3.14.

This atom is quite unique in that all the orbitals within a given principal quantum level (n) have the same energies. (When two or more orbitals have the same energy, they are said to be *degenerate*). For all other atoms, only the orbitals within a given l level (2*p*, 3*p*, 3*d*, and so on) are degenerate. If these atoms are placed in a magnetic field, the magnetic quantum number also influences the orbital energies. Each orbital in a given angular momentum level (l) has a different value of m, and therefore each orbital has a different energy in a magnetic field.

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* This is entirely analogous to the change in sign of the wave for the $n = 2$ wave for the particle confined to a line.

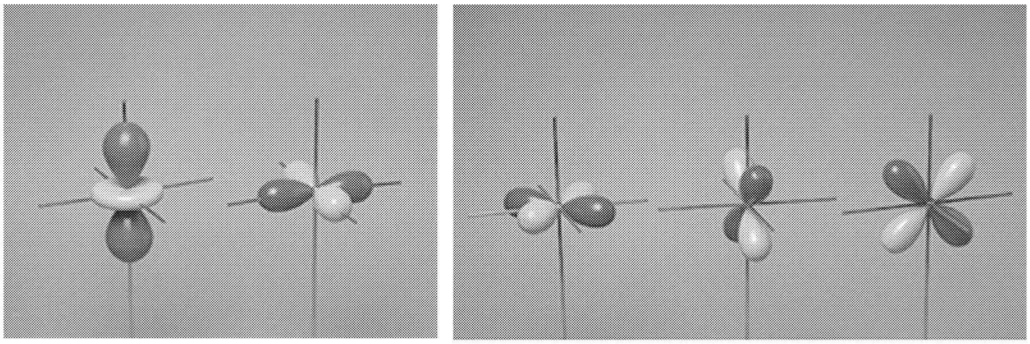


Figure 3.13 Angular location probabilities for d-orbitals.

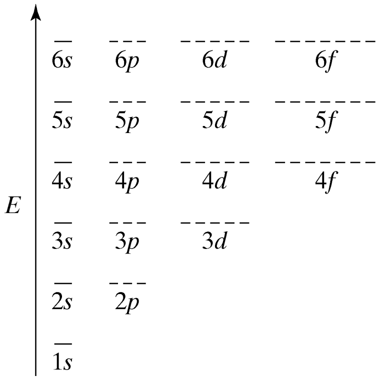


Figure 3.14 The electron energy levels for the hydrogen atom.

The wave model of the hydrogen atom, then, also explains line spectra: The electron can reside in any of the energy levels. At room temperature the electrons of the vast majority of hydrogen atoms are in the lowest energy level, the 1*s* level. At higher temperatures the electron may be in an excited level, a 2*s*, 2*p*, 3*s*, and so on, and when it reverts to a lower energy level, energy is released in the form of a photon. The energy of the photon is equal to the difference in energy between the two energy levels involved in the transition.

When hydrogen is excited in a magnetic field, the resulting line spectrum contains several features that still remain unexplained. These features can be rationalized if a fourth quantum number is introduced. This quantum number, s, seems to represent the spin of the electron, analogous to the spin of the earth on its axis, and can have only two values, $+\frac{1}{2}$ or $-\frac{1}{2}$. The two values can be interpreted as designations of spin in either the clockwise or counterclockwise direction. Thus, an electron in any orbital will have a spin quantum number of either $+\frac{1}{2}$ or $-\frac{1}{2}$, and therefore *every electron is fully characterized by four quantum numbers.*

The wave model can also be applied to atoms more complex than hydrogen. The location probability patterns of the orbitals for these atoms are similar to those for hydrogen. The relative energies of the orbitals for most atoms is shown in Figure 3.15. The exact energies for a given atom depend upon a number of factors: nuclear charge, number of electrons, and so forth.

It is possible to assign every electron in a given atom to an orbital according to the energy-level diagram above. When the **ground-state electron configuration** is being determined, every electron must be given the lowest possible energy. This must be done,

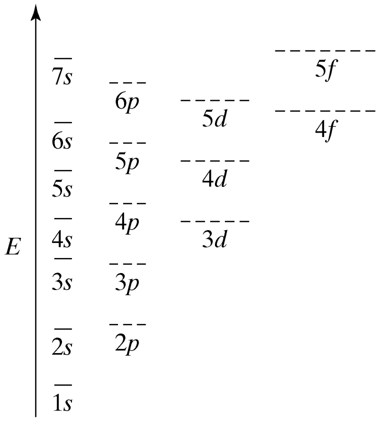


Figure 3.15 The energy levels for multi-electron atoms.

Problem 3.7

Consider the following sets of quantum numbers

	n	l	m	s
(a)	1	1	0	+1/2
(b)	2	1	1	+1/2
(c)	3	1	1	+1/2
(d)	2	0	0	−1/2
(e)	2	1	1	−1/2

1. Which set is not allowed by the wave model?
2. Which set represents an electron that is most likely to be the greatest distance from the nucleus?
3. How many of the electrons represented by these sets are *s*-electrons?
4. Which sets represent electrons that could occupy the same orbital?

Solution:

1. Set (a) is not a legitimate set because l can have the values 0 up to n-1. Thus, if n is 1, l can only be 0.
2. Set (c) which has the greatest value of n.
3. One, (d), has $l = 0$.
4. Sets (b) and (e) have identical values of n, l, and m, but different values of s.

however, within the bounds of a very fundamental law of nature, the **Pauli exclusion principle**:

Each electron within a given atom must have a
unique set of the four quantum numbers.

Therefore, two electrons can have the same set of n, l, and m values only if their s values differ, which means that only two electrons may occupy the same orbital, and to do so they must have different spin quantum numbers.

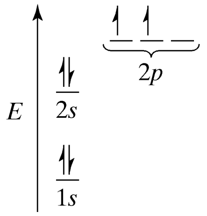
As an example, consider the second simplest atom, the helium atom. Helium has an atomic number of 2, which signifies that it has two electrons. Since we are interested in the ground-state electron configuration, the two electrons should be placed in the lowest possible energy level. This is the 1*s* orbital, and we can place both electrons in it if their spins are opposed (different s values). This configuration is written as $1s^2$, where the superscript 2 indicates the number of electrons in the orbital.

The lithium atom, with three electrons, may have only two electrons in the 1*s* level; the other goes to the next lowest level, the 2*s*. The lithium configuration is then $1s^2 2s^1$ (the superscript 1 is often omitted). Using the same procedure, the configuration of beryllium is $1s^2 2s^2$ and that of boron is $1s^2 2s^2 2p$.

With carbon a problem arises: Since there are three 2*p* orbitals of equal energy, should the sixth electron be placed into the *p* orbital that already contains an electron, or should it be placed in one of the two other *p* orbitals? In other words, if the electron is placed in the same orbital, the configuration would be $1s^2 2s^2 2p_x^2$ (the use of p_x rather than p_y or p_z is arbitrary, since the energies are the same). If the electron is placed in a second orbital, the configuration would be $1s^2 2s^2 2p_x^1 2p_y^1$. Experimental evidence indicates that the second configuration is more favorable, which seems reasonable because the electrons repel each other less if they are in different orbitals. This principle, known as **Hund's Rule**, may be formally stated as follows:

When filling a set of degenerate energy levels, the
electrons enter the orbitals singly, with spins in the same
direction (same *s* number), until the set is half filled.

In order to emphasize the spin aspect of this rule, we write the electron configuration of carbon as



Here the direction of the arrow, up or down, signifies the sign of the s value, plus or minus. Because it is inconvenient to always show the relative energies of the orbitals, we will also designate electron configurations horizontally, so that the configuration of carbon shown above becomes

$$\underset{1s}{\underline{\upharpoonleft\downharpoonright}}\quad \underset{2s}{\underline{\upharpoonleft\downharpoonright}}\quad \underbrace{\underline{\upharpoonleft}\ \underline{\upharpoonleft}\ \underline{\ \ }}_{2p}$$

Note that this procedure reveals nothing about the relative energies of the orbitals.

According to Hund's Rule, nitrogen should be given the configuration $1s^2 2s^2 2p_x{}^1 2p_y{}^1 2p_z{}^1$, or

$$\underset{1s}{\underline{\upharpoonleft\downharpoonright}}\quad \underset{2s}{\underline{\upharpoonleft\downharpoonright}}\quad \underset{2p_x}{\underline{\upharpoonleft}}\quad \underset{2p_y}{\underline{\upharpoonleft}}\quad \underset{2p_z}{\underline{\upharpoonleft}}$$

Thus, the $2p$ orbitals become half filled at nitrogen. The oxygen atom has eight electrons, and the last electron to be placed into the orbitals must be paired with an electron in one of the $2p$ orbitals. In fluorine, a fifth electron is added to the $2p$ level, and finally, with neon, whose configuration is $1s^2 2s^2 2p^6$, the level is completely filled.

Relationship of Electron Configurations to the Periodic Chart

Before we continue with our discussion of electron configurations it is important to explore their relationship to the structure of the periodic chart of the elements. If you are unfamiliar with this very important tool, take this opportunity to review some of the basic nomenclature of the table.*

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* The periodic table given in Appendix 8 consists of seven horizontal rows called **periods** and sixteen vertical **groups** or **families**. The elements within a group are similar in their chemical properties. The periods are generally referred to by number, beginning at the top; that is, period 1 consists of H and He, period 2 consists of Li through Ne, and so forth. The groups may also be referred to by number; for instance, Group 1, Group 14. An earlier convention used the letters A and B to distinguish the main group elements from the transition elements. In this convention, Group 14 was Group IVA. We will use the earlier convention in most cases because of the additional information that it provides.

The elements of the A groups are often called the **representative elements** because their properties adhere closely to the regular progression on which the periodic table is based. The elements in the B groups, which interrupt the representative elements in periods 4, 5, and 6, are called **transition elements**. These elements show considerably more deviation from the regular progression than do the representative elements.

The elements with atomic numbers 58 through 71 actually belong in the sixth period between lanthanum (atomic number 57) and hafnium (atomic number 72). These 14 elements, which have very similar properties, are called the **lanthanum series**, or simply the **lanthanides**. They are placed in a separate row rather than in the main body of the table simply to avoid making the table inconveniently wide. The elements with atomic numbers 90 through 103 are called the **actinium series** or **actinides**, and they occupy the same position in the seventh period as the lanthanides do in the sixth. Taken together, the lanthanides and actinides are sometimes called the **inner transition elements**, since they interrupt the transition series.

If we now turn our attention to the periodic chart, we find that we have just described the first two rows of elements. The first-period elements, hydrogen and helium, have their electrons in the first principal quantum level ($n = 1$), while the second-period elements, lithium through neon, have electrons in the first and second principal quantum levels. The electrons in the second principal quantum level are farther from the nucleus and are therefore the electrons involved in chemical bonding. For this reason, they are known as **valence electrons**, and the $n = 2$ level is called the **valence level**, or **shell**, for the second-period elements. (The valence level of the first-period elements is the $n = 1$ level.) The scheme shown in Figure 3.16 gives the number of valence electrons and the principal quantum number of these electrons for the elements in the first three periods.

Let us now continue this process of "building" the elements, sometimes referred to as **aufbau** (German, "building up"). The third-period elements fill the $3s$ and $3p$ orbitals; the electron configuration of phosphorus is, for example, $1s^22s^22p^63s^23p_x^{\,1}3p_y^{\,1}3p_z^{\,1}$. The energy-level diagram (Figure 3.15) indicates that the $4s$ orbital is slightly lower in energy than the $3d$ orbitals. Hence, rather than continuing to fill the third principal quantum level, the outermost electron of the first member of the fourth period, potassium, occupies the $4s$ orbital. The $4s$ orbital is filled at calcium, and at scandium the $3d$ orbitals begin to be occupied. Thus, the configuration for scandium is $1s^22s^22p^63s^23p^63d^14s^2$. (Note that in the electron configuration the orbitals are written in order of increasing n and l values, not necessarily in order of increasing energy.) Since there are five $3d$ orbitals, there are a total of 10 elements—the transition elements—whose valence electrons are in the $3d$ orbitals.

Sometimes electron configurations use the abbreviations [He], [Ne], and so on, to indicate that the configuration begins with the electron configuration of the inert gas enclosed in brackets;e.g., the configuration of Li, $1s^22s^1$, is abbreviated [He]$2s^1$. Inspection of the experimentally determined electron configurations of the first row transition elements reveals two anomalies: chromium has an outer configuration of $3d^54s^1$ rather than $3d^44s^2$, and copper is $3d^{10}4s^1$ rather than the expected $3d^94s^2$. Both anomalies reflect an extra stability associated with half-filled or filled degenerate energy levels. In other words, for chromium the extra stability of a half-filled $3d$ level more than compensates for the energy used in promoting an electron from the $4s$ to the $3d$ level. The extra stability of the filled level is also partly responsible for the nonreactive behavior of the inert gases.

When the first row of the transition elements is complete, the five $3d$ orbitals have been filled. At the element gallium, the $4p$ orbitals begin to fill; they are completely filled at the inert gas krypton. The aufbau trend of the elements from potassium to krypton is now repeated for the elements rubidium to xenon: The $5s$ orbitals are filled in rubidium and strontium, the $4d$ orbitals are filled from yttrium to cadmium, and the $5p$ orbitals become filled from indium to xenon.

The $6s$ orbitals are next in energy, according to the scheme in Figure 3.15 and the highest-energy electrons in cesium and barium are therefore in $6s$ orbitals. The scheme shows the $4f$ orbitals immediately above the $6s$ in energy, but an exception to this generalization occurs at element 57, lanthanum. The $5d$ orbital of lanthanum is lower in energy than the $4f$ orbitals, as one might expect, since lanthanum appears in the periodic table as a transition metal. The scheme now holds again, however, for element 58, cerium, with

	Main Group Elements							
Principal Quantum Number of the Valence Electrons	I	II	III	IV	V	VI	VII	VIII
1	**H** 1							**He** 2
2	**Li** 1	**Be** 2	**B** 3	**C** 4	**N** 5	**O** 6	**F** 7	**Ne** 8
3	**Na** 1	**Mg** 2	**Al** 3	**Si** 4	**P** 5	**S** 6	**Cl** 7	**Ar** 8

Figure 3.16 Number of valence electrons and the principal quantum number of these electrons for the elements in the first three periods.

configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^15s^25p^65d^16s^2$. From praseodymium to lutetium the seven 4*f* orbitals are filled, and the lanthanide elements, therefore, are the *f*-fillers.

We now return in our aufbau of the elements to the 5*d* orbitals and complete the third row of transition metals. Thallium then begins the 6*p* orbitals, which are filled at the inert gas radon. The next element, francium, has the radon configuration, denoted [Rn], plus a single 7*s* electron. The trend in configurations of the elements cesium to lutetium is now repeated with the series francium to lawrencium.

The general trends in orbital filling are summarized in Figure 3.17, which illustrates the relationship between the form of the periodic chart and the electron configurations. Elements of the first period fill the 1*s* orbital; elements of the second period fill orbitals in the second principal quantum level; elements of the third period fill orbitals in the third principal quantum level; elements of the fourth period fill orbitals in the fourth and third (3*d*) quantum levels, and so on. Elements within the same group have the same valence-electron configurations. For example, in Group IIIA, boron has the configuration $1s^22s^22p^1$, aluminum is $1s^22s^22p^63s^23p^1$, and gallium is $1s^22s^22p^63s^23p^63d^{10}4s^24p^1$. The valence-electron configuration for all three can be denoted as ns^2np^1, where *n* is 2 for boron, 3 for aluminum, and 4 for gallium.

The configurations and their relationship to the periodic chart can be summarized in still another way: Of the representative elements, Groups I and II are the *s*-fillers, while Groups III to VII and the inert gases are the *p*-fillers. The transition elements are the *d*-fillers, and the inner transition groups are the *f*-fillers.

Close scrutiny of the experimentally determined configurations will reveal a number of exceptions to the generalizations given above, but we will not attempt to explain these exceptions here. It should also be noted that the energy level scheme for an ion is usually different from that given in Figure 3.15 for the atoms. In fact, the electrons lost when an ion is formed from an atom are always the electrons that are farthest from the nucleus. In other words, the electrons lost are those at the end of the electron configuration. For example, the zinc atom has the configuration $1s^22s^22p^63s^23p^63d^{10}4s^2$; the configuration of the Zn^{2+} ion is $1s^22s^22p^63s^23p^63d^{10}$.

The realization that the structure of the periodic chart is closely related to the electron configuration of the elements not only provides an explanation for this structure, but also provides a convenient method to write electron configurations. With the periodic chart in front of you, you will find that you no longer need to rely on Figure 3.15 for the order of the energy levels, you need only follow the periodic chart (see Problem 3.8).

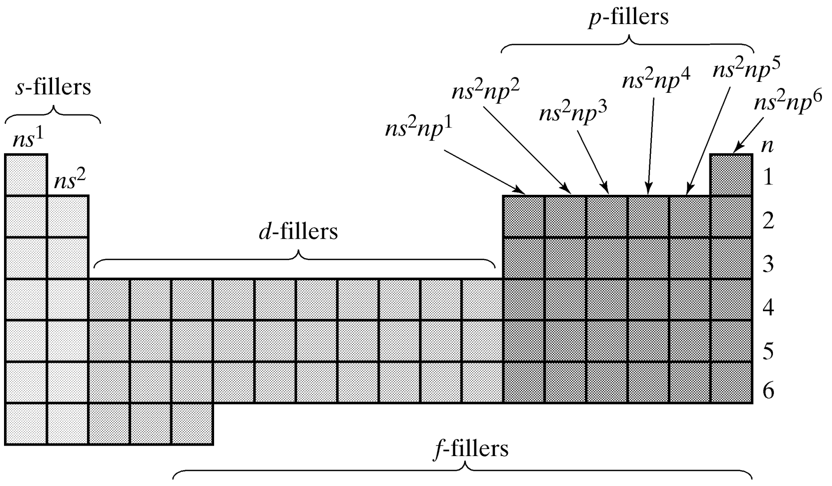

Figure 3.17 The relationship between the form of the periodic chart and the electron configurations.

Problem 3.8

Write the electron configuration for the element Ga.

Solution:

Follow the periodic chart from H to Ga, noting the types of element—*s*-filler, *p*-filler, etc.—and what period they are in. Starting with H and He, we put two electrons in the 1*s* orbital. The next two elements are *s*-fillers and are in the second period. Therefore the next part of the electron configuration is $2s^2$. The next six elements are *p*-fillers in the second period, and so we add $2p^6$. Now we are at Na, which is an *s*-filler in the third period, so we add a 3*s* electron, and then moving through the 3*p* fillers to Ar allows us to add $3s^23p^6$. Next come K and Ca, 4*s* fillers, and then the transition elements, which are *d*-fillers. Here we must remember that even though we are in the fourth period, the transition metals fill 3*d* orbitals, not 4*d* orbitals. Thus, Sc through Zn add 10 3*d* electrons. Then we get to Ga, which is a *p*-filler in the fourth period, and we therefore add a 4*p* electron. That gives us the configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^1$. Finally, we must rearrange the orbitals slightly to put them in order of increasing n:

$$\text{Ga } 1s^22s^22p^63s^23p^64s^23d^{10}4s^24p^1$$

Notice that if we want the configuration of Ga^{3+}, we now simply remove the three outermost electrons to give

$$\text{Ga}^{3+}\ 1s^22s^22p^63s^23p^63d^{10}$$

Evidence for the Wave Model

The wave model is one of the most powerful and important models in chemistry. Not only does it provide an explanation of the emission spectra of atoms, the structure of the periodic chart, and the variation in periodic trends such as ionization energies, it also is the basis for most models of the bonding between atoms in metals and molecules. However, all models are constantly being subjected to tests designed to test their validity, generality, and usefulness. One of the experimental tests of the wave model and the resulting electron configurations is obtained by using the technique called photoelectron spectroscopy.

We have previously seen that when an atom is irradiated with a photon, an electron can make a transition from one energy level to another. The energy of the photon, given by $E = h\nu$, must exactly match the difference between the two energy levels. We have also seen that if sufficient energy is imparted to an atom, the electron can leave the atom, thereby causing ionization of the atom. For example, for the hydrogen atom, ionization of the electron from the ground energy level requires 21.7×10^{-19} J or 1300 kJ/mol.

Now supppose a collection of atoms is irradiated with photons of increasing energy. When a photon has sufficient energy to cause ionization of an atom, an electron will be ejected. If the photon has more energy than required for the ionization, this energy will be imparted to the ejected electron as kinetic energy. Thus, the energy of the photon ($h\nu$) is equal to the ionization energy (IE) of the ejected electron plus its kinetic energy ($mv^2/2$):

$$h\nu = \text{IE} + mv^2/2$$

This relationship was first formulated by Einstein (see our previous discussion of the photoelectric effect) and is known as the **Einstein photoelectric law**. When ionization occurs because of irradiation with photons, it is called **photoionization**. The experimental process of determining the number of electrons ejected as the energy of the photons is increased is known as **photoelectron spectroscopy**. The experiment results in a plot of intensity (the greater the number of electrons ejected, the greater the intensity) *vs.* the ionization energy. The detector of the spectrometer determines the kinetic energy of the electrons striking the detector at each given value of hν. The ionization energy is then determined from the photoelectric law.

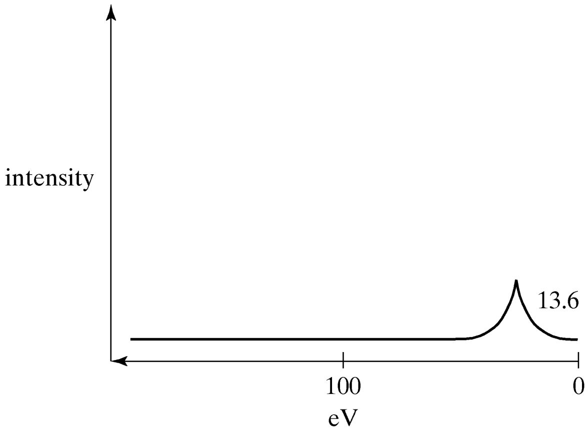

Figure 3.18 The photoelectron spectrum of hydrogen.

Figure 3.18 shows that the photoelectron spectrum of hydrogen gas contains only one peak at an ionization energy of 13.6 eV*. If the wave model is correct, this peak should correspond to the ionization of electrons from the 1*s* orbital, which, as indicated above, should require 1300 kJ of energy (13.6 eV is 13.6 eV × 96.5 kJ/eV = 1.31×10^3 kJ). Clearly there is good agreement between the model and the experimental results.

Another test of the wave model is provided by the photoelectron spectrum of atoms containing more than one electron. For these atoms, electrons in different energy levels should be ejected as the photon energy is varied, and the intensity should reflect the number of electrons in a given energy level. For sodium, with its electron configuration of $1s^22s^22p^63s^1$, there are electrons in six different orbitals. However, the 2*p* orbitals are degenerate and there are therefore only four different energy levels (1*s*, 2*s*, 2*p*, 3*s*). There are two electrons in the 1*s*, two in the 2*s*, six in the 2*p*, and one in the 3*s*; consequently, the relative intensities of the peaks in the photoelectron spectrum should be in the ratio of 1,6,2,2 for the peaks in order of increasing energy. The actual photoelectron spectrum of sodium atoms is shown in Figure 3.19, which clearly shows four peaks in the predicted intensity order. The small peak at 5.2 eV corresponds to ionization from the 3*s* orbital, while the highest energy peak at 1078 eV corresponds to ionization from the 1*s* orbital. Here again, then, is additional evidence that supports the wave model.

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* Photoelectron spectra are generally reported in units of electron volts. One electron volt is the energy obtained when an electron falls through a potential difference of one volt. One electron volt (eV) per mole is equivalent to 96.5 kJ.

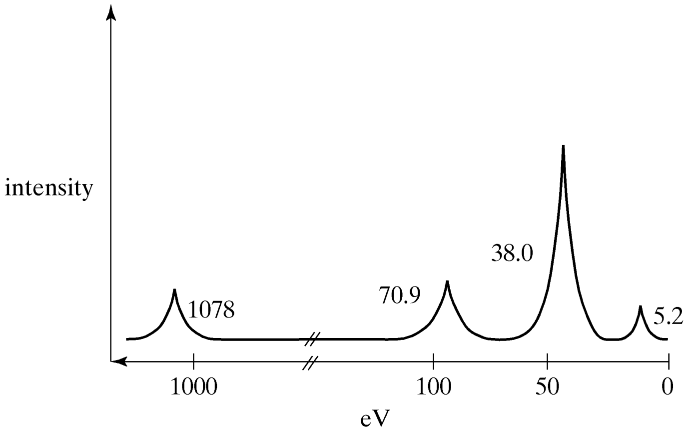


Figure 3.19 The photoelectron spectrum of sodium.

CHAPTER SUMMARY

Because much of the evidence upon which the theory of electronic structure is based comes from spectral measurements, this chapter began with a brief discussion of the nature of light and emission spectra. You should master the concepts of wavelength, frequency, electronic transitions, the Planck relationship, and the nature of an emission spectrum.

Although the Bohr model of the atom is no longer considered adequate, it was an important step toward an understanding of electronic structure. Examining the principles of this theory and its explanation of the quantization of energy will prepare you for the study of the more complex wave model that is the currently accepted theory of electronic structure.

The development of the contemporary wave model is highly mathematical, and a full treatment of it is well beyond the scope of an introductory chemistry course. But be sure that you are able to follow the qualitative treatment given in the text. A thorough understanding of the derivation of the energy of an electron confined to a line and of concepts such as the de Broglie relationship and the Heisenberg uncertainty principle will help you to understand the origin of quantum numbers.

One of your major goals in the study of this chapter should be to learn to construct the electron configurations of the various atoms. Since all electron configurations can be constructed by applying a few basic rules in a simple, orderly process, it is not necessary to memorize the configuration for any of the elements.

Ground-state electronic configurations of all the known elements can be described using seven principal quantum numbers, denoted by n, which may be thought of as seven main energy levels that electrons can occupy. The higher the principal quantum number, the farther the average distance of its electrons from the nucleus. The angular momentum quantum number, l, may be thought of as dividing these main levels into sublevels, designated s, p, d, and f. The number of **orbitals** within a given sublevel is determined by the number of different values of m (the magnetic quantum number) possible for that sublevel. For $l = 0$, there is only one possible value of m and therefore only one orbital in the s sublevel. For $l = 1$, there are three possible values of m and therefore three p orbitals in every main level. One additional quantum number is necessary for the complete description of each electron in an atom—the spin quantum number, s, which can have only two values $\left(+\frac{1}{2} \text{ and } -\frac{1}{2}\right)$.

After you have learned the relationships between the orbitals and the orbital designations, only three additional rules are necessary in order to write electron configurations: (1) the Pauli exclusion principle, which permits two electrons to have the same set of n, l, and m values only if their s values differ (allowing each orbital to contain only two electrons); (2) Hund's Rule, which states that no orbital in a given sublevel can contain two electrons until each of the orbitals in that sublevel contains one electron; and (3) the order of increasing energy of the various levels, that is, the order in which the energy levels are filled with electrons:

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f$$

This order can be determined from the periodic chart once the relationship of electron configuration to the form of the chart is understood.

To be sure that you know these rules and understand their application, practice writing electron configurations without reference to the periodic table. To write an electron configuration, all you need to know is the atomic number. For example, what is the electron configuration for the element with the atomic number 33? The atomic number tells us that there are 33 electrons in the neutral atom. By applying the rules concerning the number of orbitals and order of filling, we can conclude that the 33 electrons in this element are distributed as follows: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$.

When writing these configurations, be careful to list the orbitals in the proper sequence. For example, the electron configuration for manganese is $1s^2 2s^2 2p^6 3s^2 3p^6$

$3d^54s^2$, not $1s^22s^22p^63s^23p^64s^23d^5$. The **valence** electrons—the electrons that are used in bonding or are lost in the formation of a positive ion—always appear at the end of the configuration.

Electron configurations are also sometimes written using arrows to designate electrons and horizontal lines to indicate orbitals. For example, the configuration of silicon can be written as:

$$\text{Si}\quad \underset{1s}{\underline{\uparrow\downarrow}}\ \ \underset{2s}{\underline{\uparrow\downarrow}}\ \ \underbrace{\underline{\uparrow\downarrow}\,\underline{\uparrow\downarrow}\,\underline{\uparrow\downarrow}}_{2p}\ \ \underset{3s}{\underline{\uparrow\downarrow}}\ \ \underbrace{\underline{\uparrow}\,\underline{\uparrow}\,\underline{}}_{3p}$$

TERMS

Some additional important terms include:

Wavelength A term used to describe electromagnetic vibrations (including light); defined as the distance between crests of a wave. (The common symbol for this term is the Greek letter *lambda*, λ.)

Frequency A description of an electromagnetic vibration in terms of the number of wave crests that pass a given point in a given amount of time. Frequency, denoted by the Greek letter nu, ν, is usually expressed as vibrations, or cycles, per second. Frequency and wavelength are related by the expression $\lambda\nu = c$, where c is the velocity of the electromagnetic wave. (For light in a vacuum, $c = 3 \times 10^8$ m/s.)

Photon A quantity of electromagnetic energy, defined by the expression $E = h\nu$ where ν is the frequency and h is a constant (6.6×10^{-34} J-s) called **Planck's constant**.

Quantization of energy The occurrence of energy in terms of discrete energy packets called **quanta** (singular, **quantum**). Since only certain fixed energy levels are accessible to the electrons in an atom, an increase or decrease in electronic energy must occur in units of these quanta.

de Broglie equation An equation that relates the wave properties and the particle properties of an electron: $\lambda = h/mv$ where λ is the wavelength of the wave, m is the mass of the electron, v is the velocity of the electron, and h is Planck's constant.

Heisenberg uncertainty principle The principle that states that the position and the velocity of an electron cannot both be known with certainty. In other words, if either the position or the velocity of an electron is known accurately, the other characteristic is uncertain.

Orbital The unique description provided by a given set of n, l, and m values. No more than two electrons can be assigned to a given orbital, and these two electrons must have opposite spins (different s values).

Degenerate The term for two or more orbitals having the same energy.

Ground-state electron configuration The distribution of electrons within an atom according to energy levels, in which every electron is assigned the lowest possible energy level.

Valence electrons The electrons in the main energy level farthest from the nucleus. Valence electrons are involved in chemical bonding.

PROBLEMS

1. A ripple in a pond travels 1.0 ft per second. The distance between crests is 1.0 in. Calculate the frequency of the ripple (the number of times per second that a water molecule in the middle of the ripple would move up and down).
2. Calculate the wavelength in Angstroms of light that has a frequency of $1 \times 10^{18}\ \text{s}^{-1}$.
3. Calculate the energy in joules of one photon with the frequency of problem 2.

4. How much could a mole of the photons in question 3 raise the temperature of a liter of water if all of their energy were transferred to the water. The heat capacity of water is 4.18 J/°C.

5. A neutrino is a particle with a mass that is 16700 times less than that of an electron and it has no charge. If a neutrino was travelling through space with a velocity of 3.00×10^8 m/s, at what frequency of radiation would the neutrino be detected?

6. WFNM, Franklin & Marshall College's radio station, broadcasts at a frequency of 89.1 MHz. What is the wavelength (in meters) and the energy (in calories) of this frequency?

7. The reaction for the photochemical decomposition of NO_2, which occurs at a wavelength of 404.7 nm, is as follows:

$$2\ \text{NO2} + h\nu \longrightarrow 2\ \text{NO} + \text{O}_2$$

(a) Calculate the frequency of this light.
(b) Calculate the energy in joules of one photon of this light.
(c) Calculate the energy in joules of one mole of photons of this light.
(d) If one photon were required for the decomposition of each NO_2 molecule, how many photons would be required for the decomposition of 5 g of NO_2?

8. In the earth's upper atmosphere, sunlight with a wavelength of 210 to 310 nm reacts with ozone and is therefore prevented from reaching the earth's surface. The equation for the reaction is

$$\text{O}_3 + h\nu \longrightarrow \text{O}_2 + \text{O}$$

(a) Calculate the frequency of the light at the upper and lower limits.
(b) Calculate the energy of the light (in joules) at the upper wavelength limit.

9. A photon has an energy of 4.75×10^{-19} J. Calculate the wavelength of this photon and its color, if any.

10. Calculate the kinetic energy in joules of a 200-lb runner moving at a velocity of 20 miles per hour.

11. Distinguish carefully between
(a) an orbit and an orbital
(b) frequency and wavelength
(c) the Heisenberg uncertainty principle and the Pauli exclusion principle
(d) a wave and a particle
(e) a quantum number and an energy level
(f) an energy level and an electron configuration

12. Distinguish clearly between the Bohr model and the wave model in terms of the
(a) nature of an electron
(b) position of an electron
(c) energy of an electron
(d) size of an atom

13. (a) How would the Bohr model be different if Bohr had assumed that the angular momentum could have only one value; that is, for example, if $mvr = h$. No calculation or derivation is necessary.
(b) Would this model explain emission spectra? Explain.

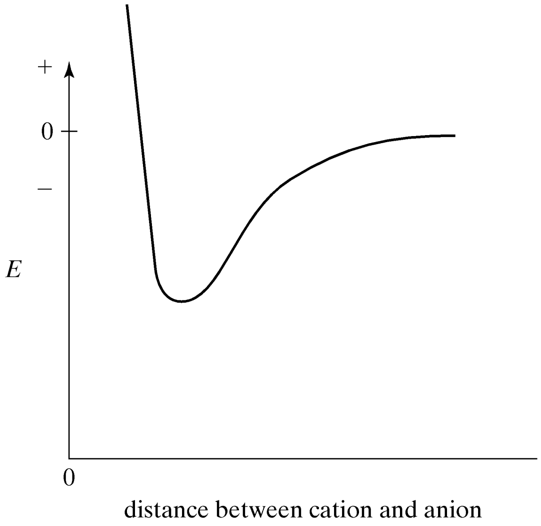
14. Use the Bohr model to calculate the radius of a hydrogen atom with its electron in the $n = 1$ orbit. Compare the radius obtained with the atomic radius of hydrogen of 40 pm.

15. Before the development of the Bohr model, the wavelengths of the lines in the visible portion of the emission spectrum of hydrogen were known to be given by the equation

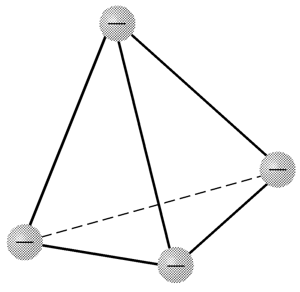
$$\frac{1}{\lambda} = 1.09678 \times 10^7\ \text{m}^{-1}\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where $n = 3, 4, 5, \ldots$ and λ is expressed in centimeters. (The number $1.09678 \times 10^7\ \text{m}^{-1}$ is known as the Rydberg constant.) Use the equation to calculate the energy of the light when $n = 4$. Then use the Bohr model to calculate the energy released when a transition from $n = 4$ to $n = 2$ occurs.

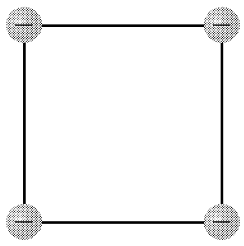
16. The following is a plot of the potential energy of a cation and anion as a function of the distance between their centers. Explain the plot.



17. Calculate the potential energy of four electrons located at the apices of a tetrahedron with distances of 2.0 Å.



18. Calculate the potential energy of four electrons located at the corners of a square with edges of 2.0 Å.



Compare the value obtained with the value obtained for the tetrahedron in problem 4. Which configuration of electrons is more stable?

19. Imagine a hydrogen atom that has only potential energy (the electron cannot move) and the separation between the proton and the electron may only have the values2

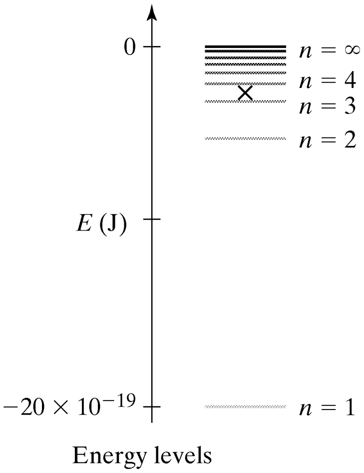
$$r = n(1\ \text{Å}),\ n = 1, 2, 3\ .\ .\ .\ .\ .$$

(a) Which of the following equations represents the potential energy of this atom?
  (1) $V = n(1\ \text{Å})$
  (2) $V = kq_1q_2/r$
  (3) $V = kq_1q_1/(n \times 1 \times 10^{-10}\ \text{m})$
(b) Calculate the energy of this atom when the electron is closest to the proton.
(c) The ionization energy of any gaseous atom is the amount of energy necessary to just remove (without supplying any excess kinetic energy) an electron from the atom. What is the ionization energy of this atom in its ground state?
(d) What is the energy of this atom in its first excited state or energy level?
(e) How much energy is required to excite the atom from its ground energy level to the first excited energy level?
(f) How could you provide this amount of energy in the laboratory?
(g) What frequency of light would be required to produce this amount of energy?
(h) What is the wavelength of this light and in what area of the electromagnetic spectrum is it found?

20. Calculate the angular momentum of a 1-g ball bearing moving at a velocity of 1 m/s around a circular track with a radius of 0.5 m. What are the units of the angular momentum?

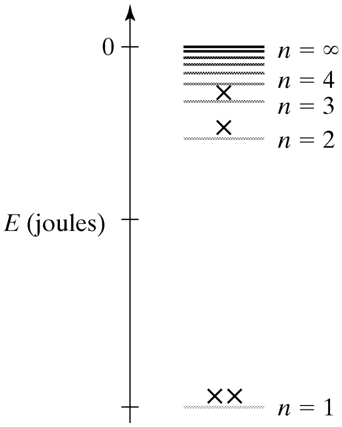
21. According to the Bohr model, what is the lowest angular momentum that an electron in the hydrogen atom could have? What is the next lowest value of angular momentum? What, according to Bohr, causes a change in the angular momentum?

22. If a hydrogen atom has the following electron configuration (the electron is designated with an x) how many lines would be expected in its emission spectrum?



Energy levels

23. What neutral atom is represented by the diagram below? Is the atom in its ground state? How many lines would be expected in its emission spectrum?



Energy levels

24. If, in a given collection of hydrogen atoms, only the first four energy levels are populated, how many lines will be observed on the emission spectrum of this collection?

25. Suppose that a hydrogen atom has energy levels given by the formula

$$E = -2 \times 10^{-11}/n \text{ ergs, where } n = 1, 2, 3,\ .\ .\ .\ .\ .$$

[Note: $h = 6.6 \times 10^{-27}$ erg-sec, $c = 3 \times 10^{10}$ cm/sec, charge on electron $= -4.8 \times 10^{-10}$ esu]

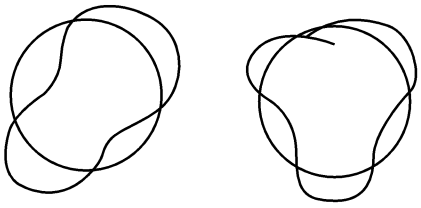
a. Determine the wavelength of light emitted when the atom relaxes from the first excited state to the ground state.
b. Assume that *all* of the energy of the atom is due to electrostatic potential energy. What is the distance between the proton and the electron in the ground state.
c. Suppose that a mole of these hydrogen atoms has just been excited and that for some atoms there is an electron in the second excited state ($n = 3$), for some the electron is in the first excited state, and other atoms have the electron in the ground state. How many lines will be observed in the emission spectrum of these atoms?

26. Suppose that the allowed wavelengths for an electron confined to a line that is 1 Å long are given by:

$$\lambda = n(1 \times 10^{-8}\ \text{cm})$$

Also assume that the electron has only kinetic energy and then derive an expression for the energy of the electron.

27. Picture the electron of the hydrogen atom as a wave that is confined to a circle surrounding the nucleus. Assume that the radius of the circle is r and that the wave must be continuous. For example, wave a below is allowed, but wave b is not.



(a) (b)

(a) Remembering that the circumference of a circle is $2\pi r$, develop a general expression for the wavelength of allowed waves on the circle.

(b) Now, use the longest wave on a circle with $r = 50$ pm (roughly the size of the hydrogen atom) and determine the velocity of the electron.

28. Use Einstein's relationship between mass and energy, $E = mc^2$, and Planck's equation to derive the de Broglie relationship.

29. The earth's mass is 5.979×10^{24} kg and its average velocity of orbit is 29.771 km/s. What is the de Broglie wavelength of the earth?

30. Calculate the wavelength of
a. an electron whose velocity is 0.12 as fast as the velocity of light
b. a 1-pound object whose velocity is 0.12 as fast as the velocity of light

31. Discuss the peculiarities of life in a world in which velocity is quantized.

32. Assume that the energy levels of a 100-g ball contained in a 1-meter, one-dimensional box are given by the equation for the electron confined to a line. Calculate the spacing between the lowest energy levels. Would the behavior of the ball be affected in any observable way by this quantization?

33. Calculate the ionization energy of hydrogen in kilojoules per mole and compare it with the experimental value.

34. How does:
a. a 1*s* orbital differ from a 3*s* orbital?
b. a 2*s* orbital differ from a 2*p* orbital?
c. a 2*p* ($l = +1$) orbital differ from a 2*p* ($l = -1$) orbital?
d. an orbital differ from an orbit?

35. List all possible sets of *n*, *l*, *m*, and *s* for $n = 4$.

36. Which of the following sets of quantum numbers are not allowed?
a. $n = 0, l = 0, m = 0$
b. $n = 3, l = 2, m = 0$
c. $n = 3, l = 3, m = 0$
d. $n = 3, l = 2, m = -3$

37. Why is there only one *s* orbital but three *p* orbitals in every major quantum level (except $n = 1$)?

38. For how many orbitals is the principal quantum number, *n*, equal to 5? Of these orbitals, how many have *l* equal to 3? How many have *m* equal to +1?

39. Which of the following transitions requires the greatest amount of energy?
a. from a 3*d* to a 4*s* orbital
b. from a 3*s* to a 3*p* orbital
c. from a 1*s* to a 2*s* orbital
d. from a 1*s* to a 2*p* orbital

40. Distinguish clearly in terms of energy and electron probability distribution between a 2*s* and a 2*p* orbital for both hydrogen and carbon.

41. Write electron configurations for the following elements or ions:
(a) F (b) K (c) Co (d) Eu (e) Fe^{2+} (f) Br^-

42. Write electron configurations for Fe^{3+}, K^+, Cl^-, Sn^{2+}, and O^{2-}.

43. Give the electron configuration for:
a. Hg b. Se^{2-}

44. Write the electron configuration for krypton. Then give the electron configurations for three negative ions and three positive ions that are isoelectronic (have the same number of electrons) with krypton. Arrange the six ions in order of increasing size and rationalize the order.

45. Which of the following is the correct order of the energies of the orbitals of the Zn^{2+} ion:
a. 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d* b. 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*

46. A half-filled or completely-filled set of degenerate energy levels seems to have some extra stability. Which is the correct electron configuration for:
1. Cu^+
 a. $1s^22s^22p^63s^23p^63d^94s^1$ b. $1s^22s^22p^63s^23p^63d^{10}$
2. Cr
 a. $1s^22s^22p^63s^23p^63d^44s^2$ b. $1s^22s^22p^63s^23p^63d^54s^1$

47. One electron resides in a 4*s* orbital, another resides in a 2*p* orbital in the same atom. Which electron has the lower energy? Which electron has a higher probability of being farther from the nucleus? Which electron is spherically "distributed" about the nucleus?

48. Discuss the difference between the electronic structures of metals and nonmetals.

49. Let us suppose that we lived in a universe in which the quantum numbers obeyed a slightly different set of rules. Suppose that

$$n = 1, 2, 3. \; . \; . \; .$$
$$l = 0, \; . \; . \; . \; n - 1$$
$$m = 1$$
$$s = +1/2, -1/2$$

and that the Pauli Principle and Hund's Rule still apply.
(a) How many *s* orbitals will there be in a given quantum level?
(b) How many *p* orbitals will there be in a given quantum level?

50. Imagine that in some far distant corner of the universe, the properties of matter are determined by laws that are slightly different from those operative on earth. For example, in this part of the universe the electronic structure of atoms is governed by the quantum numbers n, l, m, and s, but m can have values ranging from 0 to l (rather than $-l \dots 0 \dots +l$ as is true on earth). Assuming that all the other relationships (and the Pauli exclusion principle) are the same as on earth, answer the following questions about matter in this part of the universe.

(a) How many p orbitals are there in each principal quantum level?

(b) How many transition metal elements will there be in the first period that contains these elements?

Another very strange feature of matter in this part of the universe is that the model of a particle confined to a line applies to all large objects (baseballs, boulders, etc.). Assume that a baseball thrown by a pitcher in this part of the universe has only kinetic energy and that the energy levels available to it are given by

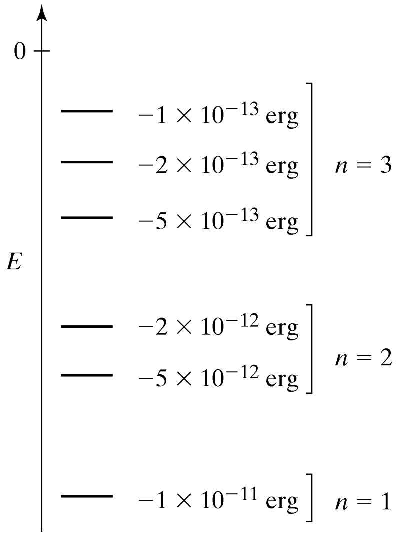
$$E = \frac{n^2h^2}{8\,ml^2}$$

(Planck's constant has a different value in this strange world: 1×10^2 J-s.)

(c) Calculate the energy of a 100-g baseball when it is in its lowest energy state and is traveling the 60 ft from the pitcher's mound to the catcher.

(d) Calculate the velocity of the baseball (in meters per second) in its second lowest energy state.

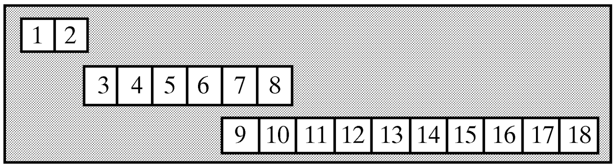
51. The following diagram gives the energy level diagram for all orbitals of the elements on the planet Obfuscate. The principal quantum number for the lowest energy orbital is 1; the principal quantum number of the next two lowest energy orbitals is 2; the principal quantum number of the highest three orbitals is 3.



a. Give the relationship between n, l, and m.
b. An atom of some element on Obfuscate contains eight electrons. Give the electron configuration for this atom.
c. Calculate the ionization energy of the atom in part b in kcal/mol.
d. Calculate the wavelength of the photon emitted when the atom in part b relaxes from the first excited state to the ground state.
e. Give a diagram of the periodic chart for the elements on Obfuscate.
f. For the element with only one electron calculate the centrifugal force, assuming that the electron has only potential energy and is in the ground state.

52. Crocodile Dundee discovered a mysterious set of 18 elements in the mouth of a crocodile in Mike's Bar. For this set of elements $n = 1, 2, 3, \dots$, $m = -l, \dots 0, \dots +l$, and $s = +1/2$ and $-1/2$ as is true for the normal elements. Dundee also found the following periodic chart for these mysterious elements (only the atomic numbers are given):

a. What is the relationship between l and n for these mysterious elements?
b. Where did Dundee find the periodic chart?

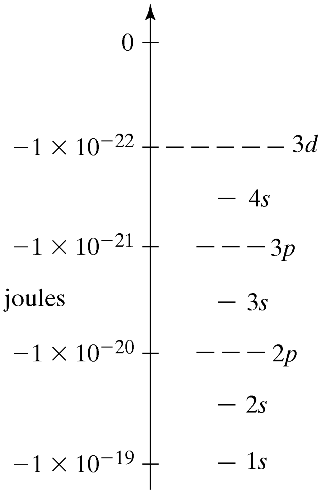


53. Suppose that a hypothetical atom has 5 electrons. The energies of the orbitals of this atom are given by the equation $E = -(10 \times 10^{-12}\ \text{erg})/n$ where $n = 1, 2, 3, 4, \dots$.

a. Give an energy level diagram *and the energies* of the 4 lowest energy orbitals. Label the diagram appropriately.
b. Calculate the ionization energy of the atom.
c. Diagram an excited state for the atom using arrows to represent electrons.
d. Calculate the wavelength of the photon emitted when relaxation from $n = 4$ to $n = 3$ occurs.

54. The Land of the Jawas contains a major deposit of the element Jawine, symbol J.

a. The electrons in this element are described by the same set of quantum numbers that describe elements on earth *except* that the spin quantum number can have the values +1/2, 0, and −1/2. Jawine has a total of 23 electrons. Populate the following energy level diagram in order to describe Jawine in its ground state.



b. Use your diagram above to calculate the first ionization energy of Jawine in kJ/mol.

c. When 1 mol of H_2 reacts with an excess of J, 50 g of J is consumed to form a compound of formula H_2J. What is the atomic weight of J?

55. Fill in the blanks.

1. When two or more orbitals have the same energy, they are said to be ____________.
2. The ____________ quantum number represents the main energy level of an atom's electron.
3. In describing an electromagnetic vibration, the term ____________ is used to denote the distance from crest to crest of a wave.
4. A bundle of electromagnetic radiation is called a ____________.
5. Because only certain fixed energy levels are accessible to electrons in an atom, this energy is said to be ____________.
6. The Bohr model of the atom positioned the electrons in ____________ around the nucleus.
7. The Heisenberg uncertainty principle states that the ____________ and the ____________ of an electron cannot both be known with certainty.
8. Two electrons in the same orbital have different ____________ quantum numbers.
9. The quantum number designated by l specifies the ____________ of the electron cloud; the quantum number m specifies the ____________ of the electron cloud.
10. That no two electrons in an atom can have the same four quantum numbers is a statement of the ____________ principle.
11. The electrons in the main energy level farthest from the nucleus are called ____________ electrons.
12. Groups ____________ and ____________ of the periodic tables are *s*-fillers.
13. Elements with electron configurations in their outer most main energy level of s^2p^6 are called ____________ ____________.
14. The 2*s* orbital has a ____________ shape.

56. Multiple-choice questions

1. The chemical properties of an element depend largely on its
   (a) mass number
   (b) ratio of neutrons to protons
   (c) electron configuration
   (d) number of naturally occurring isotopes
2. The electron arrangement $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ could <u>not</u> be that of
   (a) an inert gas (b) a positive ion
   (c) a negative ion (d) a transition element
3. Which of the following is largest?
   (a) Br^- (b) Kr (c) Rb^+ (d) Sr^{2+}
4. In general, the nonmetals are
   (a) *s*-fillers (b) *p*-fillers (c) *d*-fillers (d) *f*-fillers
5. The periodic family whose members have electron configurations ending in d^5s^2 is contained in
   (a) Group IIA (b) Group IIB
   (c) Group VB (d) Group VIIB

4 The Periodic Table

If each element had only its own specific and unique properties, it would be almost impossible to learn enough about the behavior of matter to develop a predictive science. Fortunately, this is not the case, and chemistry has become a major science within the past century. Certain similarities and regularities do exist among elemental substances, and they serve as the basis for a detailed, very useful classification of the elements.

4.1 EARLY CLASSIFICATION SCHEMES

Probably the first notable step in the evolution of this classification was provided by Johann Döbereiner in 1829. He pointed out that certain elements can be listed in groups of three with similar chemical properties. He further observed that when each group of three is listed in order of increasing atomic weight, the atomic weight of the middle member is approximately the arithmetic mean of the atomic weights of the other two. Some of these groups of three, which became known as **Döbereiner's triads**, are listed in Table 4.1. Perhaps the major significance of Döbereiner's triads was that they established the idea of groups of elements having similar properties that are in some way a function of atomic weight.

Before any significant extension of Döbereiner's classification could be made, additional developments had to occur: more elements had to be discovered so that more relationships would be apparent, and atomic weights had to be known with greater accuracy. By the 1860s these conditions had been met.

In 1864 John Newlands noted that when the known elements were listed according to increasing atomic weights, similar properties recurred in every seventh element. Seeing the similarity between this phenomenon and the musical scale, he named this relationship the **Law of Octaves**. Elements in the same vertical column have similar properties and are seven elements apart. Although his work was given little credence by the scientific community of his day, Newlands deserves credit for recognizing the periodic recurrence of properties based on increasing atomic weight—an idea that formed the basis for later classification of the elements.

In 1869 the Russian chemist Dmitri Mendeleev and the German chemist Lothar Meyer, working independently, published classification tables that were based on the same principles and were very similar. Because of the greater detail in Mendeleev's work, his bold predictions for elements not yet known at that time, and his publication of an improved table in 1871, history accords him—rather than Meyer—the major credit for this important breakthrough.

Mendeleev's classification was based on his **Periodic Law**:

> **The chemical properties of the elements are not arbitrary, but vary in a systematic way according to atomic weight.**

TABLE 4.1 Döbereiner's Triads with Approximate Atomic Weights

Li	7	Ca	40	S	32	Cl	35
Na	23	Sr	88	Se	79	Br	80
K	39	Ba	137	Te	128	I	127

When the elements are listed according to increasing atomic weight, similar properties recur periodically, so that the elements fall logically into groups, with all the elements in any group having similar properties.

The power of Mendeleev's classification has been demonstrated dramatically since 1871 by the accuracy of the predictions it enabled him to make. Scandium, gallium, and germanium are three of the elements that had not yet been discovered. Mendeleev's strict adherence to the law of periodicity that he had formulated enabled him not only to predict the existence of these elements, but even to predict some of their physical and chemical properties. All three of these elements were discovered during the next 15 years, and their properties were found to be remarkably close to those predicted by Mendeleev. A comparison of some properties predicted for germanium with those currently accepted as correct is shown in Table 4.2.

Another illustration of the great value of the periodic table—which could not be foreseen by Mendeleev—may be found in the discovery of the inert gases (helium, neon, argon, krypton, xenon, and radon). When argon was discovered in 1894 by Lord Raleigh and Sir William Ramsay, it was apparent that it did not belong in any of the vacant positions in the periodic table. This fact suggested the existence of an additional group of elements and spurred investigators to search for them. Within a half-dozen years, the entire group had been discovered.

Naturally, the periodic table has been modified since Mendeleev first formulated it. Additional elements have been added as they were discovered, the problem of the position of the actinides and lanthanides has been solved, and some of Mendeleev's misinterpretations have been corrected. The most significant alteration involves the very basis upon which the periodic law was founded. Mendeleev and his contemporaries believed that periodicity was a function of atomic weight. We now realize that periodicity is based on **atomic number**, not atomic weight. Mendeleev could not possibly have reached this conclusion, since the proton was not discovered until 1902, and atomic numbers were not determined until 1913 (by Henry Moseley). Accordingly, Mendeleev had to sometimes deviate from strict adherence to a listing according to increasing atomic weight in order to make certain elements fall into the proper groups; for instance, the inversion of iodine and tellurium. He explained these deviations as being due to inaccurate atomic weights. In this regard, he was incorrect; the determination of atomic numbers explained the inversions. In light of this later development, then, the **Periodic Law** must be restated:

The properties of the elements are periodic functions of their atomic numbers.

TABLE 4.2 A Comparison of Properties Predicted by Mendeleev (1871) with Those Currently Accepted for Germanium

PROPERTY	PREDICTED	CURRENT
Color	dark gray	grayish-white
Atomic Weight	72	72.59
Density (g/cm^3)	5.5	5.35
Atomic volume (cm^3/mol)	13	13.5
Specific heat (cal/g-°C)	0.073	0.074
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.703
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride	below 100°C	86°C
Density of chloride (g/cm^3)	1.9	1.844

Throughout the years the periodic table has taken a variety of forms. There has been the short form (closely following Mendeleev's 1871 table), the long form (in both vertical and horizontal versions), spiral tables, three-dimensional helical tables, and several others. The periodic table most commonly used today is a version of the long form, shown in Appendix 8. (Numbers above the symbols are atomic numbers and numbers below the symbols are atomic weights).

4.2 THE MODERN PERIODIC TABLE

The version of the periodic table used throughout the remainder of this book (Appendix 8) consists of seven horizontal rows called **periods** and sixteen vertical **groups** or **families**. The elements within a group are similar in their chemical properties. It should be noted that hydrogen does not show a close resemblance to any other element and might be placed in a group by itself. In our chart it is located at the top of Group IA, but in some charts it is placed at the top of both Group IA and Group VIIA, since in some of its properties it is similar to the elements of both these groups. With the exception of Group VIIIB, each group contains only one element within a period. The Group VIIIB triads, as they are sometimes called, were combined into one group by Mendeleev because of the similarity in properties, and that arrangement has been continued in modern periodic tables (Figure 4.1).

The *periods* are generally referred to by number, beginning at the top; that is, period 1 consists of H and He, period 2 consists of Li through Ne, and so forth. The *groups* may be referred to by number and letter; for instance, Group IIA, Group VIB. The A and B designations will be used throughout this book, although it should be noted that this is largely a matter of choice and is not uniform in all textbooks. In this text we will frequently refer to the A group elements by their number only.

Some groups are also designated by names: Group IA elements (excluding H) are called the **alkali metals**; Group IIA elements are called the **alkaline earth metals**; the elements of Group VIIA (excluding H) are called **halogens**; and those of Group VIIIA are the **inert** or **noble gases**. Groups may also be referred to in terms of the first element in the column: the nitrogen group, the oxygen group, and so on.

The elements of all the A groups are often called the **main group** or **representative elements**, because their properties adhere closely to the regular progression on which the periodic table is based. The elements in the B groups and those in Group VIII, which interrupt the representative elements in periods 4, 5, and 6, are called **transition elements**. These elements show considerably more deviation from the regular progression than do the representative elements.

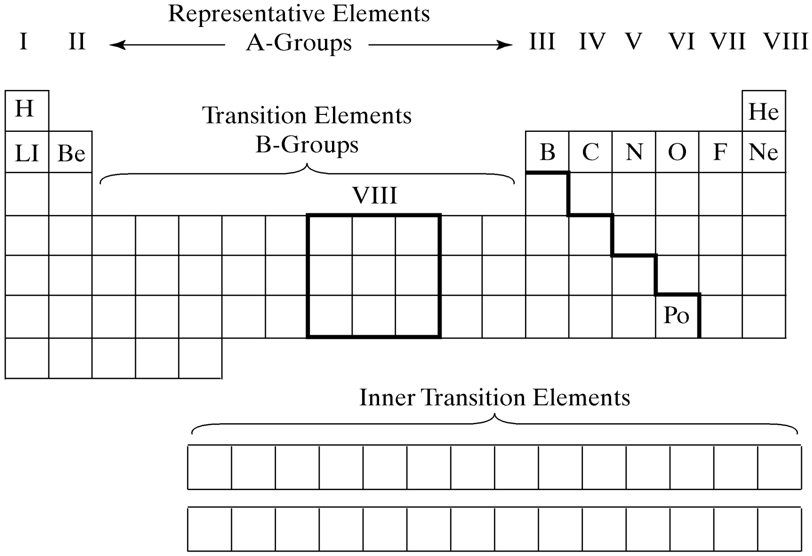


Figure 4.1 The Modern Periodic Table

The elements with atomic numbers 58 through 71 actually belong in the sixth period between lanthanum (atomic number 57) and hafnium (atomic number 72). These 14 elements, which have very similar properties, are called the **lanthanum series**, or simply the **lanthanides**. They are placed in a separate row rather than in the main body of the table simply to avoid making the table inconveniently wide. The elements with atomic numbers 90 through 103 are called the **actinium series** or **actinides**, and they occupy the same position in the seventh period as the lanthanides do in the sixth. Taken together, the lanthanides and actinides are sometimes called the **inner transition elements**, since they interrupt the transition series.

It is convenient for some purposes to classify elements as **metals** or **nonmetals**. The division between the two is indicated roughly by the stepped heavy blue line from the left of B to the right of Po in our table. The elements to the left of that line are called metals; those to the right are called nonmetals. As is described later on in this chapter, the metallic character (**metallicity**) of elements is a relative property, and the division between metals and nonmetals is not sharply defined. The elements bordering the stepped line are sometimes called **metalloids** because they show metallic behavior in some of their properties and nonmetallic behavior in others.

4.3 PERIODIC RELATIONSHIPS

It was just mentioned that elements within a given group have very similar chemical properties, and that this is particularly true of the representative elements. Members of the same group behave alike in the way they combine with other elements to form compounds, and the compounds behave similarly as well. For example, given the fact that the Group IIA element calcium combines with oxygen in an atomic ratio of 1:1 to form the compound calcium oxide (CaO), one can correctly predict that the Group IIA element strontium will also form a compound with oxygen in which the atomic ratio is 1:1 (SrO). Furthermore, calcium oxide and strontium oxide can be expected to have similar chemical properties. Likewise, knowing that carbon and chlorine form a compound in which one carbon atom is combined with four chlorine atoms (CCl_4) enables one to predict that silicon and the other Group IVA elements also form compounds with chlorine in the atomic ratio of 1:4 ($SiCl_4$, $GeCl_4$, and so on). This relationship is further illustrated in Table 4.3, where the formulas for compounds of hydrogen with elements of Groups IVA through VIIA are listed.

In addition to the various group similarities, several trends in properties can be related directly to the periodic table. Let us now examine some of these trends.

Atomic Radius

The exact size of an atom is very difficult to determine. Recall that the atom's radius is really the distance the electron cloud extends from the nucleus, and that the density of the cloud diminishes gradually as it gets farther from the nucleus, so that the boundary of the cloud is not clearly defined. Furthermore, because atoms are so small, it is not possible to measure the radius of a single atom directly. Rather, we must work with matter in bulk—large collections of atoms—where the size of an atom is influenced by electrical interactions with neighboring atoms. Thus, the size of an atom in a metallic crystal (Cu, Au) or in

TABLE 4.3 Formulas of Compounds of Hydrogen with Elements of Groups IVA Through VIIA

IVA	VA	VIA	VIIA
CH_4	NH_3	H_2O	HF
SiH_4	PH_3	H_2S	HCl
GeH_4	AsH_3	H_2Se	HBr
SnH_4	SbH_3	H_2Te	HI
PbH_4	BiH_3		

a molecule (Cl_2, N_2) is not the same as it would be if the atom were isolated. In a crystal or molecule, the atomic radius must be considered to be one-half the distance between the centers of two adjacent atoms.

Nevertheless, the atomic radii of most elements have been measured, and, although the reported values vary with the method of measurement and should be considered only approximate, these measurements are useful as a relative comparison of sizes.

Certain periodic trends in the atomic radius are obvious. Within a group, the atomic radius increases with increasing atomic number; that is, it increases from top to bottom in the periodic table. Within a period, the atomic radius tends to decrease with increasing atomic number; that is, in general it decreases from left to right in the periodic table (Figure 4.2). The representative elements follow this generalization quite closely; the transition elements show less regularity. (Rationalization of periodic trends will be discussed in Sect. 4.4)

Ionization Energy

When atoms combine to form compounds, they sometimes lose or gain one or more electrons. When they lose electrons, they become positively charged **ions**. For example, the sodium atom may lose an electron and therefore become positively charged. This ion, designated by the symbol Na^+, contains 11 protons but only 10 electrons. Positively charged ions are called **cations**; negatively charged ions are called **anions**. This process of electron removal requires the input of energy (it is endothermic); that is, work must be done in removing the negative electron from the attractive influence of the positive nucleus. The amount of energy required for electron removal varies with the particular element. It also depends on the physical state of the element, because neighboring atoms have a greater influence in the solid state, for example, than in the liquid or gaseous states. Therefore, in order to compare the energies required to ionize the various elements, they are measured in reference to the isolated gaseous atoms.

The **ionization energy** of an element is defined as the energy required to remove an electron (e^-) from an atom in the gaseous state to produce an ion, also in the gaseous state. The process may be represented as follows, using sodium as an example:

$$Na(g) \longrightarrow Na^+(g) + e^-$$

Notice that in the equation, the arrow means “to produce” or “goes to” and the subscript (g) indicates the gaseous state. Ionization energies are usually expressed in kilojoules per mole.

The periodicity of ionization energies is shown in Figure 4.3, where the first 36 elements and their approximate ionization energies (in kJ/mol) are listed. The trends revealed in these elements continue throughout the entire periodic table. Note that within a group, the ionization energy decreases from top to bottom. Also, ionization energy

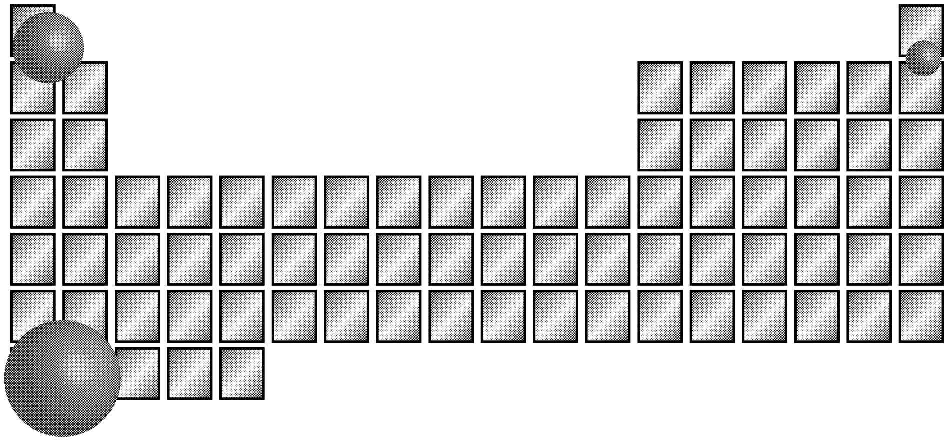


Figure 4.2 The variations in atomic radius across and down the chart.

H 1314							**He** 2372
Li 519	**Be** 900	**B** 799	**C** 1088	**N** 1402	**O** 1314	**F** 1682	**Ne** 2079
Na 498	**Mg** 736	**Al** 577	**Si** 783	**P** 1063	**S** 1000	**Cl** 1255	**Ar** 1519

Figure 4.3 Periodicity in ionization energies (kJ/mol).

generally increases within a period from left to right. A notable exception to the latter statement is the consistently lower ionization energies of the elements of Groups IIIA and VIA.

In the foregoing discussion we have dealt only with the energy required to remove *one* electron from a neutral atom; this amount of energy is known as the *first* ionization energy. It is also possible to determine the energy necessary to remove a second electron, a third electron, and so on. These amounts of energy are referred to as the second ionization energy, the third ionization energy, and so forth. Again using sodium as an illustration, the second ionization energy is the energy that must be supplied to accomplish the process:

$$\mathrm{Na}^{+}(g) \longrightarrow \mathrm{Na}^{2+}(g) + e^{-}$$

As more electrons are removed from an atom (that is, as the positive charge on the ion increases), the amount of energy required to remove yet another electron increases. In other words, in every case the second ionization energy is greater than the first and the third is greater than the second. The relationship is illustrated in Table 4.4 with the first three ionization energies of the second-period elements. It will be noted that, with two exceptions, the second and third ionization energies follow the same general trend within the period as the first ionization energy; they generally increase from left to right in the periodic table (or from top to bottom in Table 4.4). The exceptions lie in the Group IA element Li, which has the *highest* second ionization energy, and the Group IIA element Be, which has the *highest* third ionization energy.

Electron Affinity

Just as atoms may *lose* electrons to form *positive* ions during a chemical reaction, they may *gain* electrons to form *negative* ions. With few exceptions, when an atom gains an electron, energy is given off (the process is exothermic). Following the same conventions used in describing ionization energy, **electron affinity** is defined as the amount of energy

TABLE 4.4 Ionization Energies of the Second-Period Elements

	IONIZATION ENERGIES (kJ/mol)		
ELEMENT	FIRST	SECOND	THIRD
Li	519	7297	11,811
Be	900	1757	14,845
B	799	2427	3661
C	1088	2351	4619
N	1402	2858	4577
O	1314	3393	5301
F	1682	3376	6046
Ne	2079	3962	6276

evolved when a gaseous atom gains an electron to become a gaseous negative ion. The process may be illustrated with chlorine:

$$\mathrm{Cl}(g) + e^- \longrightarrow \mathrm{Cl}^-(g)$$

Like ionization energy, electron affinity may be expressed conveniently in terms of kilojoules per mole.

Values of electron affinity are difficult to determine. Since relatively few elements actually form stable negative ions, accurate values of electron affinities are known for only a few elements. On the basis of available information, however, electron affinities appear to generally increase from left to right within a period. This parallel relationship between ionization energy and electron affinity is to be expected. The more difficult it is to remove an electron from a given atom, the stronger is the attraction of that atom for electrons, and therefore the greater is the amount of energy given off when the atom gains an electron.

Electronegativity

The tendency of an element to attract electrons can be described more generally in terms of the electronegativity of the element. Electronegativity, which is related to both ionization energy and electron affinity, is defined simply as an element's attraction for electrons within a molecule.

While it is not possible to assign absolute values of electronegativities to the various elements, a scale of *relative* values can be established on the basis of an arbitrary value assigned to one element. Several different electronegativity scales have been proposed, but the one most commonly used was created by Linus Pauling. This scale, which is based on experimentally determined **bond energies** (Chapter 7), assigns the value of 4.0 to the most electronegative element, fluorine. The other elements are given values that describe their electronegativities relative to that of fluorine.

Figure 4.4 is a listing of Pauling's electronegativity values. The periodicity of electronegativities is readily apparent. In general, electronegativity increases from left to

H 2.1							
Li 1.0	**Be** 1.5		**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0
Na 0.9	**Mg** 1.2		**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0
K 0.8	**Ca** 1.0	**Sc-Zn** 1.3-1.9	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8
Rb 0.8	**Sr** 1.0	**Y-Cd** 1.2-2.2	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5
Cs 0.7	**Ba** 0.9	**La-Hg** 1.1-2.4	**Tl** 1.8	**Pb** 1.8	**Bi** 1.9	**Po** 2.0	**At** 2.2
Fr 0.7	**Ra** 0.9	**Ac-Lr** 1.1-1.7					

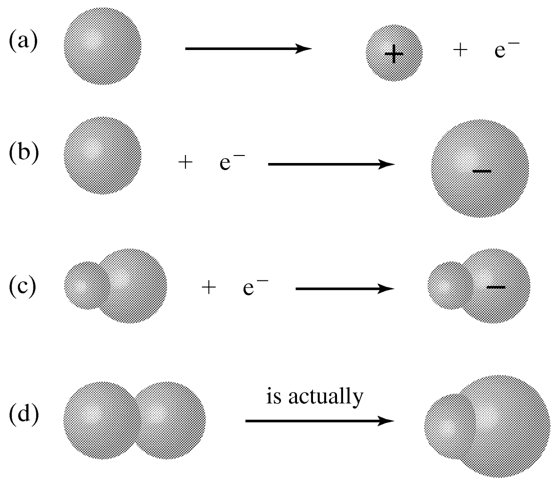
Figure 4.4 Electronegativities of the elements.

right within a period and from bottom to top within a group. There are some exceptions to this generalization, particularly among the transition elements.

Visualization 4.1

Match the following to the drawings below:

1. ionization
2. electron affinity
3. electronegativity



Solution:

a. ionization, b. electron affinity, c. electron affinity for a molecule (electron affinity usually refers to atoms, but can also be used for molecules), d. electronegativity (The diagram indicates that the real molecule has its electron density distributed as shown on the right, not equally distributed as shown on the left. Electrons are not shared equally by atoms because the one with the freater electrongegativity will draw them more onto itself.)

Metallicity and Nonmetallicity

We have already referred to the division of the elements into metals and nonmetals. Historically, the distinction between the two categories was based largely on physical properties. (Metals exhibit the properties of luster, malleability, ductility, conductivity, and so forth, while nonmetals do not.) In modern usage, the definitions are based more on chemical properties: Metals tend to form positive ions, and nonmetals tend to form negative ions. From this point of view, **metallicity** and **nonmetallicity** are entirely relative and are related to ionization energy, electron affinity, and electronegativity. The lower an element's ionization energy, electron affinity, and electronegativity, the more metallic that element is. Conversely, nonmetallicity goes with high values of these three properties. In other words, metallicity increases from top to bottom within a group and from right to left within a period, while nonmetallicity increases in the opposite directions.

Figure 4.5 summarizes the progressions of all the periodic properties just discussed.

Ionic Radius

The sizes of the stable ions formed when atoms lose or gain electrons also show periodic regularities. Positive ions (cations), which are considerably smaller than the neutral atoms from which they are formed, show an increase in radius in going down a group, but a decrease in going from left to right within a period. Negative ions (anions) are larger than

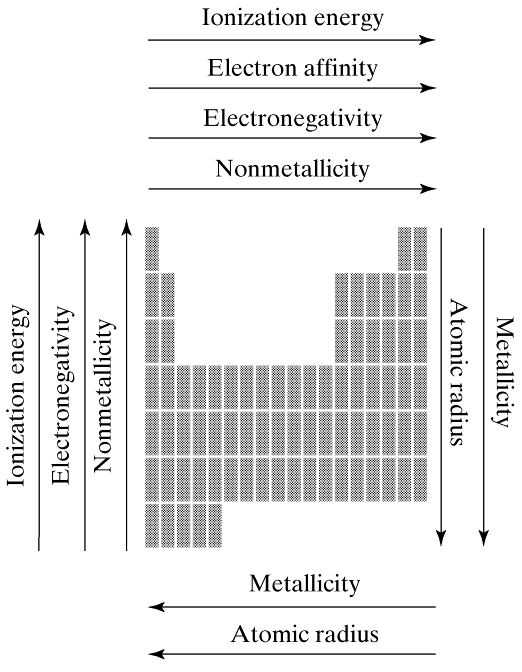


Figure 4.5 Some periodic trends, increasing in the direction of the arrows.

their parent neutral atoms, but they show the same trends as positive ions within the groups and periods.

4.4 RATIONALIZATION OF PERIODIC TRENDS

We can now use the wave model discussed in Chapter 3 to rationalize the periodic trends just discussed. Since there is a small, but finite, probability of finding an electron even at large distances from the nucleus, the size of an atom is not clearly defined in the wave model. Nevertheless, we can assume that experimentally measured atomic sizes reflect the major portion of the electron density of an atom. The variation in size (that is, the increase in going down a group and the decrease in going across a period) can be explained as follows: The "size" of an atom is determined by the location probabilities for its electrons, especially the outermost electrons. Since the greater the value of the principal quantum number, the farther from the nucleus the electron is likely to be, the increase in size in going down a group is due to an increase in the principal quantum number of the outermost electrons.

The valence electrons of all the elements within a given period have the same principal quantum number and therefore have their maximum location probabilities at roughly the same distance from the nucleus. However, in moving from left to right in a given period, the nuclear charge increases. This increase results in a greater attraction between the positively charged nucleus and the negatively charged valence electrons. The increased attraction in turn results in a smaller distance between the nucleus and the outermost electrons, that is, a decrease in the size of the atoms. Nuclear charge also increases in going down a given group, but the shrinkage due to this effect is outweighed by the increase in n. Moreover, a given outer electron does not experience the full charge of the nucleus, since it is partially shielded from this charge by the inner electrons. In general, the shielding due to a lower filled quantum level is far more effective than the shielding due to electrons within the same quantum level.

When an electron is removed from an atom to form a cation, the remaining electrons experience a greater attraction. The cation is therefore smaller than the atom from which it was formed. Conversely, when an electron is added to an atom to form an anion, the anion is larger than the atom from which it was derived.

The decrease in ionization energy in going down a group has a similar explanation. The principal quantum number of the outermost electron (the one that is lost

H 1314							**He** 2372
Li 519	**Be** 900	**B** 799	**C** 1088	**N** 1402	**O** 1314	**F** 1682	**Ne** 2079
Na 498	**Mg** 736	**Al** 577	**Si** 783	**P** 1063	**S** 1000	**Cl** 1255	**Ar** 1519

Figure 4.6 Ionization energies (kJ/mol) for the elements of the first three periods.

upon ionization) determines both its location probability and its energy. As a group is descended, the principal quantum number and the energy of the electron increase; thus, the energy required to remove the electron decreases. As a period is crossed from left to right, the distance between the outermost electron and the nucleus decreases, and the strength of the attraction increases; the energy required to remove an electron therefore increases.

While ionization energy generally increases across a period, there are two exceptions among the second-period elements (see Figure 4.6). The first exception occurs at boron, which has a lower first ionization energy than beryllium. This occurs because the outermost electron in boron is a $2p$ electron, whereas the outermost electron in beryllium is a $2s$ electron. Since the $2p$ orbitals have a higher energy than the $2s$ orbitals, and this difference in energy is not outweighed by the increased nuclear charge of boron, less energy is required to remove the $2p$ electron. The second exception occurs at oxygen, which has a lower ionization energy than nitrogen. This anomaly may be associated with the special stability of the half-filled $2p$ level of nitrogen.

Variations in electronegativity can be explained in much the same way. Electronegativity decreases in going down a group because the atomic size increases; thus an external electron is maintained farther from the nucleus and is therefore less attracted to it. Electronegativity increases across a period because of the decrease in size and consequent increase in attraction for an external electron.

The metallicity of an element is related to its tendency to form positive ions. Since the ionization energy is a quantitative measure of this tendency, trends in metallicity can be rationalized from ionization energies: The greater the ionization energy, the smaller the tendency to form a positive ion and the smaller the metallicity of the element.

CHAPTER SUMMARY

Probably no single tool is as useful in the study of chemistry as the periodic table of the elements. This classification systematically summarizes much of our knowledge about the nature of matter and has been the inspiration for new discovery. Much of our theory concerning the structure of matter has resulted from an effort to adequately account for periodic relationships.

A thorough understanding of the periodic table is essential; it will be important throughout your study of chemistry. Strive to gain an appreciation of its historical development, recognizing that the table is based on the observations of facts—the theories to explain these facts were developed later. Learn the terminology associated with the table: periods, groups, representative elements, and so on. Also learn the general periodic trends of atomic and ionic radius, ionization energy, electron affinity, electronegativity, and metallic and nonmetallic properties. You should also be able to rationalize these trends using the wave model of the atom developed in Chapter 3.

TERMS

Some important terms in this chapter are as follows:

Periodic Law A statement that the properties of the elements are periodic functions of their atomic numbers.

Periods The seven horizontal rows of the periodic table.

Groups or families The 16 vertical columns of the periodic table. Each group is designated by a number and, in most cases, by a letter (A or B); some groups are also designated by common names.

Alkali metals The group of elements designated IA in the periodic table: Li, Na, K, Rb, Cs, and Fr.

Alkaline earth metals The group of elements designated IIA in the periodic table: Be, Mg, Ca, Sr, Ba, and Ra.

Halogens The group of elements designated VIIA in the periodic table: F, Cl, Br, I, and At.

Inert gases or noble gases The members of Group VIIIA in the periodic table: He, Ne, Ar, Kr, Xe, and Rn.

Representative elements The elements of all the A groups in the periodic table. Their properties adhere closely to the regular progression on which the periodic table is based.

Transition elements The elements of the B groups in the periodic table. Their properties deviate more markedly from the regular progression of the periodic table than the properties of the representative elements.

Lanthanides The 14 elements immediately following lanthanum in the periodic table (atomic numbers 58 through 71).

Actinides The 14 elements immediately following actinium in the periodic table (atomic numbers 90 through 103).

Inner transition elements The lanthanides and the actinides.

Ionization energy The energy required to remove an electron from an atom in the gaseous state to produce a positively charged ion in the gaseous state. This is known as the **first ionization energy**. The amounts of energy required to remove a second electron, a third electron, and so on, are called the **second ionization energy**, the **third ionization energy**, and so on. For any given element, the second ionization energy is greater than the first, and the third is greater than the second. In general, ionization energies decrease from top to bottom within a group and increase from left to right within a period. (There are some exceptions to this generalization.)

Electron affinity The amount of energy given off when a gaseous atom gains an electron to become a gaseous negative ion. In general, electron affinities increase from left to right within a period.

Electronegativity The attraction for electrons shown by an atom within a molecule. The electronegativity of an element is described in terms of a relative scale on which fluorine—the most electronegative element—is assigned a value of 4.0. In general, electronegativity increases from left to right within a period and from bottom to top within a group.

Metals Elements that tend to form positive ions. In general, the lower the ionization energy, electron affinity, and electronegativity, the more metallic the element.

Nonmetals Elements that tend to form negative ions. In general, the higher the ionization energy, electron affinity, and electronegativity, the more nonmetallic the element.

Metalloids The name sometimes given to elements that have intermediate properties between those of metals and nonmetals.

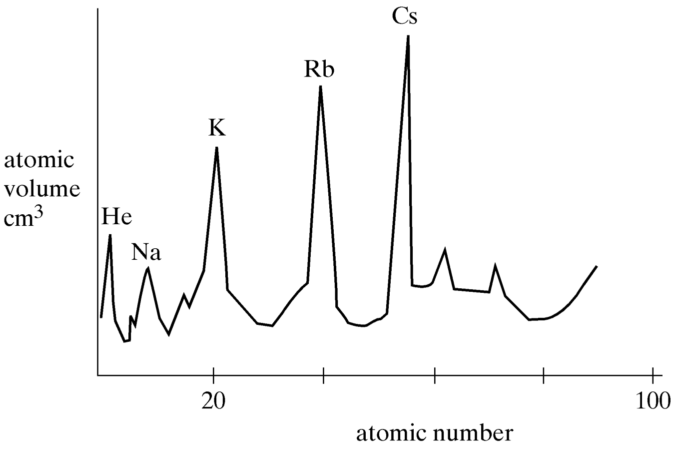
PROBLEMS

1. Indicate the meaning of each of the following terms as it applies to the periodic table:
- (a) the fourth period
- (b) the oxygen group
- (c) Group VIIB
- (d) the iron triad
- (e) the inert gases
- (f) the inner transition elements
- (g) metals versus nonmetals
- (h) representative elements
- (i) the transition elements

2. Describe the periodic trends of
- (a) atomic radii
- (b) first ionization energies
- (c) electronegativities
- (d) metallic properties

3. When Mendeleev arranged his first periodic table in 1869, he put tellurium before iodine, even though the atomic weight of tellurium is greater than that of iodine. Explain.

4. One of the first indications of a periodic variation in a property of the elements was shown by Lothar Meyer in the volume of a mole of the solid element. A crude plot of the molar volume as a function of atomic number is shown below.



Notice that the elements that we now call the alkali metals have the highest molar volume. How would you explain this observation?

5. If in the future an additional representative element is synthesized, what is the lowest atomic number it can have?

6. The space in the periodic chart for atomic number 87 was not filled in until 1939. In that year the very unstable element francium was discovered among the natural decay products of actinium. Using the following information, predict the density, melting point, and boiling point of Fr.

ELEMENT	DENSITY	mp (°C)	bp (°C)
Li	0.53	179	1331
Na	0.97	98	892
K	0.86	64	766
Rb	1.53	39	701
Cs	1.90	28	690

7. List the melting points for the second and third period elements. Are the melting points of the elements in the same group similar, but different from those in neighboring groups? If you had simply listed the melting points in order of the atomic number of the element, would you have recognized the periodic similarities?

8. The fluorine compounds of the third period elements (excluding the inert gases) have the formulas:

$$XF \; XF_2 \; XF_3 \; XF_4 \; XF_3 \; XF_2 \; XF$$

First, write the total number of valence electrons of X below each formula. Next, assume that fluorine contributes one electron to the bonding with X and write the number of electrons contributed by fluorine below the valence electrons.

a. What observation can be made by examining your table?
b. Are the first three compounds different than the other four?
c. Is it safe to assume that the second period elements form compounds of the same formulas?

9. Rationalize the following order in size:

$$Be > Li^+ > Be^{2+}$$

10. The electron affinity is defined as the heat released when a gaseous atom combines with an electron. Thus, the value of 141 kJ/mol for oxygen means that 141 kJ of heat are released in the process

$$O(g) + e^- \longrightarrow O^-(g)$$

The second electron affinity for oxygen refers to the process

$$O^-(g) + e^- \longrightarrow O^{2-}(g)$$

This value is -880 kJ/mol. What does the negative sign mean? How much heat would be released in the process

$$O(g) + 2\,e^- \rightarrow O^{2-}(g)$$

11. What would you expect the electron affinity of an inert gas to be—positive or negative?

12. What is the longest possible wavelength of light that could be used to ionize a valence electron in Li^{2+}? in Li?

13. Which requires the greater amount of energy for the removal of one electron?
(a) Be or Ca (b) S or Se
(c) Mg^+ or Mg^{2+} (d) Cl^- or Cl

14. Which has the larger radius?
(a) Mg or Ca (b) S or Cl

15. Which is more metallic?
(a) Si or Ge (b) Tl or Bi

16. Which is more electronegative?
(a) As or Se (b) Br or I

17. Which has the larger radius?
(a) Mg or Mg^{2+} (b) Fe^{2+} or Fe
(c) Cl or Cl^- (d) Na^+ or F^-

18. Arrange the following in order of increasing nonmetallicity:

Li, Ba, S, Sn, Cl, Br, O, and Na

19. Carefully explain why:
a. boron has a lower first ionization energy than beryllium.
b. nitrogen has a higher first ionization energy than oxygen.

20. Fill in the blanks
(a) The horizontal rows of the modern periodic table are called ____________; there are seven of these in the periodic table.
(b) The 14 elements following actinium are called ___________.
(c) Groups IA and IIA on the periodic table are called ____________ and ____________, respectively.
(d) The periodic table lists the elements in order of increasing ____________.
(e) The vertical columns of the periodic table are called ____________.
(f) A classification of the elements on which our modern periodic table is based is credited to ___________ ____________.
(g) ___________ is the name given to the elements in Group VIIA.
(h) The ____________ elements adhere more closely to periodic generalizations than the transition elements do.
(i) The energy required to remove an electron from a gaseous atom is called the ____________.
(j) The most electronegative element is ____________.
(k) Metals tend to form ____________ ions.
(l) When a gaseous atom is converted into a gaseous negative ion, energy is ____________.
(m) Members of the family labeled Group VIIIA on the periodic table are called ____________.
(n) If an element existed that had an atomic number of 111, it would be a member of ____________.
(o) Positive ions are _____________in diameter than their parent neutral atoms.
(p) The element in Group VA with the most metallic properties is ____________.
(q) The element in Group VIA with the smallest atomic diameter is ____________.
(r) The group of elements with atomic numbers 58 through 71 are called ____________.
(s) The alkaline earth metal with the largest first ionization energy is _____________.
(t) In general, metallic properties ____________ from left to right within a period.

21. Multiple-choice questions

1. Which of the following has the highest ionization energy?
(a) Li (b) F (c) Na (d) Cl
2. Which of the following exhibits the greatest electronegativity?
(a) Al (b) As (c) Ge (d) Si
3. Which of the following has the largest radius?
(a) K (b) K^+ (c) Ca (d) Ca^{2+}
4. Which of the following has the most metallic character?
(a) Ge (b) In (c) O (d) P
5. Which of the following has the highest ionization energy?
(a) K (b) Na (c) Na^+ (d) Rb
6. Which pair of elements are the most chemically similar?
(a) K and Ca (b) Ca and Co
(c) P and S (d) S and Se
7. Which of the following exhibits the greatest electron affinity?
(a) B (b) C (c) Li (d) O
8. Which of the following has the largest atomic radius?
(a) As (b) F (c) S (d) Sn
9. It is predictable that element 111 will be:
(a) an actinide
(b) a transition element
(c) a representative element
(d) a lanthanide
10. Which of the following has the least metallic character?
(a) F (b) Cl (c) Br (d) I

5 Ionic Compounds

In the previous chapter we have discussed the formulas of the combinations of atoms that we call compounds. Indeed, most of the matter on earth consists of compounds. In Chapters 5 through 7 we will use our knowledge of atoms to explore the internal details of the nature of compounds. In this chapter we discuss compounds that consist of ions.

5.1 FORMULAS

The composition of a compound is conveyed by its formula, a combination of the chemical symbols for the elements present in the compound. There are a number of different types of formulas, the simplest of which is the **empirical formula**. The empirical formula reveals two items of information: (a) what elements are present in the compound and (b) the lowest whole number combining ratio of the atoms of those elements. For example, the subscript 2 in the formula $MgCl_2$ indicates that this compound contains twice as many chlorine atoms as magnesium atoms. Similarly, the formula H_2SO_4 represents a compound consisting of atoms of hydrogen, sulfur, and oxygen in a ratio of 2 to 1 to 4, respectively.

The **formula weight** of a compound is analogous to the atomic weight for an element. It is simply the sum of the atomic weights of the elements shown in the empirical formula. The atomic weight of each element in the compound must be multiplied by the number of atoms of that element. Thus, for magnesium chloride, $MgCl_2$, the formula weight is $24.3 + 2(35.5)$, or 95.3. When the formula weight is expressed in grams it is referred to as the **gram formula weight** or the **molar mass**. Of course, this amount represents the weight of a mole of the compound. Thus, 95.3 g of magnesium chloride contains one mole of magnesium and two moles of chlorine atoms.

The empirical formula enables us to calculate the weight of an element in any given weight of the compound.

Problem 5.1

What weight of potassium is contained in 50.0 g of K_2SO_4?

Solution:

The formula weight of K_2SO_4 is $2(39.1) + 32.1 + 4(16.0) = 174.3$. Therefore, in every 174.3 g of the compound there are 78.2 g of potassium, and in 50.0 g of the compound there must be

$$\frac{78.2\text{ g K}}{174.3\text{ g compound}} \times 50.0\text{ g} = 22.4\text{ g K}$$

A common application of this relationship is the calculation of the **percentage composition** of a compound; that is, the percentage by weight of each element in the compound.

Problem 5.2

What is the percentage composition of $CHCl_3$?

Solution:

The formula weight of the compound is 12.0 + 1.0 + 3(35.5) = 119.5. Thus, there are 12.0 g of carbon in every 119.5 g of the compound, and therefore the percentage of carbon in the compound (the number of grams of carbon in 100 g of the compound) is

$$\frac{12.0 \text{ g C}}{119.5 \text{ g compound}} \times 100\% = 10.0\% \text{ C}.$$

Likewise, the percentages of H and of Cl are

$$\frac{1.0 \text{ g H}}{119.5 \text{ g compound}} \times 100\% = 0.84\% \text{ H}$$

$$\frac{(3 \times 35.5 \text{ g Cl})}{119.5 \text{ g compound}} \times 100\% = 89.1\% \text{ Cl}$$

By means of a calculation which is essentially the reverse of that in the preceding example, the empirical formula of a compound can be derived when its percentage composition is known. Suppose, for example, that a new compound is synthesized or isolated from some natural source. Its percentage composition can be determined experimentally in the laboratory, and from that information its empirical formula can be calculated.

Consider a compound containing only carbon and hydrogen with a percentage composition of 92.31% C and 7.69% H. These are percentages, or parts per hundred, by weight, and so 100 g (chosen to make the calculations easier) of this compound must contain 92.31 g carbon and 7.69 g hydrogen. Now the empirical formula is just an expression of the relative number of moles of the elements present in the compound, and the number of moles of carbon and hydrogen in this sample can be found by dividing these weights by the weight of one mole of the elements. In 100 g of the compound, there are

$$\frac{92.31 \text{ g C}}{12.0 \text{ g/mol C}} = 7.69 \text{ mol of carbon}$$

and

$$\frac{7.69 \text{ g H}}{1.00 \text{ g/mol H}} = 7.69 \text{ mol of hydroogen}$$

The simplest ratio of the number of moles of carbon to hydrogen is then 1:1, and the empirical formula can be expressed as CH.

A slightly more complex calculation is necessary for a compound whose percentage composition is 50.04% C, 5.59% H, and 44.37% O. Using the procedure above, for a 100-g sample we get 4.167 mol C, 5.546 mol H, and 2.773 mol O. In order to obtain the simplest mole ratio, we divide the number of moles of each element by the number of moles of the least abundant element.

$$\frac{4.167 \text{ mol C}}{2.773 \text{ mol O}} = \frac{1.503 \text{ mol C}}{1.0 \text{ mol O}}$$

$$\frac{5.546 \text{ mol H}}{2.773 \text{ mol O}} = \frac{2.00 \text{ mol H}}{1.0 \text{ mol O}}$$

Thus, the formula could be written as $C_{1.503}H_{2.000}O_{1.000}$. The formula should, however, be expressed in whole numbers by multiplying each subscript by 2. The resulting formula is $C_3H_4O_2$. The rounding off (3.006 to 3.000) for the number of carbons is justified because the percentage composition of a compound is experimentally determined and therefore subject to varying degrees of error. Usually this sort of experimental error is more or less random; thus, for most compounds, if the empirical formula were calculated from the average of a large number of percentage-composition determinations, the numbers would come quite close to exact whole numbers. Other commonly encountered coefficient ratios that are not whole numbers are multiples of the following, 0.333 (multiply by 3), 0.25 (multiply by 4), 0.20 (multiply by 5), 0.167 (multiply by 6), 0.14 (multiply by 7) and 0.125 (multiply by 8).

Problem 5.3

A compound consisting of only carbon, hydrogen, and oxygen is analyzed and found to contain 46.15% carbon and 7.69% hydrogen. Determine the empirical formula of the compound.

Solution:

For simplicity, assume we have a 100-g sample of the compound. We would then have 46.15 g carbon, 7.69 g hydrogen, and 46.16 g oxygen (100 g − 46.15 g − 7.69 g = 46.16 g). In order to determine the molar ratio, each weight must be converted to moles as follows,

$$\text{Carbon:}\quad \frac{46.15\text{ g K}}{12.0\text{ g/mol C}} = 3.85\text{ mol carbon}$$

$$\text{Hydrogen:}\quad \frac{7.69\text{ g H}}{1.01\text{ g/mol H}} = 7.61\text{ mol hydrogen}$$

$$\text{Oxygen:}\quad \frac{46.16\text{ g O}}{16\text{ g/mol O}} = 2.89\text{ mol oxygen}$$

Divide through by the lowest mole value (2.89) to determine the molar ratios,

$$\text{C to O:}\quad \frac{3.85}{2.89} = 1.33$$

$$\text{H to O:}\quad \frac{7.61}{2.89} = 2.63$$

The formula ratios are, $C_{1.33}H_{2.63}O_{1.00}$. These must be converted to whole numbers by multiplying by 3 (note that within experimental error the coefficients for C and H are both a multiple of 0.33; 4/3 for carbon and 8/3 for hydrogen) which will give the empirical formula, $C_4H_8O_3$.

In some compounds the atoms are bound together in discrete units called **molecules**. For compounds of this type, it is important to know not only the ratio of the different atoms present but also the actual number of atoms in each molecule. This information is given by the **molecular formula**. For example, the molecular formula for carbon tetrachloride (CCl_4) tells us not only that the compound consists of carbon atoms and chlorine atoms in a ratio of 1 : 4, but also that each molecule of the compound is an aggregate of one carbon atom and four chlorine atoms. For carbon tetrachloride, the empirical formula and the molecular formula are identical, but for many other compounds this is not the case. Both acetylene and benzene have the empirical formula CH, indicating that both compounds consist of carbon and hydrogen in an atomic ratio of 1 : 1. But the molecular formula for acetylene is C_2H_2 and that for benzene is C_6H_6, which indicate two quite different compounds, each with its own specific set of properties. The molecular formula is always the same as, or some whole-number multiple of, the empirical formula; for instance, $C_2H_2 = 2(CH)$ and $C_6H_6 = 6(CH)$. The calculation of a formula from percentage composition, as just described, can lead only to the empirical formula; further information—the molecular weight—is required for calculation of the molecular formula. The **molecular weight** is the sum of the atomic weights of the elements appearing in the molecular formula. Thus, the molecular weight of acetylene (C_2H_2) is $2(12.0) + 2(1.0) = 26.0$, and the molecular weight of benzene (C_6H_6) is $6(12.0) + 6(1.0) = 78.0$.

Problem 5.4

10.0 g of a compound containing carbon, hydrogen, chlorine and bromine is analyzed and found to contain 2.30 g carbon, 0.323 g hydrogen, 2.27 g chlorine and 5.11 g bromine. An additional experiment showed that the molecular weight of the compound is 312.8 g/mol. Determine the molecular formula of the compound.

Solution:

Since the absolute weights of each element in the sample of the compound are provided, we do not need to assume a 100-g sample. We can directly find the number of moles of each element in the compound by dividing the weight of each element by its atomic weight,

$$\text{C:} \quad \frac{2.30 \text{ g C}}{12.0 \text{ g/mol C}} = 0.192 \text{ mol C}$$

$$\text{H:} \quad \frac{0.323 \text{ g H}}{1.01 \text{ g/mol H}} = 0.320 \text{ mol H}$$

$$\text{Cl:} \quad \frac{2.27 \text{ g Cl}}{35.45 \text{ g/mol Cl}} = 0.0639 \text{ mol Cl}$$

$$\text{Br:} \quad \frac{5.11 \text{ g Br}}{79.9 \text{ g/mol Br}} = 0.0639 \text{ mol Br}$$

The simplest molar ratio is found by dividing through by 0.0639, giving $C_{3.00}H_{5.00}Cl_{1.00}Br_{1.00}$. Since these are all whole numbers, no further multiplication is required and this is the empirical formula. The molecular formula will be some whole number ratio of the empirical formula and this ratio is found by dividing the molecular weight by the empirical weight,

$$\frac{312.8}{156.4} = 2.0$$

The molecular formula must be twice the empirical formula, so the molecular formula of the compound is $C_6H_{10}Cl_2Br_2$.

The **gram molecular weight** is equal to the sum of the gram atomic weights of the elements in the molecular formula. Hence, 26.0 g of acetylene is one gram-molecular weight of the compound. Just as one gram atomic weight of an element contains Avogadro's number of atoms, one gram molecular weight of a compound contains Avogadro's number of molecules. Furthermore, one gram molecular weight of a compound is one *mole* of that compound and is therefore also referred to as the **molar mass**. For example, one mole of benzene weighs 78.0 grams and contains 6.022×10^{23} benzene molecules. It also contains $6 \times 6.022 \times 10^{23}$ carbon atoms and $6 \times 6.022 \times 10^{23}$ hydrogen atoms.

The relationships that exist between these various terms are demonstrated in problems 5.5–5.7.

Problem 5.5

How many molecules are there in 50.0 g of CO_2?

Solution:

The molecular weight of CO_2 is $12.0 + 2(16.0) = 44.0$. Therefore, one mole of CO_2 weighs 44.0 g, and 50.0 g is equal to

$$\frac{50.0 \text{ g CO}_2}{44.0 \text{ g/mol CO}_2} \text{ mol}$$

Since each mole contains 6.022×10^{23} molecules, the number of molecules in 50.0 g of CO_2 is

$$\frac{50.0 \text{ g CO}_2}{44.0 \text{ g/mol CO}_2} \times 6.022 \times 10^{23} \frac{\text{molecules}}{\text{mol}} = 6.84 \times 10^{23} \text{ molecules CO}_2$$

Problem 5.6

How many grams of sodium are contained in 2.50 mol of Na_2CO_3?

Solution:

Each mole of Na_2CO_3 contains 2 mol of Na, and each mole of Na weighs 23.0 g, therefore,

$$2.50 \text{ mol Na}_2\text{CO}_3 \times \frac{2 \text{ mol Na}}{1 \text{ mol Na}_2\text{CO}_3} \times \frac{23.0 \text{ g Na}}{1 \text{ mol Na}} = 115 \text{ g Na}$$

Problem 5.7

How many chlorine atoms are there in 25.0 g of carbon tetrachloride (CCl_4)?

Solution:

Since there are 6.022×10^{23} CCl_4 molecules in one mole of CCl_4, and since each molecule contains four chlorine atoms, we have

$$\frac{25.0 \text{ g CCl}_4}{154 \text{ g CCl}_4/\text{mol CCl}_4} \times \frac{6.022 \times 10^{23} \text{ molecules CCl}_4}{1 \text{ mol CCl}_4} \times \frac{4 \text{ atoms Cl}}{1 \text{ molecule CCl}_4}$$
$$= 3.91 \times 10^{23} \text{ atoms Cl}$$

5.2 THE TWO CATEGORIES OF COMPOUNDS

Table 5.1 presents the melting points, boiling points, and relative electrical conductivities at the melting point of some of the compounds formed between chlorine and the third-period elements. From these data, we can divide the compounds into two categories: One group's members have high melting and boiling points and conduct electricity in their molten state; the others have considerably lower melting and boiling points and do not conduct electricity in their molten state. These two categories are useful descriptions for many types of compounds, not just the chlorides of the third-period elements.

The internal features of a compound that are responsible for the properties that place it in one category or the other have been discussed and studied by chemists for centuries. Our present understanding of these features is based upon two models: the **ionic model** and the **covalent model**.

TABLE 5.1 Some Physical Properties of the Third-Period Chlorides

	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	Cl_2
Melting Point, °C	801	708	ca. 190	–70	–91	–78	–101
Boiling Point, °C	1413	1412	ca. 190	58	76	59	–35

▨ The molten compound conducts an electric current

Compounds of the first type, those with high melting and boiling points and so on, are classified as **ionic compounds**. According to the ionic model, these compounds consist of charged particles called **ions**. Thus the compound sodium chloride can be thought of as an orderly collection of positively charged, spherical sodium ions and negatively charged, spherical chloride ions, as shown schematically in Figure 5.1.

Probably the two most compelling pieces of evidence for this model are (a) the electrical conductivity of these compounds in the liquid state and (b) x-ray diffraction patterns of these compounds. When a battery is connected to molten sodium chloride, an electric current flows through the wires. We will find in Chapter 18 that this flow of electrons produces a chemical reaction in the sodium chloride, but for now the salient feature of this experiment is that in order to have a flow of charged particles (electrons) in the wires, there must also be a flow of charged particles in the molten sodium chloride. The charged particles in the melt are presumably sodium and chloride ions.

From an x-ray diffraction pattern (the pattern that results when a stream of x-rays is diffracted by a crystal) information about the relative locations of the nuclei of atoms in a compound can be obtained. Patterns obtained from compounds such as NaCl suggest that the electron density surrounding the atomic nuclei in these compounds is spherically symmetric. In addition, these experiments have demonstrated that in NaCl, for example, the sodium and chlorine nuclei are surrounded by 10 and 18 electrons, respectively. Since the neutral atoms have 11 and 17 electrons, respectively, the existence of ions in this compound seems to be the best explanation of the data.

The ionic model also explains the high melting and boiling points of the compounds in this category. The temperature at which a compound boils, for example, is a measure of the amount of energy necessary to separate the "particles" of the compound from their relative positions in the liquid state to their relative positions in the gaseous state. (Since gases are generally much less dense than liquids, the distances between particles in the gaseous state are much larger than the distances between particles in the liquid state.) The amount of energy required for this change in state depends on the nature of the forces between the "particles." In ionic compounds the "particles" being separated are ions, which are attracted to one another by strong electrostatic forces. As we shall see below, the "particles" of a **covalent compound** are usually molecules; thus, the more general term **molecular compound** can be substituted. The forces between two uncharged molecules are considerably weaker than those between ions. The difference in evaporation of an ionic compound and a molecular compound is shown in Figure 5.2.

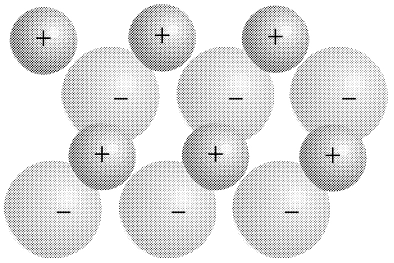


Figure 5.1 The ions in solid sodium chloride.

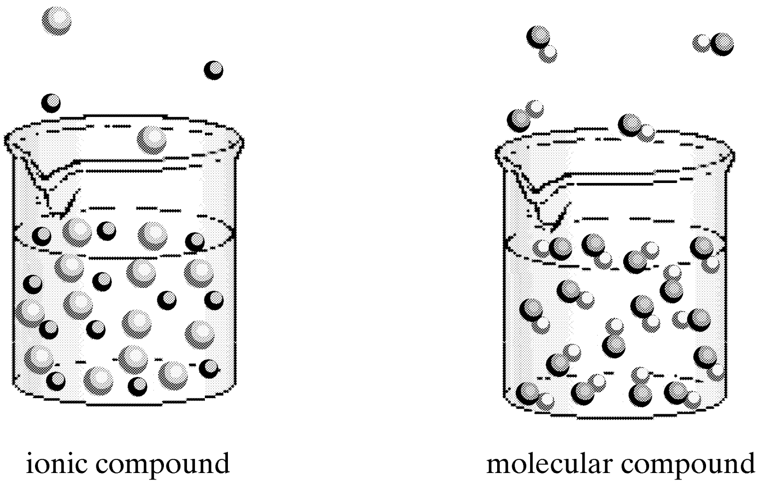


Figure 5.2 An Illustration of the Difference Between Ionic and Molecular Compounds. During evaporation, molecules remain intact, while the ions of an ionic compound move independently of one another.

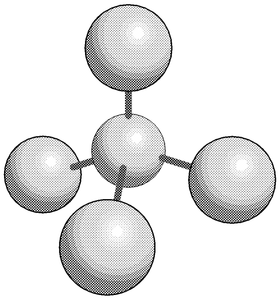


Figure 5.3 A CCl_4 molecule.

According to the covalent model, the atoms of compounds in the second category bond together by sharing electrons between them. This bonding is quite directional; that is, the atoms are held at more or less fixed angles and distances relative to one another. In CCl_4, for example, four chlorine atoms are bonded to one carbon atom in such a way that the angle between any two chlorine atoms (the Cl—C—Cl angle) is 109°. Atoms also tend to form only a certain number of covalent bonds: Carbon usually forms four bonds, while chlorine forms only one. This limitation results in aggregates of atoms (that is, molecules) that move and function as a unit. A CCl_4 molecule is shown in Figure 5.3.

Evidence for the covalent model includes (a) the nonconductivity of many liquids, which indicates the absence of charged particles, and (b) the highly directional character of the "bonds" in molecules, as evidenced by x-ray diffraction and electron microscopy (very large molecules have been "seen" in the electron microscope).

The rather low melting and boiling points for many covalent compounds have already been explained. However, not all covalent compounds have low melting and boiling points. Some consist of very long chains of atoms connected by covalent bonds. As these compounds pass from one state to another, the covalent bonds are severed, which requires a great deal of energy.

The two models—ionic and covalent—are represented in Figure 5.4. The enclosed areas in the figure represent regions of high electron density. Note that the ionic model pictures the ions as two separate "particles," with no electron density shared between them, while the covalent model shows electron density evenly shared between the two nuclei. For most compounds the disposition of electron density is somewhere between these two extremes. In Figure 5.4(c), nucleus B is surrounded by almost one extra electron and A has lost *almost* one electron, and there is definitely a sharing of some electron density. This bond is usually referred to as a **polar bond**, or as a bond with some ionic character.

The change in electron density in the A—Cl bond, where A is an element in the third period, is shown in Figure 5.5.

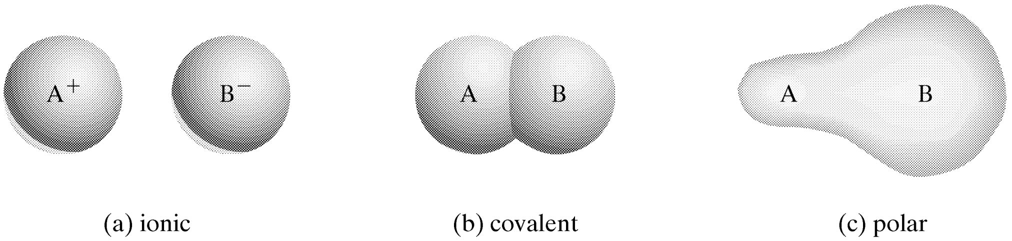


Figure 5.4 Ionic, covalent, and polar bonds.

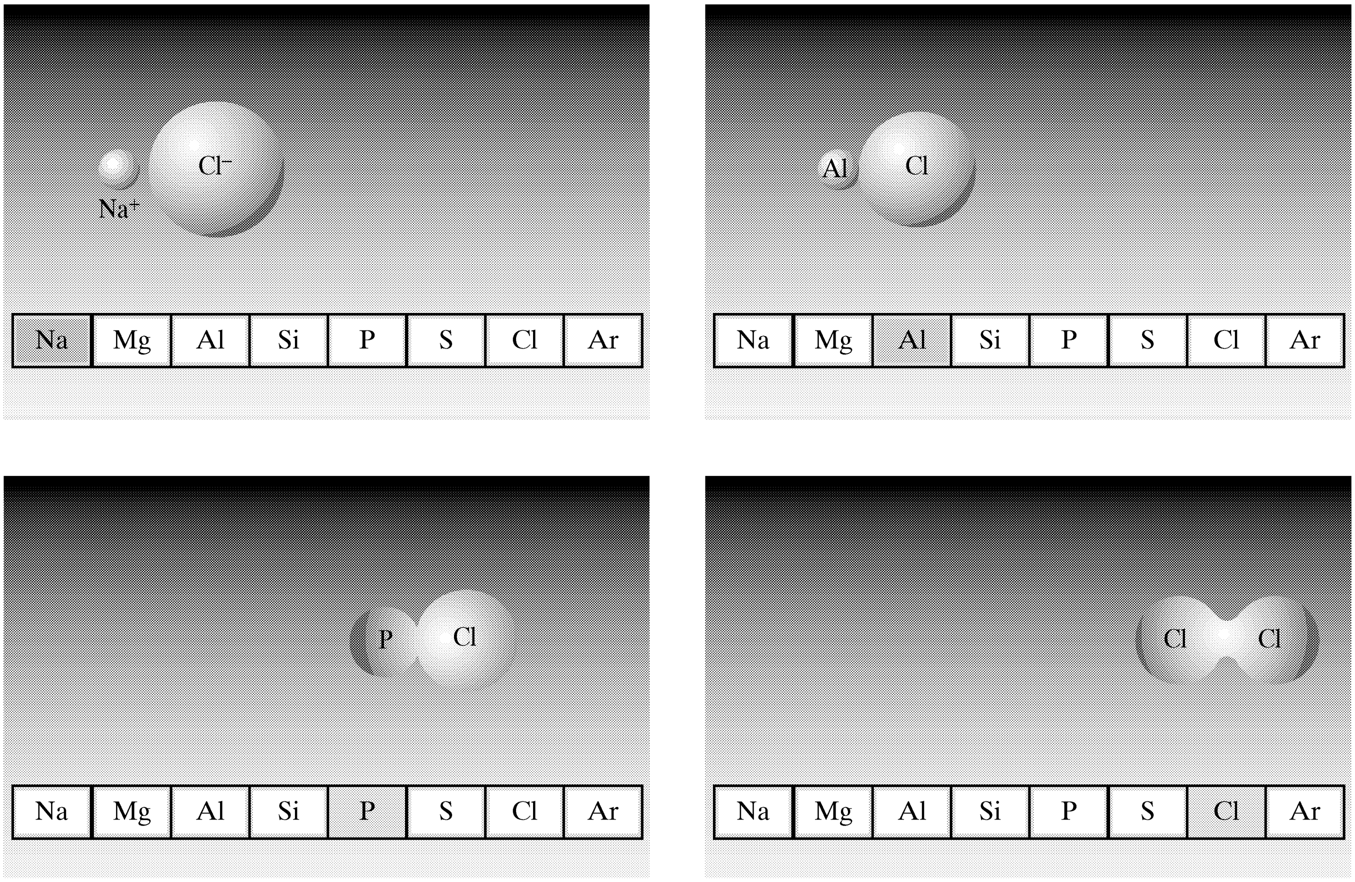


Figure 5.5 The change in electron density in the A—Cl bond, where A is an element in the third period.

We will now examine each of these models in more depth, attempting at each stage to rationalize the details of the internal microscopic structure of compounds. The remainder of this chapter will be devoted to the ionic model; the covalent model will be discussed in Chapters 6 and 7.

5.3 TYPES OF IONS

Among the first questions to arise in any discussion of the ionic model are: What kinds of compounds can be classified as ionic, and what is the nature of the ions in these compounds?

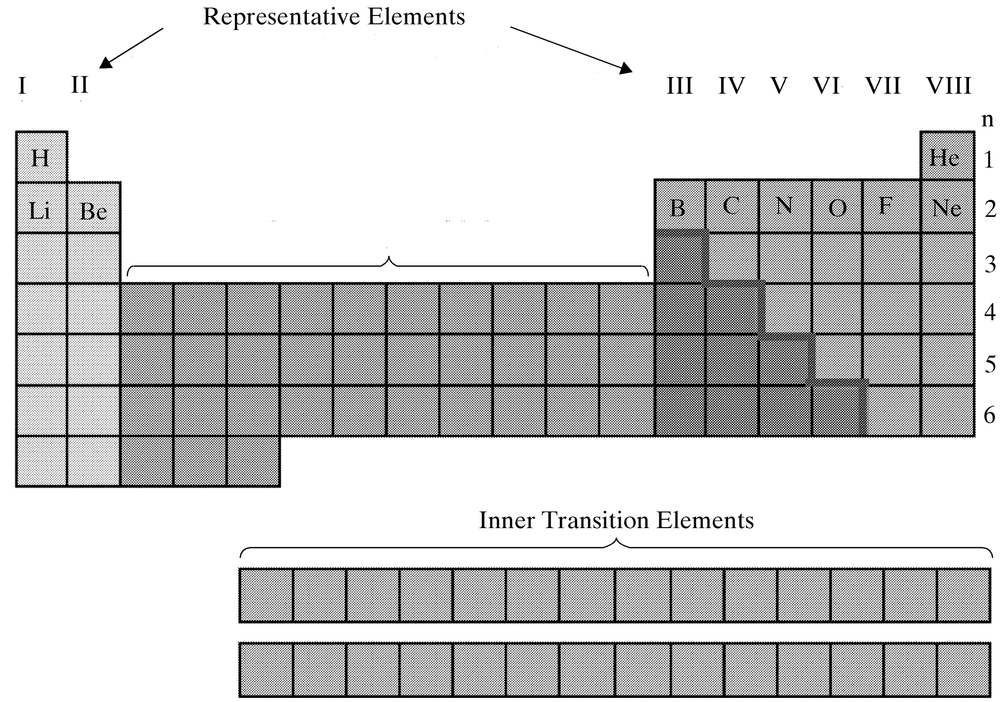
The formation of a binary (two-element) ionic compound is accompanied by a transfer of electrons from the element forming the positive ion, called the **cation**, to the element forming the negative ion, called the **anion**. Thus ionic compounds are formed when elements that lose their electrons easily—elements that have low ionization energies—combine with elements that gain electrons easily—ones that have high electron affinities. Because metals have low ionization energies, most of the compounds that have appreciable ionic character contain metallic elements. Similarly, the very electronegative nonmetals readily gain electrons, and consequently most ionic compounds have anions that contain these elements.

As an illustration, consider the process that occurs when the elementary substances sodium and chlorine are heated together. Sodium is a soft, lustrous metal, and chlorine is a greenish-yellow gas. The white, crystalline solid that forms from this heated mixture has none of the properties of either of the two original materials. The substance is sodium chloride—ordinary table salt; obviously, a chemical reaction has occurred and the sodium and chlorine atoms have undergone some sort of change.

This change may be thought of as a transfer of an electron from a Na atom to a Cl atom. The loss of one electron from Na and the gain of one electron by Cl gives each of these atoms the stable configuration of an inert gas (Ne and Ar, respectively). The Na atom from which an electron has been removed contains only 10 electrons, but its nuclear charge is still 11+. Thus, the Na atom is no longer neutral; it now has a positive charge equal to the charge of one proton. Similarly, the Cl atom, having gained an electron, contains 18 electrons but only 17 protons; it therefore carries a negative charge equal to that of one electron. The Na and Cl atoms in the heated mixture have become Na and Cl ions (symbolized by Na^+ and Cl^-, respectively). Because they have electrically opposite charges, the Na^+ and Cl^- ions attract each other; the sodium chloride crystals consist simply of aggregates of Na^+ and Cl^- particles. Since the compound is electrically neutral, there must be the same number of Na^+ and Cl^- particles, and sodium and chlorine are present in the ratio of 1:1. The formula of the compound is therefore NaCl.

Visualization 5.1

Identify the elements that are most likely to form cations on the periodic chart below.



Solution:

All of the elements to the left of the stepped line have metallic character and generally can form cations. This includes the inner transition elements.

The second question—that is, what kinds of ions are formed by the various elements—can be answered by a combination of (a) the previously formulated rule that filled quantum levels have a special stability, and (b) the ionization energies of the elements. Table 5.2 presents the ionization energies for sodium, magnesium, chlorine, and iron. Sodium has a low first ionization energy and a very high second ionization energy. It also has an electron configuration of $1s^2 2s^2 2p^6 3s^1$, which means that it will have a filled second quantum level as its outer level if it loses one electron. Thus, both the ionization energies and the inert-gas rule would predict that sodium (and all of the alkali metals) would most likely form the 1+ ion.

TABLE 5.2 Selected Ionization Energies, kJ/mol

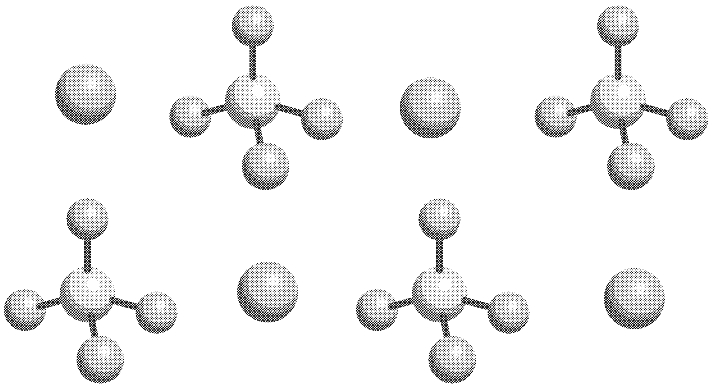
	FIRST	SECOND	THIRD
Na	498	4565	______
Mg	736	1452	7732
Cl	1255	2297	3849
Fe	761	1561	2958

For magnesium and the alkaline earth metals, the same reasoning predicts the formation of 2+ ions. Chlorine, on the other hand, certainly could lose an electron—the first ionization energy is not prohibitively high—but this would not lead to a filled quantum level, since the electron configuration of chlorine is $1s^22s^22p^63s^23p^5$. However, if it acquires an electron, chlorine will obtain the inert-gas configuration. The halogens, then, are usually present in ionic compounds as the 1– anions. Iron has an electron configuration of $1s^22s^22p^63s^23p^63d^64s^2$, and thus an inert-gas configuration cannot be achieved by loss or gain of any small number of electrons. The first, second, and third ionization energies are at most moderately high, and thus it would seem that iron could lose one, two, or three electrons. In fact, iron is found most commonly as the 2+ or 3+ ion.

Several qualifying remarks are necessary at this point. First, the feasibility of forming any particular ionic compound is a function of many factors, such as the stability of the particular arrangement adopted by the ions in the solid, as well as the ease of formation of the cation and anion. These other factors will be discussed later in this chapter. Second, the existence of ions of high charge, greater than 2+ or 2−, becomes more improbable the higher the charge. Even compounds that appear to contain a 3+ ion, such as $AlCl_3$, may be rather covalent. Third, while the discussion above has been directed toward binary compounds, many ionic compounds contain more than two elements; for example, KNO_3 and $CuSO_4$ each contain three. In most of these compounds the anion is an oxyanion; that is, the anion consists of oxygen covalently bonded to another fairly electronegative element. In $CuSO_4$, the anion is SO_4^{2-}, and in $Mg(ClO_4)_2$, the anion is ClO_4^-. The names and formulas of such anions will be discussed in the next section of this chapter. Since the bonding within these ions is covalent, their structure will be discussed in Chapters 6 and 7.

Visualization 5.2

The diagram below portrays a portion of a solid ionic compound containing the Ca^{2+} ion. Which of the following compounds is it most likely to be: $CaCl_2$, $CaSO_4$, or $Ca(ClO_4)_2$?



Solution:

Because there is a one-to-one ratio of cation to anion, the anion must have a 2– charge in order to balance the charge of the Ca^{2+}. Obviously, the anion contains four atoms covalently bonded to a central atom. The compound is $CaSO_4$.

TABLE 5.3 Common Cations

Group IA metals	1+	Co	2+, 3+
Group IIA metals	2+	Ni	2+
Al	3+	Cu	1+, 2+
Sn	2+	Zn	2+
Pb	2+	Cd	2+
Cr	2+, 3+	Ag	1+
Mn	2+	Au	1+, 3+
Fe	2+, 3+	Hg	1+,[a] 2+

[a] Actually Hg_2^{2+}

It should be clear from our discussion of iron that the charges of the ions of some elements cannot easily be predicted and must therefore be committed to memory. Table 5.3 presents the most commonly encountered metals and their common ions.

5.4 THE NOMENCLATURE OF IONIC COMPOUNDS

Chemists frequently refer to compounds by name rather than by formula, and it is therefore necessary to know how to derive names from formulas and vice versa. The name of any ionic compound is a composite of the names of its cation and anion.

Cation Names

Traditionally, cations of an element that form only one ion—for example, sodium—are named exactly like the element; thus, Na^+ is the sodium ion. Cations of elements that can form more than one ion—for example, iron—are named by adding a suffix to the root of the name from which the chemical symbol was derived. These roots are given in Table 5.4.

TABLE 5.4 Name Roots of Some Elements

ELEMENT	SYMBOL	NAME ROOT
Gold	Au	Aur-
Chromium	Cr	Chrom-
Cobalt	Co	Cobalt-
Copper	Cu	Cupr-
Iron	Fe	Ferr-
Mercury	Hg	Mercur-
Lead	Pb	Plumb-
Tin	Sn	Stann-

To distinguish between two possible ions of the same element, the suffix *-ous* is added to the root to indicate the ion of lower charge, while the suffix *-ic* indicates the ion of higher charge. The Fe^{2+} ion is therefore the ferrous ion and Fe^{3+} is the ferric ion. When there are more than two possible ions, this traditional system becomes rather unwieldy, so the International Union of Pure and Applied Chemistry (IUPAC) has proposed an alternate system. The IUPAC rule designates an ion by simply giving the name of the element followed in parentheses by the charge on the ion in Roman numerals. Thus, Fe^{3+} is iron(III).

A notable exception to these systems of nomenclature is the common cation $NH_4{}^+$, called the ammonium ion.

Anion Names

The common anions can be derived from acids. For this purpose, an acid can be defined as a substance that contains one or more hydrogen atoms that can be removed as H^+ ions by some chemical means. Generally, a hydrogen ion will not be easily removed unless it is attached to an element more electronegative than carbon. It is also generally true that the removable hydrogens are attached to the most electronegative atoms in the covalent acid. For example, the acid with molecular formula HNO_2 has the structural formula H—O—N—O, in which the hydrogen is attached to the more electronegative atom, oxygen.

The name of the anion produced when one or more hydrogen ions are removed from an acid is based on the name of the parent acid. The first step in learning to name the common anions, then, is to learn the names of the acids from which they are derived. Table 5.5 lists such acids under two categories: those that contain oxygen (oxyacids) and those that do not.

Note that the names of the first group of acids contain the prefix *hydro-* attached to the root of the name of the element (or group of elements) to which the hydrogen is attached, plus the suffix *-ic*, followed by *acid*. The names of most of the oxyacids are derived from the name of the central element, with a suffix that indicates the relative number of oxygen atoms. Thus, in the nitric acid molecule, three oxygen atoms are attached to a nitrogen according to the formula

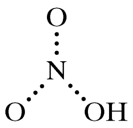


TABLE 5.5 Names of Some Acids and Their Anions

	ACIDS		ANIONS
HF	hydrofluoric acid	F^-	fluoride ion
HCl	hydrochloric acid	Cl^-	chloride ion
HBr	hydrobromic acid	Br^-	bromide ion
HI	hydroiodic acid	I^-	iodide ion
H_2S	hydrosulfuric acid	HS^-	hydrogen sulfide ion
		S^{2-}	sulfide ion
HCN	hydrocyanic acid	CN^-	cyanide ion
	OXYACIDS		
HNO_3	nitric acid	NO_3^-	nitrate ion
HNO_2	nitrous acid	NO_2^-	nitrite ion
H_2SO_4	sulfuric acid	HSO_4^-	hydrogen sulfate ion
		SO_4^{2-}	sulfate ion
H_2SO_3	sulfurous acid	HSO_3^-	hydrogen sulfite ion
		SO_3^{2-}	sulfite ion
H_3PO_4	phosphoric acid	$H_2PO_4^-$	dihydrogen phosphate ion
		HPO_4^{2-}	hydrogen phosphate ion
		PO_4^{3-}	phosphate ion
H_2CO_3	carbonic acid	HCO_3^-	hydrogen carbonate ion
		CO_3^{2-}	carbonate ion
$H_2C_2O_4$	oxalic acid	$HC_2O_4^-$	hydrogen oxalate ion
		$C_2O_4^{2-}$	oxalate ion
$HC_2H_3O_2$	acetic acid	$C_2H_3O_2^-$	acetate ion
$HClO_4$	perchloric acid	ClO_4^-	perchlorate ion
$HClO_3$	chloric acid	ClO_3^-	chlorate ion
$HClO_2$	chlorous acid	ClO_2^-	chlorite ion
HClO	hypochlorous acid	ClO^-	hypochlorite ion
$HMnO_4$	permanganic acid	MnO_4^-	permanganate ion

The nitrogen is the central atom, which accounts for the *nitr-* portion of the name. The suffixes *-ic* and *-ous* are used to designate more or less oxygen, respectively, relative to another oxyacid containing the same central element. When there are only two common acids containing the same central element, the nomenclature is straightforward. For example, HNO_3 is nitric acid and HNO_2 is nitrous acid; H_2SO_4 is sulfuric acid and H_2SO_3 is sulfurous acid.

When there are more than two oxyacids of the same element, the prefix *per-* (Latin for "complete" or "thorough") is added to the name of the *-ic* acid to indicate more oxygen, while the prefix *hypo-* (Greek for "under") is added to the name of the *-ous* acid to designate less oxygen. The chlorine oxyacids are a good example of this nomenclature:

$HClO_4$	perchloric acid
$HClO_3$	chloric acid
$HClO_2$	chlorous acid
$HClO$	hypochlorous acid

If there is only one common oxyacid of an element, it is given the *-ic* designation; for example, H_2CO_3, carbonic acid. The names of some of the acids in Table 5.5 are not derived according to this system, and at this juncture it is best to simply memorize these acids.

Having examined the nomenclature of acids, we are now in a position to derive the names of anions. When hydrogen ions are removed from acids that do not contain oxygen, the resulting ions are of the type

Cl^-	(take H^+ away from HCl)
S^{2-}	(take 2 H^+ from H_2S)

These ions are named by dropping the *hydro-* prefix of the parent acid and replacing the *-ic* suffix with *-ide*. Thus, from hydrochloric we get chloride as the name of the ion Cl^-. Table 5.6 lists four anions whose names have the *-ide* ending but are derived from compounds not usually considered as acids. Note that the names of the monatomic ions are based on the name root of the element.

TABLE 5.6 Some Additional Anions

H^-	hydride
O^{2-}	oxide
N^{3-}	nitride
OH^-	hydroxide

When hydrogen ions are removed from oxyacids, the resulting anions are given the name of the parent acid with its suffix changed—from *-ic* to *-ate* or from *-ous* to *-ite*. The chlorine oxyanions are then

ClO_4^-	perchlorate
ClO_3^-	chlorate
ClO_2^-	chlorite
ClO^-	hypochlorite

If less than all of the removable hydrogens of an acid are lost to form the anion, the number of hydrogens remaining is denoted by the word hydrogen for one, dihydrogen for two, trihydrogen for three, and so forth. The HCO_3^- ion is called the hydrogen carbonate ion; the $H_2PO_4^-$ ion is the dihydrogen phosphate ion. An older system adds the prefix *bi-* to name ions that have retained one of two hydrogens; HCO_3^- in this system is the bicarbonate ion.

Compound Names

We are now able to put the entire name of an ionic compound together by simply adding the cation name to the anion name. The compound with empirical formula $MgCl_2$ is called magnesium chloride; $RbNO_3$ is rubidium nitrate.

To name or write the formula for some compounds, it is necessary to know the charge on the ions. In the compound $FeCl_3$, the charge on the iron ion is determined by recognizing first that the sum of the charges of all ions must be zero because the compound is electrically neutral. Now, since the chloride ion always has a charge of 1− and since there are three chloride ions for every iron ion, the iron ion must have a charge of 3+. This compound is therefore ferric chloride, or iron(III) chloride.

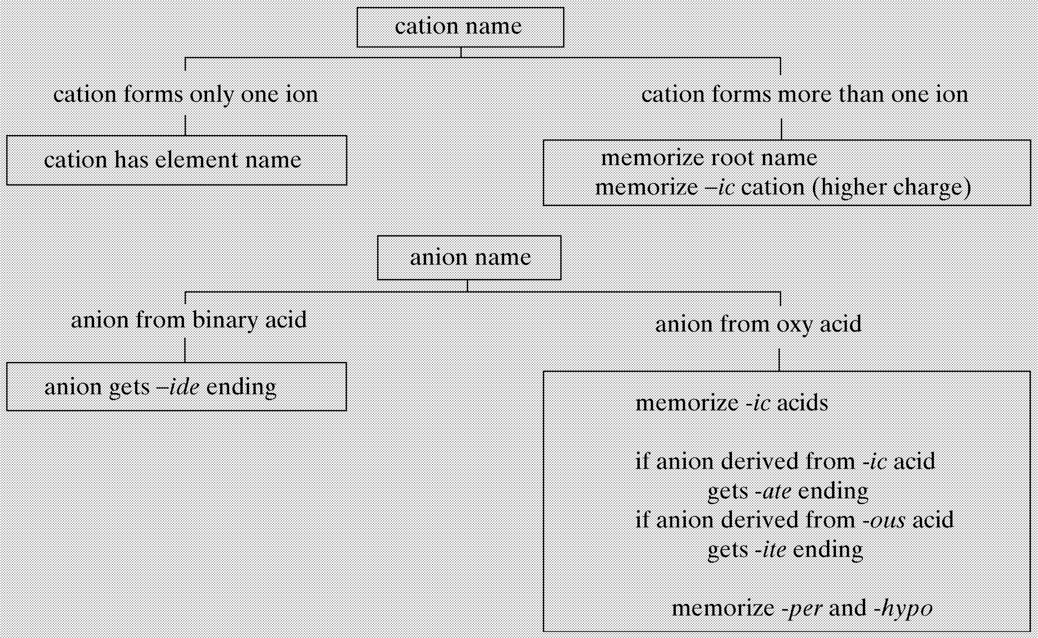
Formulas are derived from names in a similar fashion. Cobaltous nitrite is $Co(NO_2)_2$—the cobaltous ion has a charge of 2+, whereas the nitrite ion is only 1−, so there must be twice as many nitrite ions as cobaltous ions in order to preserve electrical neutrality.

Hydrates

When prepared from aqueous solution, many ionic compounds retain water molecules in their crystal structures. If the number of moles of water retained is an integral multiple of the number of moles of the compound, the water is referred to as the **water of hydration** or the **water of crystallization**, and the compounds are called **hydrates**. The compounds are named by adding the appropriate prefix—*di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, and so on—to indicate the number of moles of water per mole of compound, followed by the word *hydrate.* Thus, $BaCl_2 \cdot 2H_2O$ is barium chloride dihydrate, $Na_2CO_3 \cdot 7H_2O$ is sodium carbonate heptahydrate, and $Na_2CO_3 \cdot 10H_2O$ is sodium carbonate decahydrate.

Methodology 5.1

Name the following compounds: Cs_2SO_4, $Fe(ClO_2)_2$, and $Ba(HSO_3)_2$.
First produce a scheme for naming cations and anions.



The name for the cation in Cs_2SO_4 is cesium, and the anion name is derived from sulfuric acid by replacing the suffix -*ic* with -*ate* to give sulfate. Thus the compound is called cesium sulfate.

How would you name $Fe(ClO_2)_2$?

Start by naming the cation.

The cation name for $Fe(ClO_2)_2$ is iron(II) or ferrous, because Fe^{2+} has the lower charge of the two common iron ions.

The anion is

a. chlorate b. perchlorate c. chlorite hypochlorite

The answer is (c). The anion name is derived from chlorous acid by replacing the suffix -*ous* with -*ite* to give chlorite. The name of the compound is therefore ferrous chlorite or iron(II) chlorite.

Now determine the name for $Ba(HSO_3)_2$.

The cation name for $Ba(HSO_3)_2$ is barium, and the anion name is derived from the acid H_2SO_3, sulfurous acid. Because one hydrogen has been retained on the anion, the name of the anion is hydrogen sulfite, and the compound is barium hydrogen sulfite.

Problem 5.8

This is an excellent opportunity to practice reasoning by analogy (See Chapter 1). Table 5.5 does not contain acids such as $HBrO_4$ or H_3AsO_4, but we already know the names of acids containing central atoms in the same group ($HClO_4$ and H_3PO_4). Reason by analogy to name the compounds: $CrAsO_4$, $CuBrO_4$, $Cu(BrO)_2$.

Solution:

Because Cl and Br are in the same group, their compounds are frequently isostructural (have the same structure) and their names are analogous. Thus, $HClO_4$ is perchloric acid; $HBrO_4$ is perbromic acid. Likewise, H_3PO_4 is phosphoric acid and H_3AsO_4 is arsenic acid. $CrAsO_4$ is chromic arsenate, $CuBrO_4$ is cuprous perbromate, and $Cu(BrO)_2$ is cupric hypobromite.

✓ Check Point 5.1

Give the name of the compound $FePO_4$.

Solution:

Ferric phosphate

◇ ◇ ◇ ◇ ◇

5.5 POTENTIAL ENERGY OF IONIC CONFIGURATIONS

Let us now examine the ionic model from a microscopic view. Imagine sitting on a sodium ion in the middle of a crystal of sodium chloride. (A crystal is simply an orderly, three-dimensional arrangement of ions, atoms, or molecules in the solid state.) According to data from x-ray diffraction studies, this sodium ion is surrounded by six nearest-neighbor chloride ions. Thus it is situated at the center of an octahedron, with chloride ions at the apexes (see the close up on the right-hand side of Figure 5.6). Since there are equal numbers of sodium and chloride ions in NaCl, each chloride ion also would be surrounded by six nearest-neighbor sodium ions.

Now, our objective in sitting on the central sodium ion is to experience the forces that exist between the ions, that is, the forces that hold the ions together and make NaCl

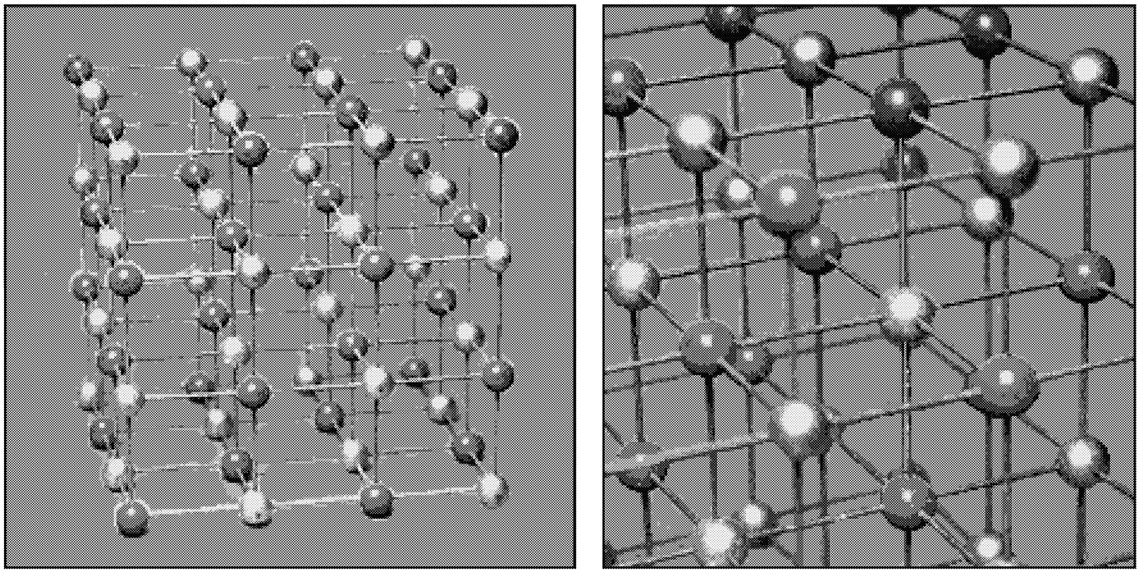


Figure 5.6 The NaCl crystal structure.

a stable compound. These forces are the electrostatic forces that exist between charged particles and, as discussed in Chapter 3, are related to the charges on the particles and the distance between them,

$$F = \frac{kq_1q_2}{r^2}$$

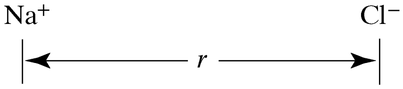
Because a given ion, such as our sodium ion seat, is surrounded by oppositely charged ions (Cl^-) that are closer than ions of the same charge (Na^+), the attractive forces are greater than the repulsive forces.

In Chapter 3 we found that the potential energy was an important part of the total energy of the hydrogen atom. The potential energy is also an important determinant of the stability of compounds. For the electrostatic interactions between ions, this energy is given by the equation

$$PE = \frac{kq_1q_2}{r}$$

This equation* will allow us to calculate the potential energy of a mole of solid sodium chloride.

Consider first just two ions—a Na^+ ion and a Cl^- ion—separated by a distance, r, which in solid NaCl is 280 pm†:



The charge on the sodium ion is one atomic unit, which is equal to 1.60×10^{-19} C. The charge on the chloride ion is equal in magnitude but opposite in sign and therefore is -1.60×10^{-19} C. The potential energy is then

$$PE = \frac{(8.99 \times 10^9 \text{ J-m/C}^2)(1.60 \times 10^{-19}\text{ C})(-1.60 \times 10^{-19}\text{ C})}{2.8 \times 10^{-10}\text{ m}} = -8.2 \times 10^{-19}\text{ J}$$

The potential energy of our Na^+ seat in the real three-dimensional sodium chloride crystal will be a sum of many terms. Our ion is attracted to six equidistant chloride ions‡ by the energy $6(kq_1q_2)/r$, repelled by 12 sodium ions situated at a distance $\sqrt{2}r$ away from our seat (this distance can be easily calculated with the Pythagorean Theorem), attracted to eight equidistant chloride ions at a distance of $\sqrt{3}r$, and so on throughout the crystal. Thus, this series will appear as

$$PE = 6\frac{kq_1q_2}{r} + 12\frac{kq_1q_2}{\sqrt{2}r} + 8\frac{kq_1q_2}{\sqrt{3}r} = \ldots$$

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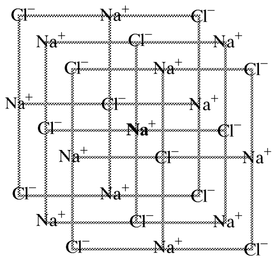
* If you do not remember this equation, return to Chapter 3 to review.
The units for the charges must be in Coulombs (a proton has a charge of 1.60×10^{-19} C), r must be expressed in meters, and $k = 8.99 \times 10^9 \frac{\text{J-m}}{\text{C}^2}$.

† Remember that pm is the abbreviation for picometer, 1×10^{-12} m. 100 pm are equal to 1 Å, a unit that is also frequently used for bond lengths.

‡ If you are having trouble seeing the nearest-neighbor ions you might try the diagram below.



The first term, in which q_1 and q_2 have different signs, will be negative; the second term will be positive, because q_1 and q_2 have the same sign; the third term will be negative; and so on. Fortunately, this infinite series converges to the value 1.75 $(kq_1q_2)/r$. The number 1.75 is called the **Madelung constant** (M) and is the sum of the coefficients of all the q_1q_2/r terms in the infinite series. The Madelung constant for any solid whose ions have the same geometrical arrangement as NaCl will have the same numerical value. The potential energy of our sodium ion can now be calculated as follows:

$$PE = -1.75\,\frac{(8.99 \times 10^{9}\ \text{J-m/C}^2)(1.60 \times 10^{-19}\ \text{C})^2}{(2.8 \times 10^{-10}\ \text{m})} = -1.4 \times 10^{-18}\ \text{J}$$

For one mole of sodium ions, this becomes

$$\begin{aligned} PE &= (6.022 \times 10^{23})(-1.4 \times 10^{-18}\ \text{J}) \\ &= -8.4 \times 10^{5}\ \text{J/mol} \end{aligned}$$

If we want the potential energy of a mole of NaCl we must also include the potential energy of a mole of chloride ions, which is identical to that of a mole of sodium ions. The addition of these two energies, however, would count each electrostatic interaction in the crystal twice. Thus, the sum must be divided by two.

$$\begin{aligned} PE &= -\frac{(8.4 \times 10^{5}\ \text{J} + 8.4 \times 10^{5}\ \text{J})}{2} \\ &= -8.4 \times 10^{5}\ \text{J/mol} \end{aligned}$$

Actually, this is still not quite the potential energy of a mole of crystalline NaCl. Our calculation up to this point has treated the ions only as point charges. In fact, the electron clouds of the closely packed ions repel one another somewhat. This repulsion leads to an increase in the potential energy; that is, the potential energy becomes less negative due to the positive energy added by the repulsions. The magnitude of these repulsions depends upon the nature of the ions in the crystal, but they can be approximated as 10% of the point charge potential energy. Thus, for NaCl the repulsions contribute about $0.10 \times 8.4 \times 10^{5}$ J to the potential energy. The total potential energy is therefore

$$\begin{aligned} PE &= (-8.4 \times 10^{5} + 0.84 \times 10^{5})\ \text{J/mol} \\ &= -7.6 \times 10^{5}\ \text{J/mol} \\ &= -760\ \text{kJ/mol} \end{aligned}$$

This amount of energy represents the negative of the work required to separate one mole of sodium and chloride ions from their positions in the crystal to infinite distances from one another. Although in reality it is impossible to separate the ions by infinite distances, the separation they undergo as the compound passes from the solid state to the gaseous state is very nearly equivalent, since the distance between the ions in the gaseous state is much greater than the distance in the solid. The energy evolved when the solid is formed from its constituent ions in the gaseous state is called the **lattice energy** (see Figure 5.7) and can be determined from experimental data. (Loosely defined, a lattice is a regular arrangement of atoms, ions, or molecules.)

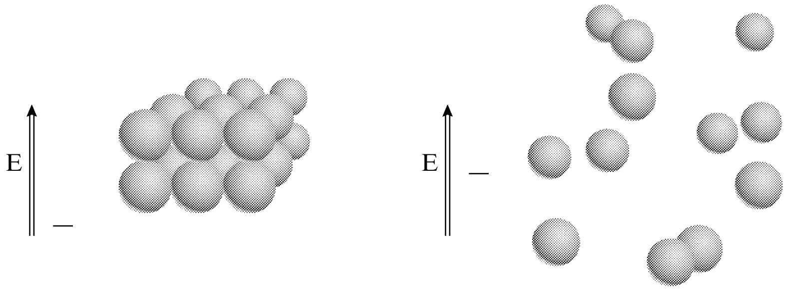


Figure 5.7 The energy change during the formation of an ionic solid (left) from its constituent ions in the gas phase (right).

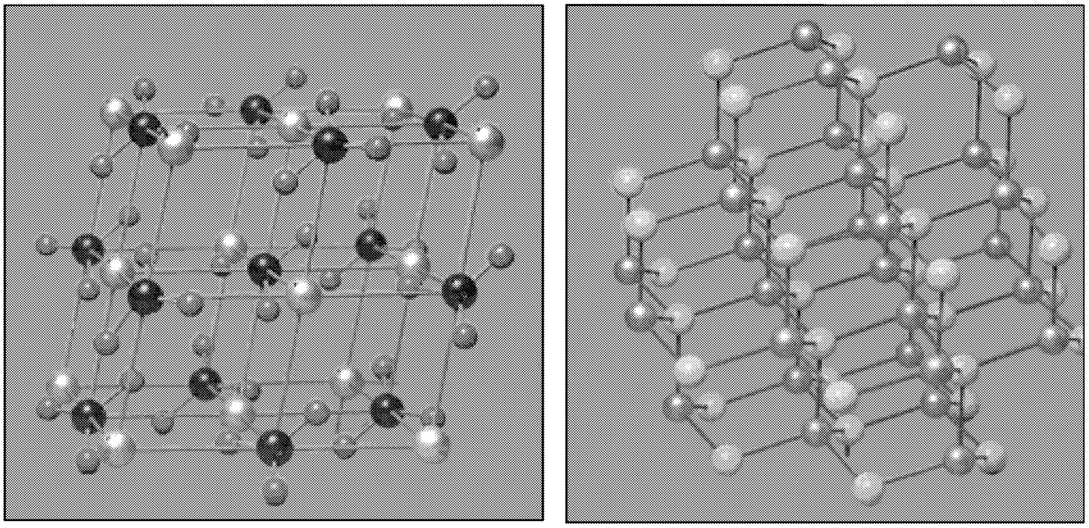

calcium carbonate zinc sulfide (zinc blende)

Figure 5.8 The calcite ($CaCO_3$) and zinc blende (ZnS) lattices.

For sodium chloride, the experimentally determined lattice energy is 770 kJ/mol. The good agreement between the calculated and experimental lattice energies is additional evidence for the existence of ions* in these compounds.

The structures of most ionic compounds are not as simple as that of sodium chloride (several other structures are shown in Figure 5.8), but because the Madelung constant takes into account the geometrical arrangement of the ions, the same procedure can be used to calculate the lattice energy of more complex structures (see Problem 5.9).

Problem 5.9

Assuming that CaF_2 is ionic, calculate its lattice energy.

Solution:

In order to do the calculation we need to know two things about CaF_2; a) the distance between the ions in the crystal lattice, and b) the geometrical arrangement of ions in the lattice. Although it would be nice to have the experimentally determined (x-ray diffraction) distance between the centers of the ions, we can use the sum of the ionic radii given in Appendix 9 as a good approximation. The sum of these radii [$r(Ca^{2+}) + r(F^-)$] is 233 pm or 2.33×10^{-10} cm.

The Madelung constant for the geometrical arrangement of the ions in CaF_2 has been determined to be 2.52. Every compound that has this particular arrangement of ions has the same Madelung constant.

Continued on next page

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* In other words, we have used a simple model that portrays NaCl as consisting of charged particles whose potential energy can be determined with the simple Coulomb expression. (This expression is only valid if the distances between the charges are large compared to the size of the charges, an assumption that we make here.) Because our calculated potential energy is in good agreement with the experimentally determined lattice energy, we have additional reason to believe that NaCl does indeed contain ions. Of course, this agreement could just be coincidental. We should also note that there are other factors, such as London dispersion forces (see Chapter 9), that contribute to the total potential energy of NaCl. We also know, however, that these other factors make a minor contribution to the potential energy.

Problem 5.9 *Continued*

The potential energy is

$$PE = \frac{2.52(8.99 \times 10^{9}\ \text{J-m/C}^{2})(2 \times 1.60 \times 10^{-19}\ \text{C})(-1.60 \times 10^{-19}\ \text{C})}{(2.33 \times 10^{-10}\ \text{m})}$$

$$= -5.0 \times 10^{-18}\ \text{J}$$

Note that the value of q_1 includes a factor of 2 to account for the 2+ charge on the Ca ion. Now, we add 10% for repulsive forces,

$$PE = -5.0 \times 10^{-18}\ \text{J} + 0.10 \times 5.0 \times 10^{-18}\ \text{J} = -4.5 \times 10^{-18}\ \text{J}$$

Finally, we convert to kJ per mole,

$$PE = -4.5 \times 10^{-18}\ \text{J} \times 6.022 \times 10^{23}\ \text{x}\ (1\ \text{kJ}/1000\ \text{J}) = -2.7 \times 10^{3}\ \text{kJ/mol}$$

Our treatment above suggests that lattice energy is a function primarily of three factors: (1) the charge on the ions, (2) the distance between the centers of the ions, and (3) the arrangement of ions in the solid (which determines the Madelung constant). Among the alkali halides, the Madelung constant is virtually the same (1.75 to 1.76, depending on the type of lattice). The decrease in lattice energy in the series LiF > NaF > KF and NaF > NaCl > NaBr, as shown in Table 5.7, is due solely to an increase in interionic distance within these series (the greater the distance, the lower the absolute value of the potential energy). The Madelung constant for the alkaline earth oxides and sulfides is also 1.75; the much larger lattice energies for these compounds are due, then, to the greater charge on the oxide and sulfide ions. Since q_1 and q_2 for the alkaline earth oxides and sulfides are both twice what they are for the alkali halides, the alkaline earth lattice energies should be roughly four times as large. Indeed, NaCl and CaS both have an interionic distance of 280 pm, and the lattice energy of CaS is very nearly four times that of NaCl.

The lattice energy, then, is a measure of the stability of the crystalline solid *with respect to its constituent gaseous ions.* Thus it would appear that the greater the charge on the ions and the smaller the ions, the more favorable the formation of the solid. However, the stabilities (and ease of formation) of crystalline ionic substances are usually measured relative to their constituent elements, not their gaseous ions.* Hence, as indicated before, the ease of formation of an ionic compound from its elements is a function of the energy required to form the gaseous cation and anion, as well as the energy released in the formation of the ionic lattice. Thus, while ions of high charge and small size result in large lattice energies, a large amount of energy is also required for their formation from the elements. The calculations necessary to predict the stability of ionic compounds will be discussed in Part Three of this book.

The lattice energy is directly related to physical properties such as melting point, boiling point, and hardness, since these properties depend upon the strength of the electrostatic forces that hold the ions in their lattice positions. For example, the lattice energy of LiF is greater than the lattice energy of LiBr because the fluoride and lithium ions are

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* The lattice energy is the amount of energy evolved when the solid is formed from the gaseous ions, as indicated by the equation

$$\text{Na}(g)^{+} + \text{Cl}(g)^{-} \longrightarrow \text{NaCl}(s)$$

This should not be confused with a traditional method of measuring the stability of any compound, which uses the constituent elements in their elemental forms as the reference or starting point. If we use this measure (called the heat of formation or the free energy of formation), we are concerned with the equation

$$\text{Na}(s) + 1/2\ \text{Cl}_2(g) \longrightarrow \text{NaCl}(s)$$

(Note that elemental sodium is a solid, whereas elemental chlorine exists as diatomic molecules in the gaseous phase.)

TABLE 5.7 Selected Lattice Energies and Interionic Distances

COMPOUND	LATTICE ENERGY kJ/mol	DISTANCE pm
LiF	1008	201
NaF	904	231
KF	803	266
NaCl	770	281
NaBr	736	298
MgF_2	2908	202
MgO	3925	210
MgS	3297	254
CaO	3519	240
CaS	3038	283

smaller and consequently more strongly attracted to one another. For the same reason, the melting point of LiF is higher than that of LiBr; that is, a higher temperature (more energy) is required to permit the ions in the LiF crystal to flow—to reach the liquid state.

Methodology 5.2

Which compound—MgF_2 or BaF_2—has the higher melting point?

First, think about what determines the melting point of an ionic compound.

Many of the physical and chemical characteristics of ionic compounds are affected by their potential energies. The lower the potential energy of a compound, the greater the energy required to separate the ions to infinity. Although melting does not involve separating the ions to infinity, it does involve separating the ions from their positions in the solid state to the liquid state, where they are free to move. The potential energy is therefore one (not the only one) of the factors that determines how much energy is required to cause melting to occur.

How is the potential energy of an ionic compound related to its lattice energy?

The lattice energy is the energy required to move the ions from their lattice positions in the solid to the gaseous state. Because the separations in the gaseous state are so large compared to those in the solid state, this is equivalent to the amount of energy required to separate the ions to infinity—the negative of the potential energy. Thus, lattice energy = −potential energy.

Will a high lattice energy result in a low melting point or a high melting point?

A high lattice energy corresponds to a large negative potential energy. The more negative the potential energy, the more strongly the ions are attracted to one another in the solid and the greater the energy required to melt the compound. Thus, the higher the lattice energy, the higher the melting point.

What factors determine the lattice energy?

Because the lattice energy is just the negative of the potential energy it is determined by Mq_1q_2/r, where M is the Madelung constant. Fortunately, for most qualitative comparisons, the Madelung constant can be ignored; this is particularly true for compounds that have the same type of formula (for example, all have a formula of the type AB). Thus, generally, we need only consider q_1, q_2, and r.

The greater the charge of the ions, the higher the lattice energy; and the smaller the distance between the ions, the higher the lattice energy.

Continued on next page

Methodology 5.2 Continued

Do we have to worry about q_1, q_2, and r in comparing the lattice energies of MgF_2 and BaF_2?

The charge on the Mg^{2+} and Ba^{2+} ions are clearly the same—+2. Both compounds contain fluoride as the anion and therefore q_2 is also the same for both compounds. The only factor to consider then is r, which is determined by the size of the ions. As you can see from the periodic chart, the Ba^{2+} ion is larger than the Mg^{2+}, and therefore the distance from the center of the Mg^{2+} ion to the center of the fluoride ion in MgF_2 is less than the distance in BaF_2.

How does r affect the lattice energy?

As r increases the lattice energy decreases; that is, as the denominator gets larger the value of q_1q_2/r decreases. Thus, the lattice energy is greater for MgF_2, and MgF_2 therefore has the higher melting point.

Can you think of a pair of compounds that would illustrate the effect of q_1 and q_2?

NaCl and $MgCl_2$. In this pair, q_1 for $MgCl_2$ is twice that of q_1 in NaCl, whereas q_2 is the same. The distance r is a little smaller in $MgCl_2$ because the Mg^{2+} ion is smaller than Na^+. Usually the effect of the charges outweighs a small change in r. For these two compounds both the charges and the distance operate to give $MgCl_2$ the greater lattice energy.

Problem 5.10

For each of the following pairs of compounds determine which compound has the higher melting point:

a. LiF, LiI

b. NaCl, $MgCl_2$

c. Na_2O, Na_2CO_3

Solution:

It is important to realize that each of these compounds is treated as if it were 100% ionic, an assumption that is certainly not true for each—especially for LiI, which has considerable covalent character. We have previously seen that the melting point of an ionic compound is determined by its lattice energy. Moreover, we know that lattice energy is a function of the Madelung constant, the charges on the ions, and the distance between the centers of the ions. In most cases, the charges on the ions and the distance between the ions are more important factors; indeed, the Madelung constant can generally be ignored when making predictions of relative lattice energies. Thus,

a. For these two compounds, the charges on the cations are the same and the charges on the anions (fluoride and iodide) are the same. Hence, the only factor that must be considered is the distance between the ions. Because the iodide ion is larger than the fluoride ion, the distance is greater for LiI and consequently the lattice energy of LiF is greater (remember r appears in the denominator of the expression for potential energy; a larger r means a less negative potential energy).

b. For these compounds, the main difference is the +1 cation in NaCl as opposed to the +2 cation in $MgCl_2$. Therefore, q_1 in the expression $PE = -\mathrm{M}\,kq_1q_2/r$ for $MgCl_2$ is twice that of q_1 in the expression for NaCl. This difference far outweighs any difference in the distance between the ions (which is smaller for $MgCl_2$, because the Mg^{2+} ion is smaller than the Li^+ ion). Hence, $MgCl_2$ has the higher lattice energy and the higher melting point.

c. Like part (a), the charges for the cations (q_1) are the same, as are the charges for the anions (q_2). Thus, any difference must be due to the sizes of the ions: O^{2-} is smaller than $CO_3{}^{2-}$ and therefore the lattice energy for Li_2O is greater than that Li_2CO_3.

✓ Check Point 5.2

Which compound has the higher melting point—$MgCl_2$ or MgO?

Solution:

MgO

◇ ◇ ◇ ◇ ◇

5.6 IONIC LATTICES

An ionic compound adopts a geometrical arrangement (lattice) of ions in such a way as to minimize the potential energy of the solid. The potential energy, in turn, is a function of three factors:

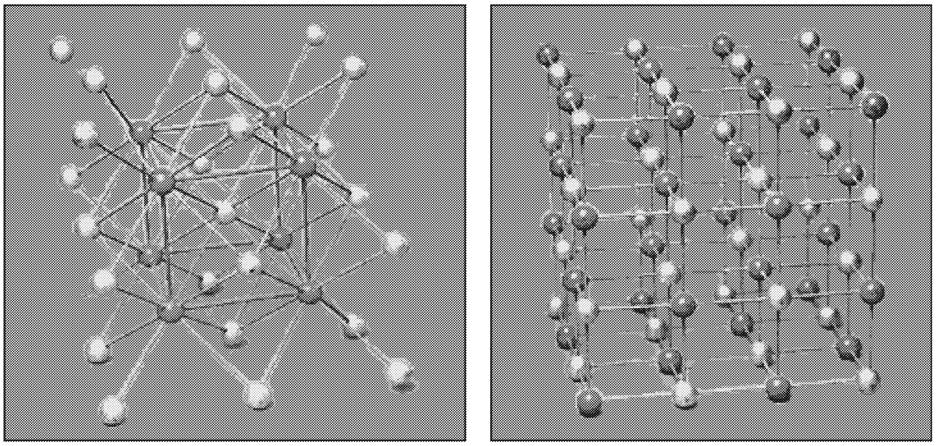
1. The cation-anion distance; the smaller this distance, the lower the potential energy; i.e., the more negative the potential energy
2. The coordination number—that is, the number of equidistant ions of opposite charge; the greater the coordination number, the lower the energy
3. The cation-cation and anion-anion distances; the smaller these distances, the greater the repulsions and the higher the energy of the crystal

Thus, in general, the greater the number of anions that can be squeezed around a cation without causing significant repulsions between the anions, the more stable the crystal.

In order to see how these factors work in more detail, let us examine several lattice structures of simple ionic compounds of the AB type. These lattices are the cesium chloride lattice and the sodium chloride lattice, which are shown in Figure 5.9.

In the cesium chloride lattice, each ion has a coordination number of eight, since each ion is surrounded by eight ions of opposite charge at the corners of a cube. In actuality, the ions are very nearly touching , so that the large Cs^+ ion fits snugly into the center of a chloride cube. For a smaller cation, such as Na^+, this structure would allow the anions to move even closer, resulting in more repulsion, and the cation would "rattle around" in the remaining space. Thus, in order to minimize anion-anion repulsion and the cation-anion separation, the crystal lattice assumes the sodium chloride structure (see Figure 5.10). In this type of lattice the coordination number is six; the cation is surrounded by six anions at the apexes of an octahedron. The coordination number, therefore, is smaller than that of the cesium chloride lattice, but the potential energy is also lower. Thus, the size of the cation relative to the size of the anion controls the arrangement of ions.

The favored lattice for a given ratio of cation to anion radii (r^+/r^-) can be determined with simple geometry by treating the ions as hard spheres. Using this method, it can be shown that when the ratio is between 1.00 and 0.73, the cesium chloride structure


cesium chloride

sodium chloride

Figure 5.9 The cesium chloride and sodium chloride lattices.

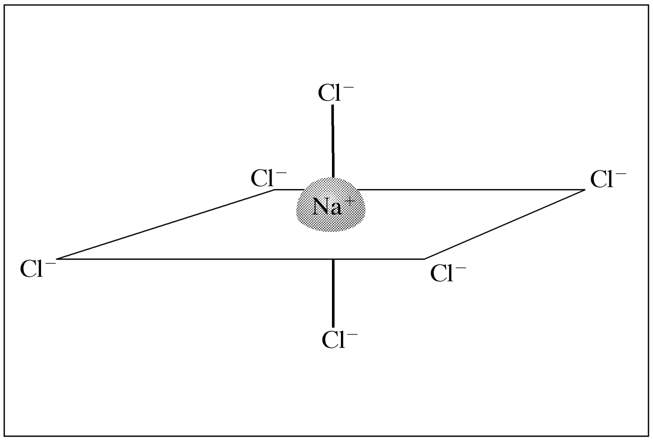


Figure 5.10 The Dependence of Lattice Geometry on Relative Ion Size. When the size of the cation decreases, the repulsions between the anions increase, and the total potential energy of the lattice can be decreased (thereby making the lattice more stable) by a change in geometry. In the new octahedral arrangement of ions, the distances between the anions are smaller.

is favored, whereas a ratio between 0.73 and 0.41 indicates a sodium chloride lattice. When the ratio is even lower, between 0.41 and 0.24, the zinc blende structure, where the coordination number is four, is favored. Table 5.8 lists the crystal lattices of some AB-type compounds and their radius ratios as derived from the ionic radii of Appendix 9. The data here clearly illustrate that the radius ratio rules provide only a rough guide to crystal structure.

An alternative method of rationalizing the structures formed by ionic compounds will be discussed in Chapter 8.

TABLE 5.8 Structure of Some Ionic Compounds

COMPOUND	RADIUS RATIO, r^+/r^-
CsCl Structure	
CsCl	0.94
CsBr	0.87
TlCl	0.83
TlI	0.68
NaCl Structure	
LiI	0.34
NaI	0.46
RbI	0.68
CsF	1.28
MgO	0.51
MgS	0.39
Zinc blende Structure	
AgI	0.52
BeS	0.16
ZnS	0.41

CHAPTER SUMMARY

Investigation of the properties of compounds indicates that, with some exceptions, compounds may be divided into two categories. A different model is required to describe each category. Compounds of the first type, called **ionic compounds**, consist of charged atoms or groups of atoms called **ions**. In compounds of the second type, called **covalent** or **molecular compounds**, electron-sharing atoms form aggregates that move and function as discrete units called **molecules**. The focus of this chapter was on ionic compounds; covalent compounds will be discussed in Chapter 6.

As the first step toward understanding how and why ionic compounds are formed, consider the electron configurations of the inert gases. These elements have the configuration s^2p^6 in their outermost energy level. The uncombined, neutral atoms of the inert gases are extremely stable; that is, they do not tend to combine readily with other atoms.

It seems, then, that the external electron structure s^2p^6 exhibits great stability. The atoms of other elements that do not have this structure can obtain the inert gas configuration (and, thus, greater stability) by losing or gaining a small number of electrons.

Using the inert-gas rule to predict the formation of ionic compounds is an oversimplification. Actually, the formation of any particular ionic compound is a function of many factors, including the ionization energy of the metallic atom, the electron affinity of the nonmetallic atom, and the lattice energy of the compound (the energy released when the ions unite to form the crystalline solid). Not all stable ions have an inert-gas electron configuration. For example, although iron cannot achieve an inert-gas configuration by losing or gaining a small number of electrons (the configuration of the iron atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$), it does form stable 2+ and 3+ ions.

The inert-gas rule can be used, however, to predict the ionic charges of **monatomic** (one-atom) ions of the **representative** elements. Group IA elements in the periodic table form ions with a 1+ charge; Group IIA elements form 2+ ions; Group VIA elements form 2− ions; and Group VIIA elements form 1− ions. (Ions with a charge greater than 2+ or 2− are much less common.) The formulas of ionic **binary** compounds (consisting of only two elements) of the representative elements can also be easily predicted. For example, if Na forms a 1+ ion and S forms a 2− ion, then the formula for the ionic binary compound of sodium and sulfur must be Na_2S.

Many of the **transition** elements form positively charged monatomic ions. However, their charges are not as predictable as those of the representative elements. In fact, a number of the transition metals form more than one stable ion. These ions cannot be deduced; they must be memorized (see Table 6.3).

Not all ions are simply charged atoms. Some ions are charged groups of atoms called **complex ions** (ClO_3^-, SO_4^{2-}, NO_3^-, and so on). Complex ions must also be memorized; since they may be considered to be derived from parent acids, you should memorize the names and the formulas of these acids as well.

The ions in an ionic compound are arranged in an orderly, three-dimensional pattern that is called the crystal **lattice**. Because ions are electrically charged, electrostatic attractions and repulsions exist within the lattice. The ions of a given compound adopt a particular arrangement largely to balance these attractive and repulsive forces and thus achieve a minimum potential energy. The Coulomb expression for the potential energy of two ions is fundamental to an understanding of ionic forces. A review of Chapter 3, where this expression was developed, will enable you to apply the Coulomb expression to the calculation of the potential energy of simple ionic configurations.

As a final step in your study of this chapter, you should learn what factors contribute to the stability of the ionic solid and know how to predict the type of lattice (sodium chloride, cesium chloride, or zinc blende) formed by simple ionic compounds of the AB type.

TERMS

Some important terms in this chapter include:

Binary compound A compound containing only two different elements.

Atomic unit of charge The charge on a single proton or a single electron. This charge is equal to 1.60×10^{-19} C.

Madelung constant An ion in an ionic lattice is attracted by all the ions of opposite charge and repelled by all the ions of like charge. The total potential energy of a given ion, then, is the sum of an infinite series of positive and negative terms of type A (kq_1q_2/r). The solution to this series for all the A terms is called the **Madelung constant** (**M**). For the alkali halides and the alkaline earth oxides and sulfides, the value of this constant is approximately 1.75.

Lattice energy The energy emitted when a solid ionic compound is formed from its constituent ions in the gaseous state. Lattice energy may also be thought of as the energy required to separate one mole of ions from their positions in the crystal to infinite distances from one another.

PROBLEMS

1. Consider a compound with empirical formula AB_2. What physical or chemical properties would help to classify this compound as ionic or covalent?

2. A compound contains only carbon and hydrogen. When it is burned in oxygen, all of the carbon is converted to CO_2 and all of the hydrogen is converted to water. Complete combustion of a 440-mg sample produced 0.0300 mol of CO_2 and 0.0400 mol of H_2O.
(a) Determine the number of moles of carbon and hydrogen in the sample.
(b) Determine the empirical formula of the compound.
(c) If the molecular formula is the same as the empirical formula, what is the molar mass of the compound?

3. What is the mass of aluminum in 1.0 kg of each of the following compounds?
(a) $AlCl_3$ (b) $KAl(SO_4)_2 \cdot 12H_2O$

4. How many grams of boron are contained in 6.00 g of borax, $Na_2B_4O_7 \cdot 10H_2O$?

5. Determine the percentage composition of the following compounds:
(a) LiBr (b) FeF_3 (c) K_2CO_3

6. Calculate the empirical formulas of compounds with the following percentage compositions:
(a) 46.68% N, 53.32% O
(b) 85.62% C, 14.38% H
(c) 75.92% C, 6.37% H, 17.70% N
(d) 58.53% C, 4.09% H, 11.38% N, 25.99% O

7. A certain compound has an empirical formula of CH_2O and a molecular weight of approximately 90. How many moles and how many molecules are there in 50.0 g of the compound? How many carbon atoms are there in 50.0 g of the compound?

8. Determine the molecular formula of the following compound: 40.00% C, 6.72% H, 53.29% O, molecular weight = 180

9. Elemental analysis of sulfathiazole, a sulfa drug, gave the following results: 42.35% carbon, 3.53% hydrogen, 16.48% nitrogen, 12.55% oxygen, and 25.18% sulfur. Calculate the empirical formula for sulfathiazole.

10. A sample of chloroform ($CHCl_3$) weighing 150 g contains
(a) how many moles of $CHCl_3$?
(b) how many chloroform molecules?
(c) what weight of carbon?
(d) how many chlorine atoms?
(e) how many moles of hydrogen?

11. How much do one million carbon monoxide (CO) molecules weigh?

12. Potassium chloride and titanium(IV) chloride were allowed to react in fused antimony trichloride. The analysis of the product was K, 23.1%; Ti, 14.2%; Cl, 62.7%. What is the empirical formula of the compound?

13. A compound containing iron, carbon, and oxygen has two moles of ions per mole of compound. The carbon and oxygen are present in a 1 : 3 ratio.
(a) Is it likely that this is an ionic compound?
(b) If the compound is ionic, which element is present as the cation?
(c) Can you guess at the formula of the anion?
(d) Predict the formula of the compound.
(e) Is the fact that the compound is water insoluble sufficient to eliminate the presence of ions?

14. The melting points (°C) of the fluorides of the second-period elements are

LiF	BeF_2	BF_3	CF_4	NF_3	OF_2	F_2
842	800	−127	−184	−207	−224	−220

What conclusions can you draw about the bonding and structure of these compounds?

15. Discuss the use of ionization energies in predicting the most common cation charge for an element.

16. Name the following compounds:
(a) $CaCO_3$ (b) Cu_2SO_4 (c) $FeCl_3$
(d) Li_3PO_4 (e) CoF_2 (f) $Cu(OH)_2$
(g) K_2SO_3 (h) $ZnBr_2$ (i) NH_4NO_3

17. Name the following compounds:
(a) NaH_2PO_4 (b) $FeCl_3 \cdot 6H_2O$
(c) Cs_2HPO_4 (d) NiO
(e) $NaHCO_3$ (f) $LiClO_2$
(g) $Ba(ClO_4)_2$ (h) $RbHSO_3$
(i) $Na_2CO_3 \cdot 7H_2O$ (j) Na_4C
(k) BPO_4 (l) $HgSO_4$

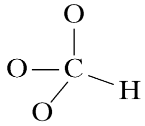
18. Name the following acids:
(a) H_2CO_3 (b) $HClO_2$ (c) H_3PO_4
(d) H_2SO_3 (e) $HClO_4$ (f) H_3PO_3
(g) HClO (h) HNO_2 (i) $HC_2H_3O_2$
(j) $H_2C_2O_4$ (k) HNO_3 (l) H_2SO_4

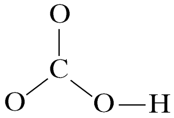
19. Write the formula for each of the following compounds:
(a) potassium carbonate (b) cesium chlorate
(c) hypochlorous acid (d) sodium bromide
(e) hydrosulfuric acid (f) strontium sulfite
(g) copper(II) phosphate (h) cuprous chloride
(i) nickel(II) permanganate (j) chromic sulfate
(k) mercuric nitrate (l) lithium bromate
(m) indium(III) oxide (n) aluminum hydroxide
(o) bismuth(III) chloride (p) ferric nitrite
(q) silver sulfide (r) gold(I) cyanide
(s) hydrofluoric acid (t) rubidium hydrogen sulfite
(u) barium dihydrogen phosphate

20. Use your knowledge of the periodic chart and nomenclature to give formulas for the following compounds:
(a) bromous acid (b) sodium bromite
(c) hypoiodous acid (d) barium periodate
(e) arsenous acid (f) selenic acid
(g) ferric arsenate (h) bromic acid

21. Write formulas for each of the following:
(a) ferrous hydroxide (b) zinc oxalate
(c) iodic acid (d) aluminum tellurate
(e) ammonium acetate

22. Which of the following is the correct structure for the hydrogen carbonate ion?

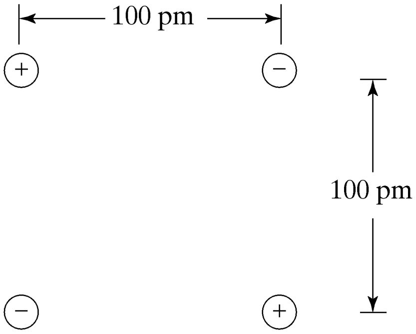
(a)


(b)


23. If CrO_4^{2-} is the chromate ion, what is:
(a) MoO_4^{2-} (b) WO_4^{2-}
(c) VO_4^{3-} (d) MnO_4^{2-}

24. Write electron configurations for the ions in each of the following compounds: cupric chloride, ferric oxide, and manganese(II) sulfide.

25. Calculate the total potential energy in joules of two protons and two electrons situated at the corners of a square as follows:



26. Account for the following trends in lattice energies:
(a) LiF > NaF > KF (b) NaF > NaCl > NaBr
(c) MgF_2 > NaF (d) MgO > MgF_2

27. Consider a compound in which the bonds are predominantly ionic-$CaCl_2$.

a. Predict the geometry of gaseous ionic $CaCl_2$.
b. Calculate the amount of energy necessary to separate the ions in the "molecule" to infinity. You will have to consider two Ca^{2+}—Cl^- attractions and one Cl^-—Cl^- repulsion. The Ca—Cl bond length in $CaCl_2$ is 2.5 Å.
c. The energy calculated in b) is not the CaCl bond dissociation energy, however, since this is defined as one-half the energy required for the process

$$CaCl_2(g) \longrightarrow Ca(g) + 2Cl(g)$$

Using the data from b) and the following information, calculate the average CaCl bond dissociation energy.

$$Ca(s) \longrightarrow Ca^{2+}(g) + 2e^- \qquad \Delta H = 414 \text{ kcal/mol}$$
$$Cl(g) + e^- \longrightarrow Cl^-(g) \qquad \Delta H = 283 \text{ kcal/mol}$$

d. The experimental CaCl bond energy is 113 kcal/mol. Compare your result with this value and rationalize the difference.
e. Sometimes the difference between calculated "completely ionic" and experimental dipole moments is taken as a measure of the ionic character of a bond. Why is this procedure impossible for $CaCl_2$?

28. Strontium oxide has the sodium chloride structure. Calculate its lattice energy in kilojoules per mole, using the sum of the ionic radii as the interionic distance.

29. Calculate the lattice energy in kJ/mol of silver iodide assuming that it has the sodium chloride structure and a distance between the centers of the ions of 3.35 Å.

30. Given the following reactions, find the lattice energy of KI:

$$K^+(g) + I^-(g) \longrightarrow KI(s) \qquad U \text{ (lattice energy)}$$
$$K(s) \longrightarrow K(g) \qquad \Delta H_a = 89.6 \text{ kJ/mol}$$
$$K(g) \longrightarrow K^+(g) + e\text{-} \qquad \Delta H_{IE} = 418.9 \text{ kJ/mol}$$
$$I_2(s) \longrightarrow 2\,I(g) \qquad \Delta H_a = 213.6 \text{ kJ/mol}$$
$$I(g) + e^- \longrightarrow I^-(g) \qquad \Delta H_{EA} = -295.2 \text{ kJ/mol}$$
$$K(s) + 0.5\,I_2(s) \longrightarrow KI(s) \qquad \Delta H_f = -328 \text{ kJ/mol}$$

31. Magnesium oxide crystallizes in the same lattice arrangement as sodium chloride. Predict whether the melting point and lattice energy of MgO are higher or lower than those of NaCl. Give reasons for your predictions.

32. The following equations show changes in energy that occur when one mole of the compound is converted completely to product:

$$CuCl(s) \longrightarrow Cu^+(g) + Cl^-(g) \qquad \Delta E = 979 \text{ kJ/mol}$$
$$Cu^+(g) \longrightarrow Cu^+(aq) \qquad \Delta E = -593 \text{ kJ/mol}$$
$$Cl^-(g) \longrightarrow Cl^-(aq) \qquad \Delta E = -378 \text{ kJ/mol}$$

The energy change for the dissolution of cuprous chloride in water

$$CuCl(s) \longrightarrow Cu^+(aq) + Cl^-(aq)$$

can be obtained by adding the energy changes for the three equations [notice that the equations add to give the equation above]. If the energy change is negative it means that energy (heat) is given off; if the energy change is positive it means that energy is absorbed from the environment.

(a) Calculate ΔE for the dissolution.
(b) Is heat given off or absorbed during the reaction?
(c) Which of the three steps above is the lattice energy?
(d) Now do the same analysis for AgCl, using the following equations:

$$AgCl(s) \longrightarrow Ag^+(g) + Cl^-(g) \qquad \Delta E = 916 \text{ kJ/mol}$$
$$Ag^+(g) \longrightarrow Ag^+(aq) \qquad \Delta E = -473 \text{ kJ/mol}$$
$$Cl^-(g) \longrightarrow Cl^-(aq) \qquad \Delta E = -378 \text{ kJ/mol}$$

(e) All other factors being equal, it is usually true that the more positive the energy change for the dissolution (that is, the more heat that must be absorbed by the reactants), the less favorable the dissolution process. If this assumption is correct, which compound—CuCl or AgCl—is less soluble?
(f) Rationalize the fact that the lattice energy for AgCl is lower than that for CuCl.

33. Essentially all salts of the alkali metals are soluble in water. Many of the salts of other metals, particularly carbonates, sulfides, sulfites, and phosphates, are insoluble. Explain the difference.

34. A Group II carbonate has a greater hardness than $BaCO_3$. What can you conclude?

35. Use the radius ratio rules to predict the lattice structure of each of the following ionic compounds:
(a) KBr (b) NaI (c) BeSe (d) MgO

36. How much energy is required to move two protons that are initially 1.0 cm apart to a distance 1.0 mm apart?

6

Covalent Compounds

The electrostatic forces that stabilize ionic compounds were discussed in Chapter 5. In this chapter, we will find that the same forces are responsible for the stability of covalent compounds, but in a more complex manner. The covalent bond is a result of shared electron density. We will first discuss the role of this shared electron density in stabilizing the covalent bond and then elaborate upon three models that are used to explain how electron density is distributed in molecules.

6.1 THE STABILITY OF COVALENT COMPOUNDS

If we consider the very simple molecule, H_2, for example, we find that its energy is 431 kJ/mol lower than the energy of its constituent hydrogen atoms. The greater stability of the molecule may seem surprising, since the distance between the nuclei in the molecule is much smaller, resulting in greater electrostatic repulsions.

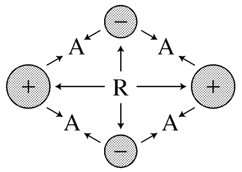


Figure 6.1 A representation of the attractions and repulsions in the H_2 molecule.

There is clearly an additional factor that determines the difference between the potential energies of the molecule and of the separated atoms. This factor is a result of the considerable amount of shared electron density in the molecule. Because nearly two electrons are attracted to each hydrogen nucleus in H_2, the electrostatic attractions are greater than in the separated hydrogen atoms. Furthermore, the magnitude of these attractions is greater than the magnitude of the counteracting repulsions. The total attractions (A) and repulsions (R) in the H_2 molecule are represented schematically in Figure 6.1. (The electrons are not, of course, stationary; nor are there exactly two electrons located in exactly this way between the nuclei.)

As we have seen in Chapter 3, these electrostatic interactions lower the potential energy of the molecule. Of course, the total energy of any system is the sum of the potential and kinetic energies. But according to the laws of wave mechanics, the increase in kinetic energy of the electrons of the H_2 molecule relative to the hydrogen atoms is only half of the corresponding decrease in potential energy. Consequently, it is the lower potential energy of the H_2 molecule that is responsible for its greater stability.

While we have now succeeded in rationalizing the stability of H_2 and covalent molecules in general, we are far from developing models of the covalent bond that will enable us to understand and predict the properties of these substances. Before turning our attention to several of these models, let us discuss some of the properties of covalent compounds.

6.2 MOLECULAR PARAMETERS

Because most covalent compounds consist of molecules—aggregates of atoms, intimately and (usually) strongly bound, that function as units in the solid, liquid, and gaseous states—it will be useful at this point to examine some properties that can be used to characterize and identify molecules.

Bond Length

For our present purposes, we will assume that the atoms constituting a molecule remain in fixed positions relative to one another. The distance between the centers of two adjacent atoms is called the **bond length**. For example, in CH_4, in which four hydrogen atoms are attached to a central carbon atom, the distance between any hydrogen nucleus and the carbon nucleus has been found to be 194 pm. If the molecule contains more than two elements, as in formaldehyde (H_2CO), then more than one bond length will be present in the molecule.

Bond angle can be defined as the angle between any two adjacent internuclear lines. In CH_4, the angle between any two adjacent C—H bonds (strictly speaking, the hypothetical lines connecting the carbon and hydrogen nuclei) has been determined to be 109.5°. In carbon dioxide, O···C···O, the bond angle is 180°; in other words, the atoms lie on a single line and the molecule is said to be linear. In formaldehyde there are two different bond angles: The H···C···O angle is 121°, and the H···C···H angle is 118° (see Figure 6.2, where dotted lines are used to portray internuclear lines).

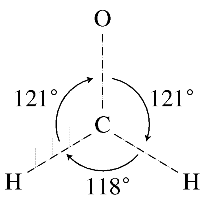


Figure 6.2 The bond angles in formaldehyde.

Bond Energy

For a diatomic molecule, the **bond energy** is the amount of energy necessary to dissociate one mole of the gaseous compound into its gaseous atoms. Thus, the dissociation of one mole of H_2 into hydrogen atoms requires 431 kJ/mol.

$$H_2 \longrightarrow 2\,H \qquad \text{bond energy} = 431\ \text{kJ/mol}$$

The energy required to dissociate H_2O into its neutral constituent atoms is 925 kJ/mol.

$$H_2O \longrightarrow 2\,H + O \qquad \text{energy change} = 925\ \text{kJ/mol}$$

Since there are two O—H bonds, the *average* O—H bond energy in water is 925/2 = 462.5 kJ/mol. The bond energy for any given set of atoms, say OH, depends on the nature of the remainder of the molecule, but generally, the variation from one molecule to another is small enough that a set of empirical average bond energies can be tabulated (see Appendix 2).

Bond Polarity

The electron density between the atoms of most covalent compounds is not shared equally by the atoms. In a bond between atoms A and B, the electron density is shared equally only if A and B are the same element or have the same electronegativities. Since electronegativity, as Linus Pauling originally defined it, is "the power of an atom within a molecule to attract electrons to itself," it seems reasonable to assume that the greater the difference in electronegativity between A and B, the more unequal the sharing of electrons will be. (See Chapter 4 for the Pauling electronegativity scale.) This is illustrated in Figure 6.3, where the transition from diatomic chlorine (Cl_2) to NaCl is demonstrated.

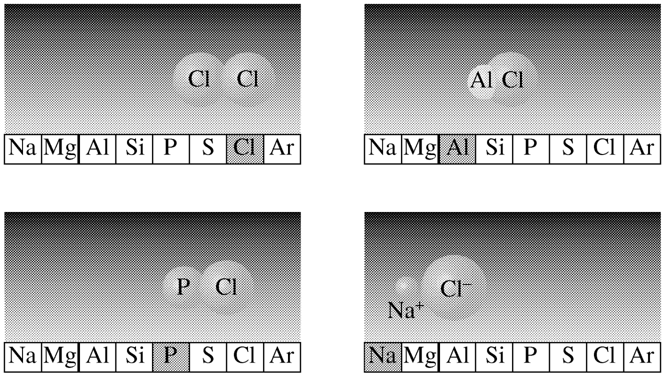


Figure 6.3 The change in electron density and bond polarity from Cl_2 to NaCl.

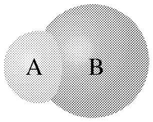


Figure 6.4 A Polar Bond

It is sometimes convenient to think of a polar bond as a mixture, or **hybrid**, of the equal-sharing case (such as Cl_2) and the ionic case (such as NaCl). Thus, a 60–40 hybrid (as portrayed in Figure 6.4) of the equal-sharing case with the ionic case would be said to have 40% ionic character.

The inequality of the electron distribution, or **polarity**, of a diatomic molecule is often measured by its **dipole moment**. Mathematically, the dipole moment (μ) of a neutral molecule is given by the product of the amount of charge (q) that has been unequally distributed in the molecule, and the distance (d) between the unequal charges:

$$\mu = qd$$

The dipole moment of our hybrid above can be calculated as follows: An ionic character of 40% means that 0.4 electron charge has been transferred from A to B and q is therefore $0.4 \times (1.6 \times 10^{-19}\text{ C})$ or 0.64×10^{-19} C. If we assume, for computational simplicity, that the AB internuclear distance is 100 pm, or $d = 1.0 \times 10^{-10}$ m, the dipole moment is

$$\mu = (0.64 \times 10^{-19}\text{ C}) \times (1.0 \times 10^{-10}\text{ m}) = 0.64 \times 10^{-29}\text{ C-m}$$

The quantity 0.334×10^{-29} C-m is called a **Debye** (1.0 D), in honor of Peter Debye, who did much of the early work on dipole moments. Thus, the dipole moment of 0.64×10^{-29} C-m is

$$\frac{0.64 \times 10^{-29}\text{ C-m}}{0.334 \times 10^{-29}\text{ C-m}} = 1.9\text{ D}$$

It is important to realize that if one electron had been completely transferred from A to B (as we imagine for NaCl), the dipole moment would be $(1.60 \times 10^{-19}\text{ C}) \times (1.0 \times 10^{-10}\text{ m}) = 1.6 \times 10^{-29}$ C-m or 4.8 D. From this value, the percentage of ionic character of our hybrid can be calculated from the dipole moment as

$$\frac{1.9\text{ D}}{4.8\text{ D}} \times 100 = 40\%$$

Problem 6.1

Suppose that a diatomic molecule with a bond length of 200 pm has a dipole moment of 2.0 D. Calculate the percent ionic character in the bond.

Solution:

A dipole moment of 2.0 D is $2.0 \times (0.334 \times 10^{-29}\text{ C-m}) = 0.668 \times 10^{-29}$ C-m. In order to calculate the amount of charge unequally distributed, we divide this number by the bond length:

$$\mu = qd \quad q = \frac{\mu}{d} = \frac{0.668 \times 10^{-29}\text{ C-m}}{2.00 \times 10^{-10}\text{ m}} = 0.334 \times 10^{-19}\text{ C}$$

If the bond were ionic, one whole electron (or two or three) would have been transferred. Because the charge on one electron is 1.6×10^{-19} C, the percent ionic character is

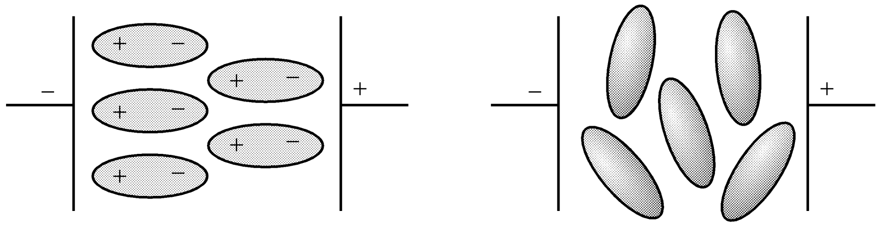
$$\frac{0.334 \times 10^{-19}\text{ C}}{1.6 \times 10^{-19}\text{ C}} \times 100 = 21\%$$

We could have also solved the problem by first determining the dipole moment of a molecule with 100% ionic character:

$$\mu = qd = (1.6 \times 10^{-19}\text{ C})(2.0 \times 10^{-10}\text{ m}) = 3.2 \times 10^{-29}\text{ C-m} = 9.6\text{ D}$$

Then, as above,

$$\frac{2.0\text{ D}}{9.6\text{ D}} \times 100 = 21\%$$



Alignment of polar molecules

Random distribution of molecules with no dipole moment

Figure 6.5 Experimental measurement of dipole moment.

Experimentally, dipole moments are determined by observing the effect of the compound on the capacitance (the ability to store charge) of a capacitor containing the compound in solution. The plates of the capacitor are oppositely charged, as shown in Figure 6.5. Molecules with equal electron distribution, that is, with no dipole moments, will orient themselves randomly in the electric field of the capacitor. On the other hand, molecules with uneven electron distributions have positive and negative ends (they do not, however, contain ions) and therefore align themselves with the electric field of the capacitor. The greater the separation of charge in the molecule, the greater the alignment in the capacitor and the greater the effect on the capacitance of the capacitor. (The attraction of water, a polar molecule, to a charged rubber rod is shown in Figure 6.6.) The measured capacitance of the solution can be converted *via* a series of mathematical relationships to dipole moment.

Table 6.1 presents dipole moments of some molecules. In the hydrogen halide series, the decrease in ionic character (and thus the decrease in q) from HF to HI greatly outweighs the increase in internuclear distance d attributable to the increase in size of the halogen. In the polyatomic molecule CO_2, however, the dipole moment is zero, even though the difference in electronegativity between carbon and oxygen is large and the carbon-oxygen bonds are therefore polar. Clearly bond polarity is not the only factor determining the dipole moment of a polyatomic molecule; the spatial disposition of the bonds may also be critical. The charge distribution of the linear CO_2 molecule is shown in Figure 6.7, where the negative ends of the C—O bonds are indicated by the heads of arrows and the positive ends are located at the carbon. Thus, while each C—O bond is polar and has a **bond dipole**, these two dipoles cancel, and the molecule has no net dipole moment. The same type of reasoning can be used to explain the zero dipole moments of BF_3 and CF_4 (we will return to this in Chapter 7).

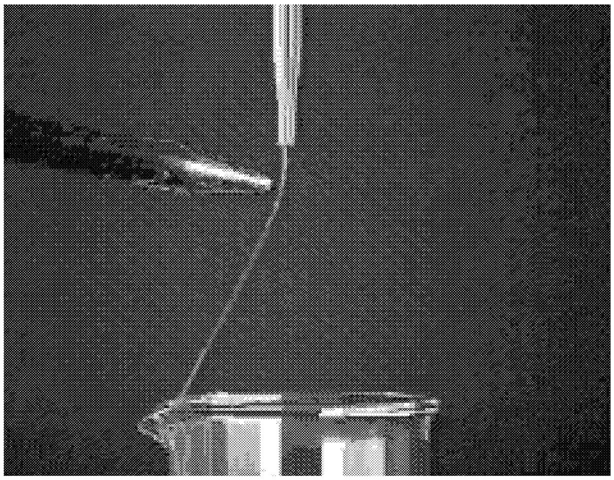


Figure 6.6 The attraction of a stream of water to a charged rubber rod.

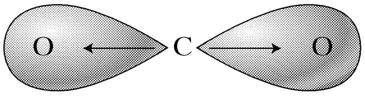


Figure 6.7 The charge distribution in the CO_2 molecule.

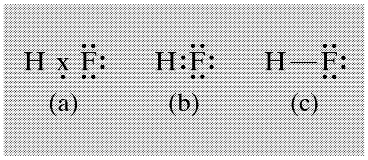
TABLE 6.1 Some Dipole Moments

COMPOUND	DIPOLE MOMENT(D)
H_2	0
HI	0.38
HBr	0.79
HCl	1.03
HF	1.98
N_2	0
NO	0.16
CO_2	0
H_2O	1.87
BF_3	0
CF_4	0

6.3 THE LEWIS MODEL

One of the earliest theories of covalent bonding was developed by the American chemist Gilbert N. Lewis, just before the advent of wave mechanics. It remains one of the simplest and most useful models of the electronic structure of covalent materials. Lewis believed that the inert-gas rule, which was of such importance in the ionic model, could also be applied to covalent situations. Since the valence shell of an element is the outermost quantum level that is populated by electrons, most atoms achieve an inert-gas configuration when eight electrons are present in their valence shell (the **octet rule**). This octet of electrons, according to Lewis, can be attained by the **sharing** of electrons. Since the valence shell of hydrogen is the first quantum shell, it cannot achieve an octet, but can attain the inert-gas configuration of helium with two electrons.

The Lewis theory can be illustrated with the hydrogen fluoride molecule. Fluorine, with an electron configuration of $1s^2 2s^2 2p^5$, has seven electrons in its valence shell (the $n = 2$ quantum level). Thus, it needs only one more electron to fill its octet. Hydrogen, which has one electron in its valence shell, also requires only one to fill its shell. Thus, if each atom shares one electron with the other, both will be satisfied. This approach is generally represented by an electron dot formula, which shows the disposition of electrons about each atom. Several ways of writing the **electron dot formula** for HF are shown below. In part (a) the hydrogen electron is designated by an x and the fluorine electrons by dots. But, of course, electrons are indistinguishable, and in part (b) all are designated by dots. In part (c) the shared pair of electrons is represented by a dash; this is the convention we will use in most cases.



(a) (b) (c)

Let us examine the electron dot formula for HF more closely. First, note that the two shared electrons count as electrons of the valence shells of both atoms. That is, the shared pair is part of the hydrogen valence shell and also part of the fluorine valence shell. This shared **pair** of electrons is called a **bond** and provides the electron density responsible for the decrease in potential energy of the molecule relative to the individual constituent atoms.

Second, observe that the six unshared electrons around the fluorine are arranged in groups of two, indicating that the spins of these electrons are paired. The wave model predicts that paired electrons can approach each other more closely than unpaired electrons and it is reasonable to suggest spatial proximity by these groupings. Consequently, the

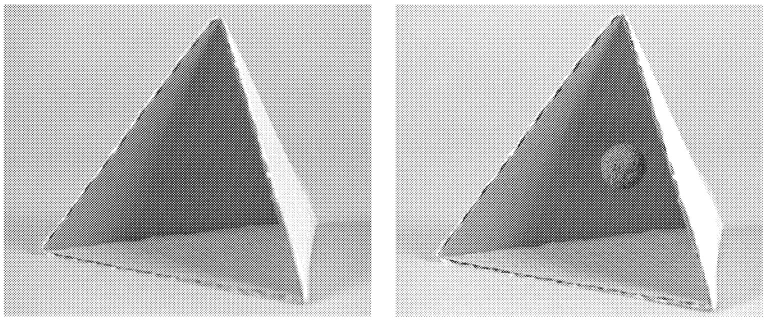


Figure 6.8 The tetrahedron, shown with a central nucleus on the right.

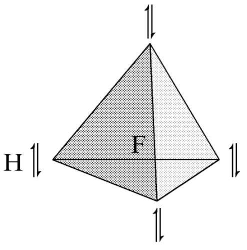


Figure 6.9 The tetrahedral distribution of electron pairs around the fluorine in HF.

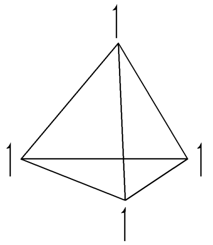
octet of electrons can be thought of as four pairs of electrons. The three pairs of electrons around the fluorine are referred to as **nonbonded electrons**, **lone pairs**, or **unshared pairs**.

Third, the four pairs of electrons constituting any octet can be visualized as being positioned at the apexes of a tetrahedron, because this arrangement of electrons minimizes the repulsions between them. This blatantly artificial particle conception allows some interesting predictions. The solid geometric figure of the tetrahedron is shown in Figure 6.8 both with and without a nucleus in the center.

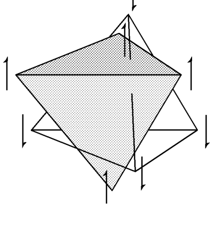
The tetrahedron of electrons about the fluorine nucleus (the symbol F here denotes the fluorine nucleus and its 1*s* electrons) is shown in Figure 6.9 with the hydrogen nucleus sharing a pair of electrons.

Visualization 6.1

An interesting way to visualize the eight electrons around a nucleus is as two sets of four electrons. Each set has the same spin (for example, all up) with each electron at the corner of a tetrahedron.



When the octet is achieved, two tetrahedra must be superimposed. The tetrahedra should be staggered, however, to minimize the repulsions between the electrons.

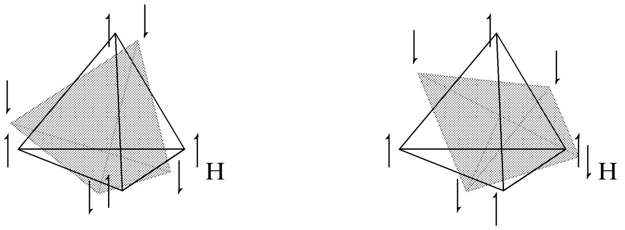


This model was proposed by J. W. Linnett and is known as the double quartet theory. It has several advantages over the simpler Lewis model: it minimizes repulsions between electrons and it is able to provide explanations for bonds that are difficult to explain with the Lewis model.

Continued on next page

Visualization 6.1 *Continued*

When another nucleus is brought up to the double quartet, what do you imagine happens to them? For example, suppose an H^+ approaches the figure above. Which of the following figures best represents how the double quartet would react to the perturbation caused by the H^+?



Solution:

The approaching nucleus draws the double quartet together at one corner because of the attraction of the electrons to the nucleus, but the other electrons (on the face opposite the H) are staggered to minimize their repulsions. Thus, the diagram on the right is favored by the double quartet model.

In order to write the electron dot formula for any molecule, it is necessary to know its structural formula. One rule for establishing the structural formula can be illustrated with the water molecule. For H_2O, there are two conceivable arrangements of the atoms:

H···H···O and H···O···H

According to the Lewis theory, each bond between atoms in a covalent molecule is formed by a pair of shared electrons. Since the valence shell of hydrogen can accommodate only two electrons, the first structural arrangement, in which hydrogen is attached to *two* atoms, is quite unlikely.* In general, the structural formula for the compound must be known, or must be established by rules similar to the one just stated, before an appropriate electron dot formula can be written.

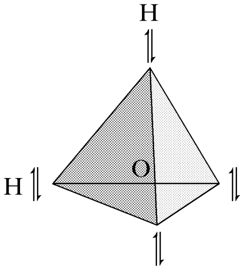


Figure 6.10 The tetrahedral distribution of electron pairs about the oxygen in H_2O.

Thus, the structural formula for water is H···O···H and we can proceed to write the electron dot formula. Oxygen has six valence electrons and each hydrogen has one. There are therefore eight electrons to distribute in such a way as to place an octet of electrons about oxygen and two about each hydrogen. Since each H—O bond must contain two electrons, the proper formula can only be

$$\mathrm{H{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{-}H}$$

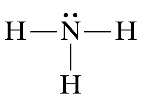
The most favorable distribution of the electrons about the oxygen is again at the apexes of a tetrahedron, as shown in Figure 6.10.

The principal value of any model of bonding is its usefulness in explaining and predicting various properties of matter. It should be clear that the Lewis theory predicts a certain bond angle for H_2O. Since the angle between lines drawn from the center of a tetrahedron to the apexes is 109.5°, this would be the predicted angle. The experimental value found for the bond angle in H_2O is 104.5°, which is in fair agreement with the predicted value.

---

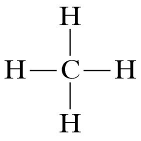
* Although we will almost always assume that hydrogen can be bonded to only one atom, this is not always the case. In some compounds hydrogen is bonded to two atoms, but these bonds have unusual properties. In other cases, hydrogen is covalently bonded to one atom and interacts weakly with another. This occurs frequently and is called hydrogen bonding.

By a process similar to that for H_2O, the electron dot formulas for ammonia (NH_3) and methane (CH_4) can easily be written as



$$\begin{array}{ccccc} H & - & \ddot{N} & - & H \\ & & | & & \\ & & H & & \end{array}$$

and

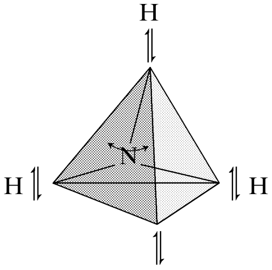


$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

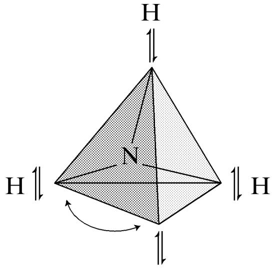
Their predicted three-dimensional structures are presented in Figure 6.11. Note that the predicted bond angles for these **isoelectronic** molecules (molecules with the same number of electrons) are all the same—109.5°.

Visualization 6.2

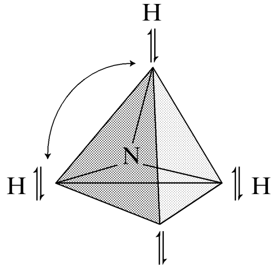
Which diagram portrays the bond angle of 107° in ammonia?



(a)



(b)



(c)

Solution:

Part (a) shows the angle on a face of the tetrahedron (60°); part (b) shows the angle between an N—H bond and the lone pair of electrons; part (c), the correct answer, shows the angle between two N—H bonds.

The diatomic molecules F_2, O_2, and N_2 present a somewhat different case. The electron dot formulas for F_2 and O_2 are easily seen to be

$$:\underset{\cdot\cdot}{\ddot{F}}-\underset{\cdot\cdot}{\ddot{F}}:$$

$$:\!\underset{\cdot}{\dot{O}}::\underset{\cdot}{\dot{O}}\!: \quad \text{or} \quad :\!\underset{\cdot}{\dot{O}}-\underset{\cdot}{\dot{O}}\!:$$

In N_2, since nitrogen has only five valence electrons, each atom must share three electrons with its partner, producing the formula

$$:N\vdots\vdots N: \quad \text{or} \quad :N\equiv N:$$

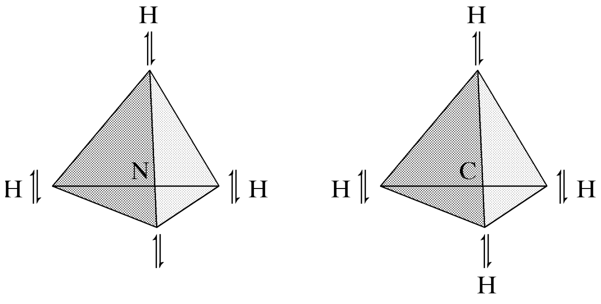


Figure 6.11 The tetrahedral distribution of electron pairs in NH_3 and CH_4.

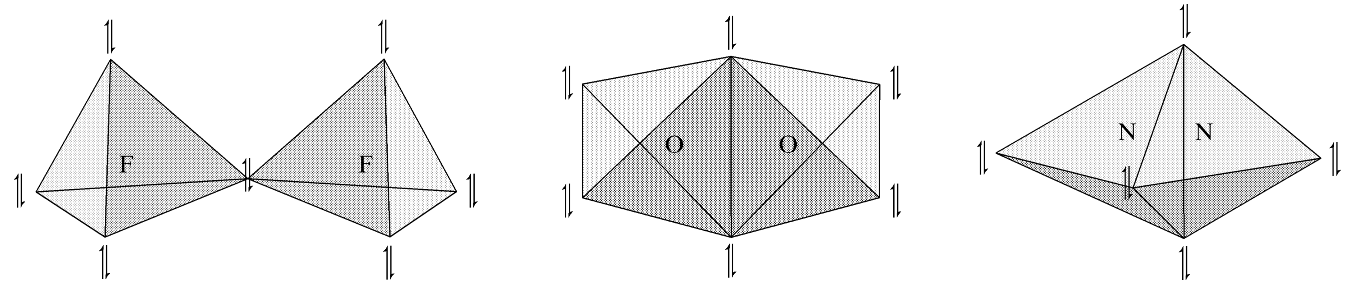


Figure 6.12 The disposition of electrons according to the Lewis Model in F_2, O_2, and N_2.

Thus, the oxygen molecule is held together by two bonds, referred to as a **double bond**. Since this means a greater amount of electron density between the nuclei and consequently a lower potential energy, the molecule should be more stable than a similar molecule held together by only a single bond, such as F_2. The N_2 molecule, which contains a **triple bond**, should be even more stable than O_2.

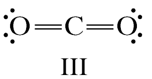
Here again is a test of the Lewis theory. The theory predicts that the order of stability of the three molecules should be $N_2 > O_2 > F_2$. The experimental measure of a molecule's stability with regard to dissociation is bond energy, and the bond energies of these molecules are: N_2, 941 kJ/mol; O_2, 494 kJ/mol; F_2, 155 kJ/mol. Thus, the theory's predictions have been borne out by experimental data.

The electron positions for F_2, O_2, and N_2 according to the Lewis model can again be visualized with sets of tetrahedra. The configurations shown in Figure 6.12 were constructed by surrounding each atom with a tetrahedron of electrons in such a way that the shared electrons become part of both tetrahedra. In F_2, the tetrahedra are joined at the apexes; in O_2, on an edge; and in N_2, on a face.

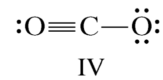
Let us now examine some polyatomic molecules. Two structural formulas for carbon dioxide are possible:

$$\underset{\text{I}}{\mathrm{O\cdots C\cdots O}} \qquad \text{and} \qquad \underset{\text{II}}{\mathrm{C\cdots O\cdots O}}$$

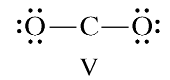
Reasonable electron dot formulas can be written for both structures, and so as far as our present discussion extends, there is no way of deciding between them. It is usually true, however, that *for compounds of general molecular formula* AB_n—CO_2, SO_3, CCl_4, NH_3, and so on—*the A atom is the central atom and the B atoms are attached only to it, not to each other*. Thus, I represents the structure of CO_2. There are two good electron dot formulas for this structure, shown here as III and IV. Formula V is not a good electron dot formula because the valence shell of carbon does not contain eight electrons.


$$\mathrm{\underset{\cdot\cdot}{\ddot{O}}=C=\underset{\cdot\cdot}{\ddot{O}}}$$

III


$$\mathrm{:O\equiv C-\underset{\cdot\cdot}{\ddot{O}}:}$$

IV


$$\mathrm{:\underset{\cdot\cdot}{\ddot{O}}-C-\underset{\cdot\cdot}{\ddot{O}}:}$$

V

An intriguing question at this point is: Which electron dot formula, III or IV, best describes the *true* electronic structure of CO_2? Formula III predicts two equivalent C—O bonds, which are the same in every regard—length, strength, and so on. Formula IV predicts two unequal linkages; the C—O linkage with the triple bond would be stronger (and shorter) than the C—O linkage with the single bond. In fact, the experimentally determined structure for CO_2 has two exactly equivalent linkages, and therefore electron dot formula III provides the best Lewis description of CO_2.

As another application of the rule for compounds or ions of type AB_n, consider the structural formula of the nitrite ion, $[\mathrm{O\cdots N\cdots O}]^-$. This species has a 1− charge,* and therefore a total of $6 + 5 + 6 + 1 = 18$ electrons must be distributed about the three nuclei in such a way as to give each atom an octet of valence electrons. A suitable electronic structure is

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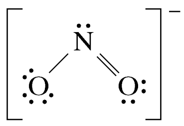
* A charge of 1− means that the ion has one more electron than it would if it were the neutral molecule NO_2; it does not mean that one electron has been subtracted.

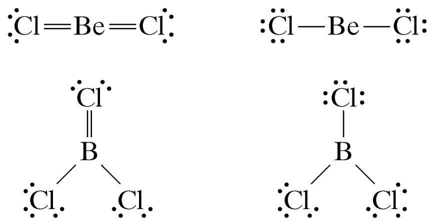


The minus sign is placed outside the brackets to indicate that the negative charge is associated with the entire grouping, not necessarily with any one atom. The electron dot formula predicts unequal N—O linkages, whereas in fact the linkages in NO_2^- are equivalent in every way. A means of modifying the theory to account for this experimental fact will be discussed later in this chapter.

Exceptions to the Octet Rule

The majority of compounds obey, or appear to obey, the octet rule. Compounds that do not obey this rule fall into one of two categories: those with atoms whose valence shells contain fewer than eight electrons, and those with atoms whose valence shells contain more than eight electrons.

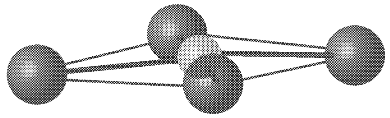
Several compounds of the elements of Group IIA and Group IIIA can be placed in the first category. Consider, for example, the species $BeCl_2$ and BCl_3. For both compounds, at least two electron dot formulas are possible.



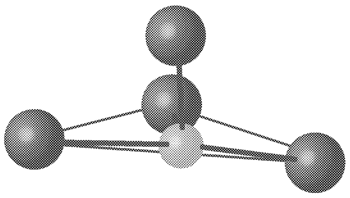
The left-hand representations satisfy the octet rule for each atom, while those on the right portray electron-deficient central atoms. For BCl_3, the experimentally determined bond lengths and energies indicate that the first formula is probably the better description. For $BeCl_2$, on the other hand, the evidence suggests that the electron-deficient representation is the better one.

Visualization 6.3

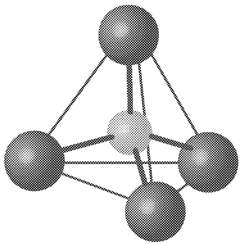
Although structural evidence favors the structure that obeys the octet rule for BCl_3, the formula with an electron-deficient atom is useful for explaining some of the reactions that BCl_3 undergoes. For example, BCl_3 reacts with chloride ion to form the species BCl_4^-. Which diagram below best represents the structure of this ion?



(a)



(b)



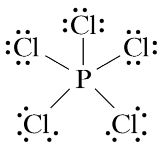
(c)

Solution:

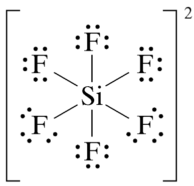
Structure (c) best represents the geometry of the BCl_4^- ion. The tetrahedron provides more space about the boron than any of the other geometries.

The valence shells of the atoms of the second period are restricted to a maximum of eight electrons. Elements of periods 3 through 6, however, have valence quantum levels that can hold more than eight electrons. For instance, phosphorus has its valence electrons in the third major quantum level, where the *s*, *p*, and *d* orbitals are available for bonding; therefore, phosphorus can accept more than eight electrons in its valence shell.

As an example, consider the following electron dot formula for PCl_5, in which phosphorus has 10 electrons in its valence shell:



Similarly, the species SiF_6^{2-} has 12 electrons about its central atom:



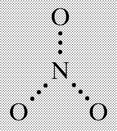
The spatial disposition of the electrons in molecules that do not obey the octet rule is governed by the same factor that determines the tetrahedral arrangement in the octet structures: minimization of the repulsions between electron pairs. The geometry of molecules will be treated in more detail in Chapter 7.

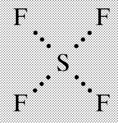
Methodology 6.1

Write electron dot formulas for NO_3^- and SF_4.

The first step is to determine the structural formula for each species; that is, which atoms are attached to which other atoms. Write a structural formula for both species.

Both NO_3^- and SF_4 are examples of the AB_n type of ion or molecule, with the B atoms attached only to the central atom A.

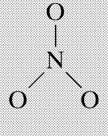


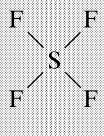


The second step is to count up the total number of valence electrons that must be distributed around the atoms in each molecule.

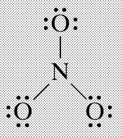
For NO_3^- this number is 24 (five for nitrogen, plus six for each of the three oxygens, plus one extra electron). For SF_4 the number is 34 (six for sulfur and seven for each fluorine).

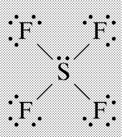
The third step is to connect each pair of attached atoms with a single bond.





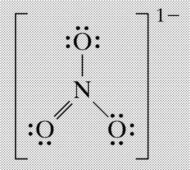
The remainder of the electrons (remember that each bond is two electrons) are positioned about the terminal atoms so that each terminal atom has an octet of electrons. If there are any electrons left over, they are placed on the central atom.





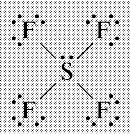
Finally, in order to obtain an octet around each atom (when possible), use a pair (or two pairs) of electrons on a terminal atom to form a double (or triple) bond to the central atom.

For NO_3^- this can be accomplished only with the following electron dot formula (note the use of brackets and placement of the minus sign to indicate a net negative charge of 1 on the ion):



After the formula is complete, it should be checked by counting the total number of electrons and the number around each atom.

For SF_4 it is not possible to place only eight electrons around each atom. Since four pairs must be used for the S—F bonds, 34 − 8 = 26 are left to distribute about five atoms. The four electron pairs around the sulfur give it an octet and also contribute two to each fluorine. Thus only 4 × 6 = 24 electrons are needed to fill the octet around the fluorines. There are therefore two electrons more than would be required for octets around each atom. These two electrons must be placed on the sulfur, because fluorine is a second-period element and cannot hold more than eight electrons in its valence shell. Thus the electron dot structure for SF_4 is

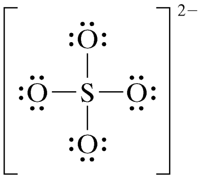


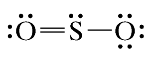
Problem 6.2

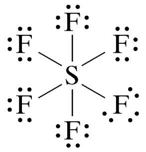
Write electron dot formulas for each of the following species:

(a) SO_4^{2-} (b) SO_2 (c) SF_6

Solution:







Check Point 6.1

How many lone pairs are there on the central atom of O_3 and BrF_3?

Solution:

1 for O_3 and 2 for BrF_3

◇ ◇ ◇ ◇ ◇

6.4 THE NOMENCLATURE OF COVALENT COMPOUNDS

Our knowledge of the Lewis model now enables us to write structural formulas for covalent compounds. Before continuing with an analysis of the other models for these compounds, let us examine some of the rules used for naming simple binary compounds.

Simple covalent compounds containing two elements are named by giving first the name of the more electropositive element. This is followed by the *-ide* form of the other element (root + *-ide*), with a prefix to indicate the number of atoms of this element in the molecular formula. The following names serve as an illustration:

CO	carbon monoxide
CS_2	carbon disulfide
BF_3	boron trifluoride
$SiBr_4$	silicon tetrabromide
PCl_5	phosphorus pentachloride
SF_6	sulfur hexafluoride
B_2Cl_4	diboron tetrachloride

In the last example a prefix is also used to indicate the number of atoms of the more electropositive element.

Some very common compounds are known exclusively by their common or trivial names; examples include H_2O, water, and NH_3, ammonia.

The nomenclature of the many compounds formed by carbon is discussed in the Descriptive Chemistry booklet, The Nomenclature of Organic Compounds found in the electronic version of this text.

Problem 6.3

Give formulas for each of the following:

(a) carbon dioxide

(b) phosphorus triiodide

(c) disulfur dichloride

Solution:

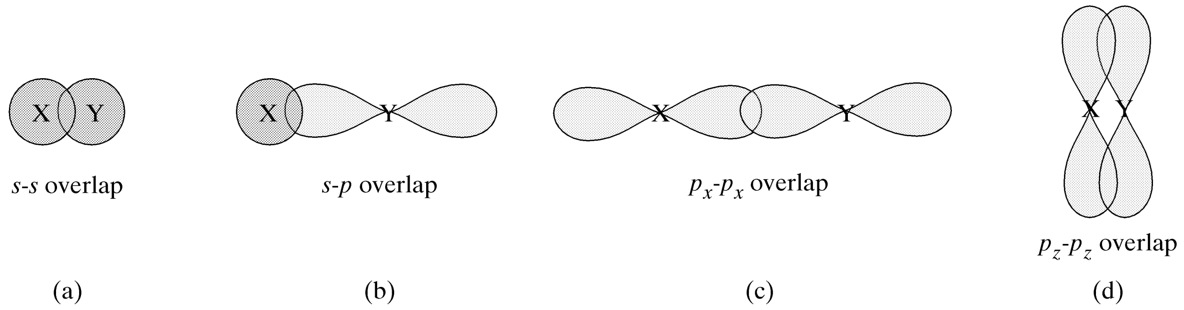
(a) CO_2 (b) PI_3 (c) S_2Cl_2

6.5 THE VALENCE BOND MODEL

The creation of wave mechanics in the 1920s led to the development of two models of bonding in covalent compounds—the valence bond model and the molecular orbital model. The valence bond theory was formulated primarily by W. Heitler and F. London in the early 1930s and was later extended and popularized by Linus Pauling, who wrote the classic treatise *The Nature of the Chemical Bond*.

The **valence bond theory** retained the idea of the electron-pair bond from the Lewis model, but its origin is described in terms of atomic orbitals—a wave concept. As its basic assumption, the theory uses the idea that a bonding orbital (a bond) between two atoms is formed when an atomic orbital on one atom physically overlaps an atomic orbital on the other atom. The two electrons populating this bonding orbital must have their spins paired (the Pauli principle).

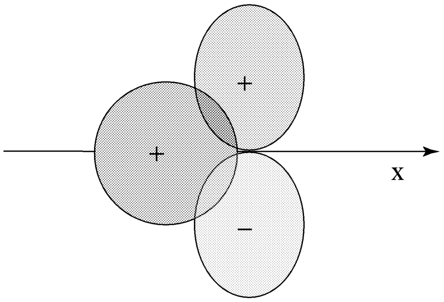
There are many different types of atomic orbitals, and their overlap in various combinations leads to several types of bonding orbitals. Some of the possible combinations of two orbitals are pictured in Figure 6.13, where the nuclei of the two atoms involved are labeled X and Y. The overlap of two s orbitals, an s orbital and a p_x orbital, and two p_x orbitals are shown in parts a, b, and c, respectively. (We have arbitrarily defined the x axis as the internuclear axis; this convention will be followed throughout.) Each of these orbital overlaps produces a buildup of electron density along the internuclear axis, and the resulting bond is called a sigma (σ) bond. The overlap between two p_z orbitals results in concentrations of electron density above and below the internuclear axis. This type of bond is termed a pi (π) bond. The overlap of two p_y orbitals, where the electron density is concentrated above and below the plane of the paper, also produces a π bond.



s-*s* overlap (a)
s-*p* overlap (b)
p_x-p_x overlap (c)
p_z-p_z overlap (d)

Figure 6.13 Some orbital overlap schemes.

In Chapter 3, we have shown that an orbital is a wave mechanical description of the energy and location probability of an electron. Because they are wave mechanical descriptions, orbitals are mathematical equations similar to those that can be used to describe an electron confined to a line. Consequently, in some regions of space, these orbitals have positive signs, and in others negative signs. *S*-orbitals have positive signs everywhere, whereas *p*-orbitals have one lobe with a positive sign and the other with a negative sign. In order to create a bonding orbital, the parts of the orbitals that overlap must have the same sign (analogous to constructive interference of waves). For example, let us ask whether overlap of an *s* orbital with a p_z orbital results in a bond (the *x* axis is the internuclear line)? The diagram below shows that the interaction of the *s* orbital (which has a positive sign everywhere) with the positive lobe of the p_z orbital is exactly canceled by the interaction with the negative lobe. Thus, there is no build-up of electron density, and no bond can be formed from this combination of orbitals.



A bonding orbital has no physical meaning unless it is populated by two electrons. In terms of electron population, orbitals can overlap to form bonds under the following circumstances: (a) when an orbital containing *one* electron on atom X can overlap with an orbital containing *one* electron on atom Y, or (b) when an orbital containing *two* electrons on atom X can overlap with an *empty* orbital on atom Y. These two situations are shown in Figure 6.14, using the convention of Chapter 3 to denote orbitals. Note that the electrons in both cases have their spins in opposite directions.

Therefore, to describe the bonding of any species in terms of valence bond theory, we begin with the valence electron configuration of each atom in the molecule and then decide which orbitals can overlap. The molecules F_2, O_2, and N_2 provide a convenient starting point for our discussion.

Each of the fluorine atoms in F_2 has one half-filled *p* orbital that can be used to form a single bond (Figure 6.15). Because the p_x orbitals extend toward each other and can therefore overlap to a greater extent (forming a stronger bond), these orbitals rather than

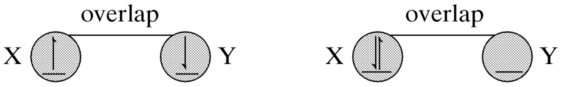


Figure 6.14 Population of overlapping orbitals.

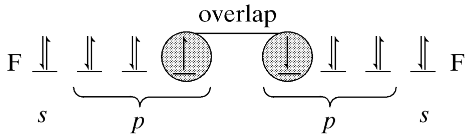


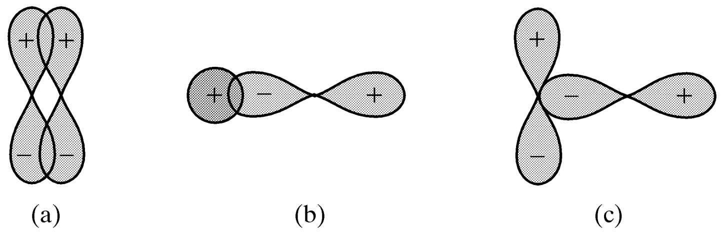
Figure 6.15 Overlap diagram for F_2.

the p_y or p_z orbitals will form the bond in F_2. (In fact, it has been shown experimentally that a π bond rarely forms without an accompanying σ bond.) In addition, each fluorine has six nonbonding electrons distributed by pairs in the 2*s*, $2p_y$, and $2p_z$ orbitals. The electron dot formula corresponding to this description is

:F̤̈—F̤̈:

Visualization 6.4

Each of the following diagrams depicts the overlap of orbitals in F_2 to form a sigma bond. What is wrong with each?



Solution:

The overlap of two p_z orbitals in part (a) leads to a π bond. Pi-bonds are generally not formed unless a sigma bond is already present (the sideways overlap is less effective than end-to-end overlap). The overlap of an *s* and a p_x will produce a sigma bond. (In the diagram the negative end of the *p* orbital overlaps with the positive *s* orbital and no bond is formed. This can be remedied by simply switching the signs of the lobes of the *p* orbital so that there is reinforcement of the positive ends of the orbitals.) Our overlap diagram shows that the half-filled orbital is a *p* orbital, however, and the overlap of two p_x orbitals produces more electron density between the nuclei because the *p* orbitals extend toward one another. In part (c), a p_x overlaps with a p_z and, as discussed above, the reinforcement produced by interaction of the negative parts of the two orbitals is canceled by interaction of the positive end of the p_z with the negative end of the p_x.

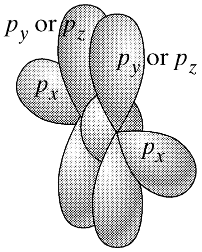


Figure 6.17 Formation of π-bond through overlap of p_y or p_z orbitals.

We begin our valence bond description of O_2 by writing the valence electron configurations for both oxygen atoms (Figure 6.16). Each atom has two half-filled orbitals that can be overlapped to form a double bond. Thus, in addition to the overlapping p_x orbitals, which form a σ bond, we now also have a π bond formed by overlap of either the p_y or p_z orbitals, as shown in Figure 6.17. The corresponding electron dot formula is

:Ö=Ö:

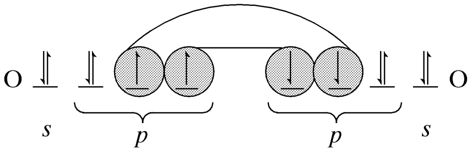


Figure 6.16 Overlap diagram for O_2.

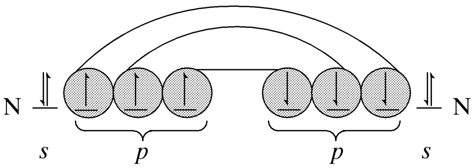


Figure 6.18 Overlap diagram for N_2.

The description of N_2 follows the same procedure (Figure 6.18). There are now three half-filled p orbitals to overlap, resulting in a σ bond and two π bonds. The two π bonds are oriented at right angles to each other because perpendicular p orbitals—a p_y and a p_z—are used to form the π bonds.

Bond Order

We have previously asserted that the greater the electron density between two atoms, the greater the electron-nuclei attractions and therefore the lower the potential energy of the molecule. If we define **bond order** as one-half the number of electrons between the nuclei (indeed, bond order is just a more sophisticated way of expressing the number of bonds between two atoms), we can now state an important generalization:

The greater the bond order, the higher the bond dissociation energy and the shorter the bond length.

This is reasonable according to theory because the greater the electron-nuclei attractions, the stronger the bond and the smaller the internuclear distance.

Table 6.2 presents the bond energies and bond lengths, along with the bond orders, for N_2, O_2, and F_2. These parameters are also presented for ethane, ethene, and ethyne, which also have bond orders of 1, 2, and 3, respectively. These and similar data clearly substantiate our generalization. A comparison of the bond energies and bond lengths of F_2 and ethane, which have the same bond orders, also reveals, however, that the generalization must be used with care. It certainly cannot be interpreted to mean, for example, that two bonds with the same bond order will have the same bond energies and bond lengths. This would be only approximately true even for bonds containing very similar atoms (atoms with similar electronegativities, size, and so on).

The data of Table 6.2 can also be used to develop another generalization, namely, that

species with the same number of electrons (isoelectronic species) have the same bond orders and roughly similar molecular parameters.

Diatomic fluorine and ethane have the same number of electrons and the same bond orders; diatomic oxygen and ethene are isoelectronic and have O—O and C—C bond orders of 2; and diatomic nitrogen and ethyne are isoelectronic and have N—N and C—C bond orders of 3. As we have seen in our discussion of the Lewis model, and thus far in our discussion of the valence bond model, the number of valence electrons determines the type of bonding adopted by the molecule, and this generalization, therefore, is not surprising.

TABLE 6.2 A Comparison of Bond Energies and Lengths with Bond Order

	BOND ORDER	BOND ENERGY kJ/mol	BOND LENGTH pm
F_2	1	155	142
O_2	2	494	121
N_2	3	941	109
$H_3C{-}CH_3$	1	347	153
$H_2C{=}CH_2$	2	615	134
$HC{\equiv}CH$	3	812	120

TABLE 6.3 Selected Isoelectronic Species

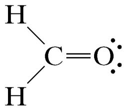
SPECIES	BOND LENGTH pm	BOND ENERGY kJ/mol
$:\ddot{O}=\ddot{O}:$	121	494
	(CO) 121	(CO) 623
$H-\ddot{N}=\ddot{O}:$	(NO) 121	(NO) 527
$:N\equiv N:$	109	941
$H-C\equiv N:$	(CN) 116	(CN) 644
$:C\equiv N:^-$	115	–
$:C\equiv O:$	113	1075
$:N\equiv O:^+$	106	–

Table 6.3 presents bond lengths and bond energies for other compounds isoelectronic with O_2 and N_2. Here, the similarities in bond lengths for isoelectronic species are obvious; the bond energies, however, are more widely divergent.

Hybridization

Our treatment of valence bond theory to this point leads to a description of bonding in the water molecule that does not agree with the structural parameters for the molecule. According to the valence configurations for oxygen and hydrogen (Figure 6.19), two 2*p* orbitals in the oxygen atom are available for overlap with the 1*s* orbitals in the hydrogen atoms. Since two *p* orbitals are oriented at 90° to each other (part (b)), the angle between the two oxygen-hydrogen bonds should also be 90°. However, the experimentally determined bond angle is 104.5°.

When this discrepancy was first noted, it was suggested that oxygen, because of its greater electronegativity, attracts a considerable amount of the electron density in the O—H bonds, leaving the hydrogen nuclei rather exposed. The partially exposed nuclei would then repel each other, resulting in a widening of the bond angle. This proposed repulsion was later shown to be inadequate to account for a widening of almost 15°.

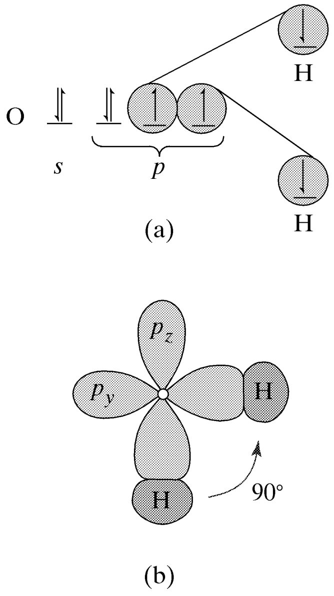


Figure 6.19 Overlap diagram for water.

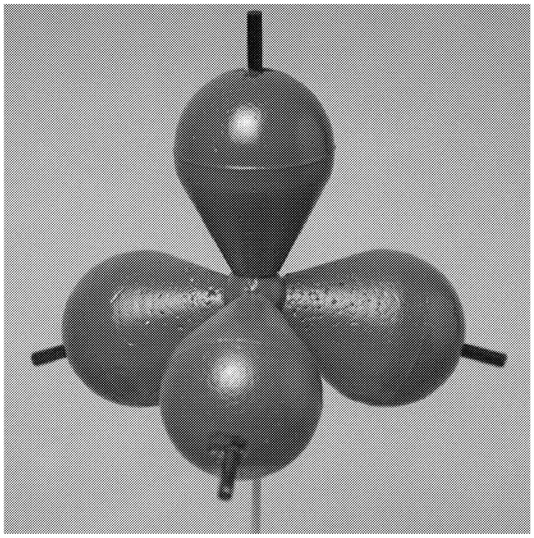


Figure 6.20 The four sp^3 hybrid orbitals.

The explanation that is currently accepted as an integral part of valence bond theory is based on the concept of **hybridization** of atomic orbitals. During our discussion of the modern view of the atom in Chapter 3, we found that the orbital is a mathematical construct. It is a consequence of wave mechanics that orbitals can be mathematically combined according to certain rules to produce a new, different set of orbitals. It can be shown that if, for example, an s orbital, a p_x orbital, a p_y orbital, and a p_z orbital are combined according to the rules of quantum mechanics, four different combinations are possible and each combination describes a new orbital. These four new orbitals are named according to the orbitals that were used in their creation and thus are termed sp^3 orbitals. There are, then, four sp^3 orbitals, or, since this combining process is usually referred to as hybridization, four sp^3 hybrid orbitals.

The spatial disposition of the four sp^3 orbitals is completely different from the spatial disposition of the individual s and p orbitals. As is shown in Figure 6.20, the sp^3 orbitals have their maximum electron density directed toward the apexes of a tetrahedron.

Figure 6.21 also reveals that each of the four orbitals has the same energy. Indeed, the four sp^3 hybrid orbitals are identical in every way except their orientation in space.

Other combinations of orbitals are also possible. Hybridization of one s and one p orbital produces two sp hybrid orbitals, which are directed toward the opposite ends of a straight line, as shown in Figure 6.22. The angle between the orbitals is therefore 180°. A combination of one s and two p orbitals produces three sp^2 orbitals, whose regions of maximum electron density are directed toward the corners of an equilateral triangle. The angle between any two adjacent sp^2 orbitals is therefore 120°.

A combination of one s orbital, three p orbitals, and one d orbital produces five sp^3d orbitals, which are directed toward the corners of a trigonal bipyramid (Figure 6.23). The

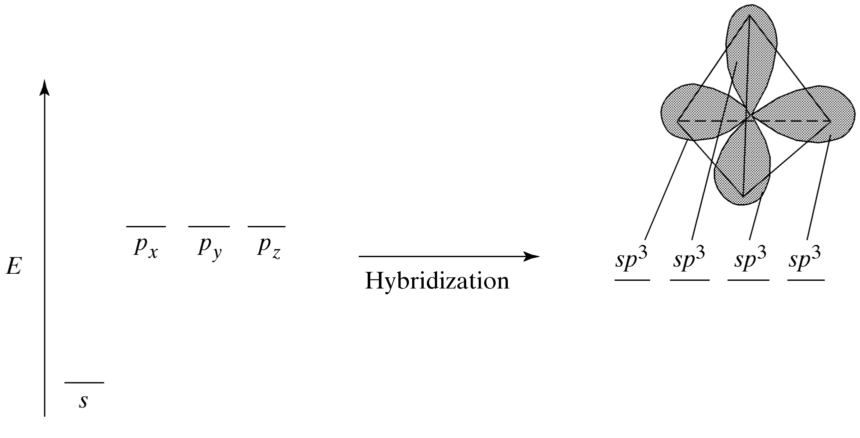
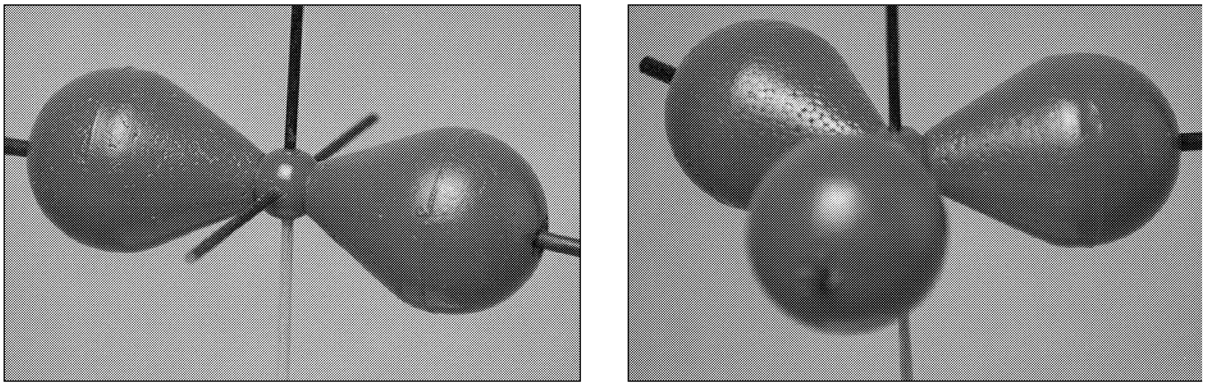


Figure 6.21 The hybridization of one s and three p orbitals to form four sp^3 hybrids.



sp hybrid orbitals

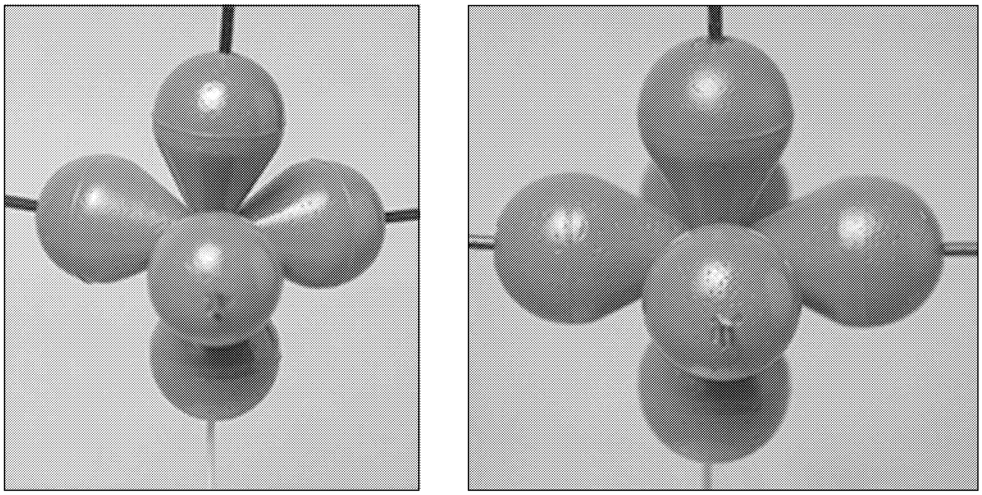
sp^2 hybrid orbitals

Figure 6.22 *sp* and sp^2 hybridization.

trigonal bipyramid is a unique geometrical figure, since it alone (of the figures discussed here) produces two different angles between the orbitals. The angle between the orbitals in the equatorial plane is 120°, while the angle between an axial orbital and an equatorial orbital is 90°. The energies of the five sp^3d orbitals are also unique in that there are two energy levels, with the two axial orbitals having the higher energy. The other common type of hybridization is sp^3d^2. These orbitals are directed toward the apexes of an octahedron (Figure 6.23); the angle between any two adjacent sp^3d^2 orbitals is therefore 90°.

Before we leave our general discussion of hybridization, we must add one qualifying remark: Orbitals can be combined effectively only when they have similar energies. Thus, we would not expect a carbon atom to utilize sp^3d orbitals in bonding, because this would mean that the 2*s* and the three 2*p* valence orbitals would combine with a 3*d* orbital, which has a much higher energy. Hybridization, therefore, is restricted to valence shell orbitals.

Let us now return to our dilemma with the bond angle in H_2O. If the oxygen uses sp^3 hybrid orbitals to overlap with the 1*s* orbitals of the two hydrogen atoms (see Figure 6.24), we would expect the tetrahedral angle of 109.5°. This prediction is certainly closer to the actual value of 104.5° than our previous prediction of 90° and is an important modification to the valence bond model.



sp^3d hybrid orbitals

sp^3d^2 hybrid orbitals

Figure 6.23 sp^3d and sp^3d^2 hybridization.

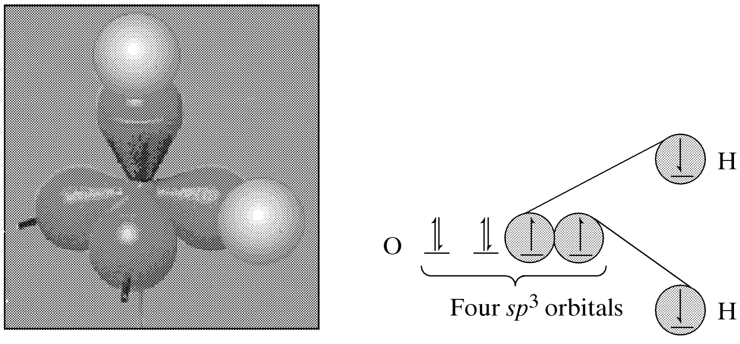


Figure 6.24 The use of sp^3 hybridization to rationalize the bond angles in water.

The isoelectronic species NH_3 and CH_4 can be treated in the same way, using sp^3 hybrid orbitals on the central atom. Figure 6.25 shows models of these molecules as well as H_2O. The experimental bond angles in NH_3 and CH_4 are 107° and 109.5°, respectively.

The derivation of the valence bond description of methane (CH_4) deserves elaboration. There are only two unpaired electrons in the valence configuration of carbon:

$$\mathrm{C}\ \underset{s}{\underline{\uparrow\downarrow}}\ \underset{p}{\underline{\uparrow}}\ \underset{p}{\underline{\uparrow}}\ \underset{p}{\underline{}}$$

Since methane has four C—H bonds, we need *four* unpaired electrons on the carbon to overlap with the unpaired electrons on the four hydrogens. The bond angle of 109.5° is an obvious manifestation of sp^3 hybridization, and thus we can hybridize the carbon orbitals and populate them according to Hund's rule:

$$\mathrm{C}\ \underbrace{\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{sp^3\ \text{orbitals}}$$

As a result of the equal energies of the sp^3 orbitals, there are four unpaired electrons on carbon after hybridization. An alternative analysis of the change in electronic structure of carbon involves the promotion of an electron from an s orbital to a p orbital prior to hybridization.

$$\overset{\text{promote}}{}\ \mathrm{C}\ \underset{s}{\underline{\uparrow\downarrow}}\ \underset{p}{\underline{\uparrow}}\ \underset{p}{\underline{\uparrow}}\ \underset{p}{\underline{}} \longrightarrow \mathrm{C}\ \underset{s}{\underline{\uparrow}}\ \underset{p}{\underline{\uparrow}}\ \underset{p}{\underline{\uparrow}}\ \underset{p}{\underline{\uparrow}} \xrightarrow{\text{hybridization}} \mathrm{C}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}$$

Let us now examine the bonding in a hydrocarbon, using ethene (C_2H_4) as the example. Ethene, the simplest hydrocarbon with a C=C bond, is a planar molecule (Figure 6.26). The C—C—H angle in ethene is 120°, which is indicative of sp^2 hybridization. We shall therefore create three sp^2 hybrids, leaving one p orbital at each carbon. This p orbital is oriented perpendicularly to the plane containing the three sp^2 hybrid orbitals.

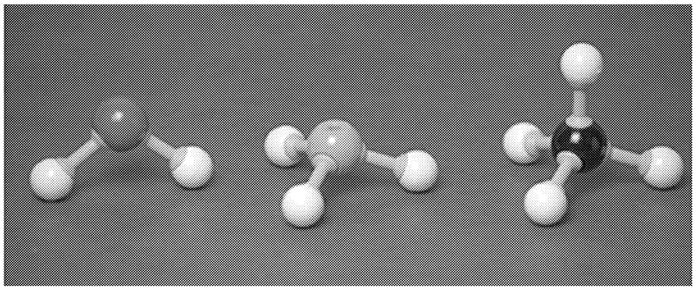


Figure 6.25 Models of water, ammonia, and methane.

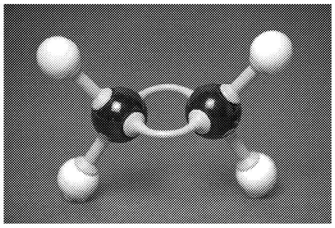


Figure 6.26 A Model of Ethene

Because we have defined the molecular plane as the xy plane, the sp^2 hybrids must be in this plane (the C—H and C—C bonds are constructed with the hybrids). Therefore the p orbital not used in the hybridization is the p_z orbital.

According to Hund's rule, the electron configuration at each carbon should be

$$\mathrm{C}\ \underbrace{\underline{\upharpoonleft\downharpoonright}\ \underline{\upharpoonleft}\ \underline{\upharpoonleft}}_{sp^2}\ \underset{p_z}{\underline{\quad}}$$

But this provides only two unpaired electrons, whereas we need at least three for the two C—H bonds and the C—C linkage. Promotion of one electron to the p_z orbital will provide the required orbital schematics (Figure 6.27). The planar geometry of the molecule is fixed by the overlap of the two p_z orbitals, which must be parallel in order to overlap effectively (see Figure 6.27).

The use of hybridization in molecules that do not obey the octet rule can be illustrated with PCl_5, phosphorus pentachloride, and the species SiF_6^{2-}. Phosphorus pentachloride has a trigonal bipyramidal geometry with the phosphorus at the center of the bipyramid. This geometry requires the use of sp^3d hybrid orbitals, which can be produced by hybridization of the s orbital, three p orbitals, and one of the d orbitals that exist in the valence shell (the third quantum level) of phosphorus:

$$\mathrm{P}\ \underbrace{\underline{\upharpoonleft}\ \underline{\upharpoonleft}\ \underline{\upharpoonleft}\ \underline{\upharpoonleft}\ \underline{\upharpoonleft}}_{\text{five } sp^3d \text{ orbitals}}$$

After hybridization, these orbitals can be populated with the five valence electrons of phosphorus and then overlapped with the single half-filled p orbital of each chlorine.

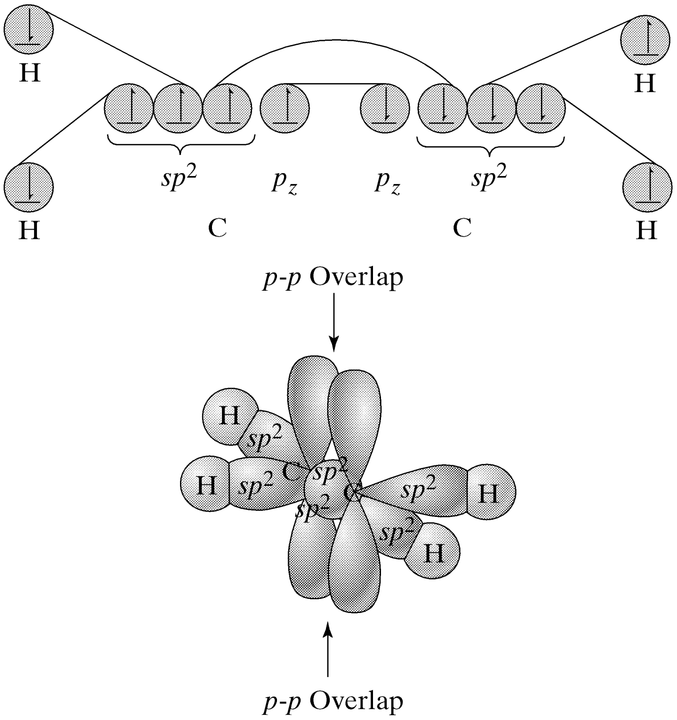
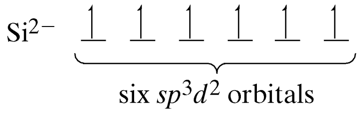


Figure 6.27 The valence bond description of the bonding in ethene.

For the species SiF_6^{2-}, which has octahedral geometry, we begin by arbitrarily assigning the two extra electrons (which give the species a 2− charge) to silicon. Since the octahedral geometry requires sp^3d^2 hybridization at the silicon, the six electrons of the fictitious Si^{2-} ion are placed in these hybrid orbitals:

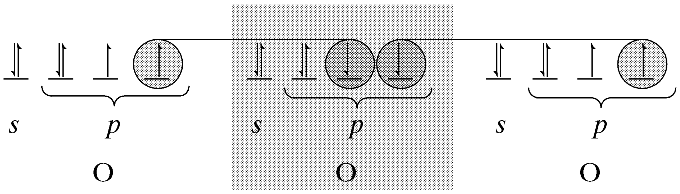


These hybrids can then be overlapped with the single half-filled orbital on each fluorine to produce the final description of SiF_6^{2-}. The same final disposition of electrons can be obtained by beginning the valence bond visualization with one silicon atom, four fluorine atoms, and two fluoride ions.

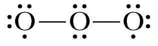
Resonance

The ozone molecule (O_3), one of the constituents of smog, provides a convenient introduction to yet another feature of the valence bond model. This molecule contains two identical oxygen-oxygen linkages with bond lengths of 128 pm. The bond angle is 117°.

We begin, as usual, with the valence electron configuration for each oxygen.



Since the central oxygen must bond to two oxygens, the overlap just pictured seems logical. However, the electron dot formula corresponding to this description would be

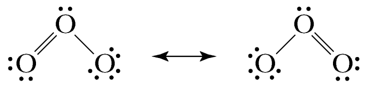


Clearly, the octet rule is not obeyed for the outer atoms.

A description that does obey the octet rule can be obtained by transferring an electron from the central oxygen to one of the outer oxygens (naturally, this is just a kind of electron bookkeeping system and should not be interpreted as the formation of ions). If we then recognize that the 117° bond angle is indicative of sp^2 hybridization, we can describe the molecule as shown in Figure 6.28.

While this description certainly obeys the octet rule and is in agreement with the 117° bond angle, it does not account for the observed equal bond lengths. The formula above predicts two unequal linkages, the double bond being shorter than the single bond in accord with our bond-order generalization.

However, the description in Figure 6.28 is rather arbitrary at any rate, for we could have decided to place the double bond between the central oxygen and the other oxygen:



If we were to combine or hybridize these two structures, we would get a hybrid that has equal bonds. This process, especially for the purpose of "seeing" the equalization of

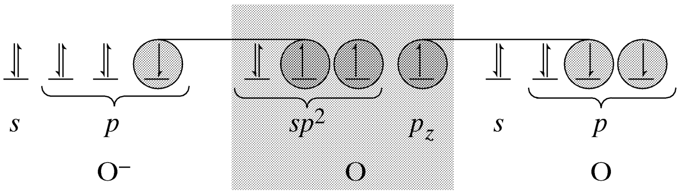


Figure 6.28 The overlap diagram for O_3.

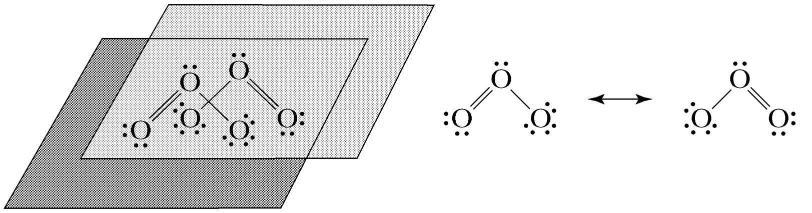


Figure 6.29 Resonance hybridization in O_3.

bonds, is probably best visualized as a superimposition of the one structure on the other, as in superimposing two transparent images (Figure 6.29).

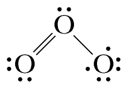
This fusion of two (or more) valence bond representations is somewhat analogous to the concept of hybridization, except that entire electronic descriptions rather than just atomic orbitals are mathematically combined. The process is known as **resonance hybridization**; the individual structures that are hybridized are called **resonance forms** or **resonance contributors**. The double-headed arrow is used to indicate resonance hybridization.

The formation of resonance hybrids is sometimes likened to the creation of a rhinoceros by hybridization of a unicorn and a dragon. Just as the "resonance contributors" in this analogy are mythical creatures and have no physical reality, resonance forms such as either of the O_3 contributors do not actually exist. The analogy is not quite perfect, however, because the *real* creature, the rhinoceros, is presumed to result from the hybridization. In the case of molecular resonance hybridization, the resulting electronic hybrid is very likely not a perfect description of the electronic structure of the *real* molecule. In fact, the most that can be said of the resonance hybrid is that it is a better representation of the electronic structure of the real molecule than either of the individual resonance contributors.

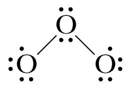
Let us now return to the ozone hybrid. Each of the resonance forms has one π bond. The resonance hybrid, however, has the two π electrons **delocalized**, or smeared out, over two linkages. Each O—O linkage, then, has a total of three electrons (two σ electrons and one π electron), or a bond order of 1.5. Our bond order-bond length generalization would now predict a bond length somewhere between the length observed for an oxygen-oxygen single bond and an oxygen-oxygen double bond. The bond length in O_2, to which we have previously ascribed a bond order of 2, is 121 pm, while the O—O bond length in hydrogen peroxide, which has an O—O linkage best described as a single bond, is 148 pm. The experimentally determined bond lengths for O_3 are 128 pm, which is indeed between the measured double and single bond lengths for oxygen.

Visualization 6.5

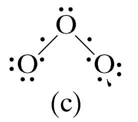
Which of the following would be the best electron dot formula if only one could be used to describe O_3?



(a)



(b)



(c)

Solution:

Formula (a) shows two bonds of different bond orders and therefore different bond lengths. Since O_3 has two bonds of equal length, this formula is not a good description. Formula (b) indicates that the O—O bond has a bond order of one, whereas the experimentally observed bond length of 121 pm is evidence for a bond order greater than one. Formula (b) also does not obey the octet rule. Formula (c), although somewhat strange in appearance, does obey the octet rule (the single electron above the bonds counts in the octet of both attached atoms) and it suggests that the O—O bond has a bond order of 1.5 (three electrons shared by two atoms) and that the O—O bonds are equal in length and energy.

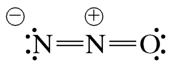
The delocalization of electrons as represented by resonance has yet another consequence—it generally results in a decrease in energy. This decrease in energy can be rationalized with the electron-confined-to-a-line model discussed in Chapter 3: The greater the distance (d) available to the electron, the lower the energy given by the equation

$$E = \frac{n^2h^2}{8md^2}$$

In a molecule that is best represented as a resonance hybrid—one that has some electron delocalization—the difference between the energy expected for a given resonance contributor and the true energy of the molecule is called the **resonance energy**. This is presumably a measure of the degree to which the molecule has been stabilized by delocalization.

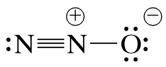
The energy expected for the dissociation of one mole of the resonance form $O{=}O{-}O$ to three moles of monatomic oxygen is 992 kJ. The dissociation of one mole of **ozone** to three moles of monatomic oxygen actually requires 1109 kJ. Ozone is therefore 113 kJ more stable than predicted on the basis of one resonance form; that is, the resonance energy of ozone is 113 kJ/mol.

Dinitrogen oxide, N_2O (which is used as an anesthetic and as the propellant gas in "whipped" cream containers), is a linear molecule with an $N{-}N$ bond length of 113 pm and an $N{-}O$ bond length of 119 pm. The linear structure is indicative of *sp* hybridization at the central nitrogen. By reasoning similar to that used for ozone, we can write the following electron dot formulas:



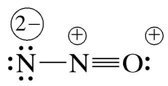
$\overset{\ominus}{:\ddot{\mathrm{N}}}{=}\overset{\oplus}{\mathrm{N}}{=}\ddot{\mathrm{O}}:$

(I)



$:\mathrm{N}{\equiv}\overset{\oplus}{\mathrm{N}}{-}\overset{\ominus}{\ddot{\underset{..}{\mathrm{O}}}}:$

(II)



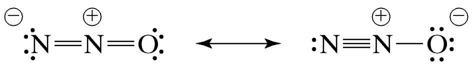
$\overset{2\ominus}{:\ddot{\underset{..}{\mathrm{N}}}}{-}\overset{\oplus}{\mathrm{N}}{\equiv}\overset{\oplus}{\mathrm{O}}:$

(III)

The charges in the formulas above are **formal charges** and are determined for any given atom by counting its nonbonded electrons plus one-half of its shared electron pairs. This sum is then subtracted from the number of valence electrons in the neutral atom. The difference is the formal charge.* For example, in structure I, the valence shell of the end nitrogen contains four nonbonded electrons and four shared electrons. The valence shell of a neutral nitrogen atom contains five electrons. The formal charge of this nitrogen is then $5 - \left(4 + \frac{4}{2}\right) = -1$. As the name implies, this number does not represent the actual distribution of electrons, because electronegativity differences have not been taken into account. In many cases, however, the number does represent an approximate idea of the electron distribution. Formal charge does not imply the existence of ions, and is usually encircled to avoid confusion.

The question at this point is, which structure, or combination of structures, is the best representation of the electronic structure of N_2O; that is, which structure, or combination of structures, provides the best explanation of the physical and chemical properties of N_2O? To answer this question, we again make use of our bond-order generalization. A comparison of the bond lengths in N_2O with those expected for the $N{\equiv}N$, $N{=}N$, $N{=}O$, and $N{-}O$ bonds (tabulated in Table 6.4) suggests an $N{-}N$ bond order of 3 or slightly less and an $N{-}O$ bond order of 2 or slightly greater.

None of the electronic structures I, II or III shows $N{-}N$ and $N{-}O$ bond orders of about 3 and 2, respectively. In addition, structure III would appear to be quite unlikely because of the positive formal charges on adjacent atoms (the charge distribution implied by these formal charges would be electrostatically unfavorable). A resonance hybrid of forms I and II, however, will produce a reasonable representation of the electronic structure of N_2O,



$$\overset{\ominus}{:\ddot{\mathrm{N}}}{=}\overset{\oplus}{\mathrm{N}}{=}\ddot{\mathrm{O}}: \longleftrightarrow :\mathrm{N}{\equiv}\overset{\oplus}{\mathrm{N}}{-}\overset{\ominus}{\ddot{\underset{..}{\mathrm{O}}}}:$$

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* For those who relish formulas,

$$F = v - (n + s/2)$$

where F is the formal charge of a particular atom, v is the number of valence electrons of that neutral atom, n is the number of non-bonded electrons on that atom, and s is the number of electrons that atom shares with other atoms.

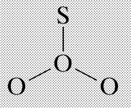
TABLE 6.4 A Comparison of Bond Lengths (pm) in N_2O with Some Standards

	N—N BOND LENGTH	N—O BOND LENGTH
N_2O	113	119
Standards	N═N 124	N—O 146
	N≡N 110	N═O 120

Assuming that the two forms contribute equally, the hybrid would have N—N and N—O bond orders of 2.5 and 1.5, respectively. Since compounds whose electron dot formulas indicate no formal charge are being compared to formulas with formal charges, the bond length-bond order rule can be expected to hold only approximately.

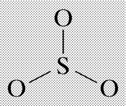
Methodology 6.2

The dipole moment of SO_3 is zero. Is it possible for the structural formula to be

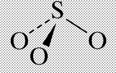


or S---O---O---O?

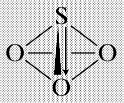
No, neither structural formula is sufficiently symmetrical to allow the bond moments to cancel and produce a dipole moment of zero. The structural formula that will produce a symmetrical molecule and also follows the rule for compounds with the AB_n structure is



Will the following structure allow for cancellation of the S—O bond moments?

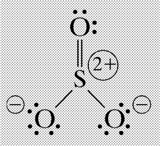


No, in this structure the bonds point down toward the corners of a pyramid and the bond moments add to form a resultant that runs from the center of the sulfur to the middle of the base of the pyramid.



Only a trigonal planar structure where all atoms lie in the same plane and the oxygens are at the corners of an equilateral triangle will allow the bond moments to cancel.

Now write an electron dot formula for the compound.



Does this formula produce equivalent S—O bonds?

No, one bond is a double bond, the other two are single bonds and are therefore longer and weaker than the double bond.

What effect do the formal charges have?

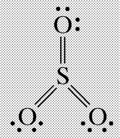
Continued on next page

Methodology 6.2 Continued

The formal charges are an approximate indication of electron excess or deficiency. When adjacent atoms have opposite formal charges they tend to be attracted more than would be the case if the formal charges were zero. This attraction leads to bond shortening.

Is it possible to write formulas that have no formal charges?

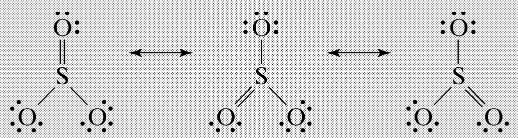
Yes, we could write a structure that would have three S═O bonds.



This structure has no formal charges but it also does not obey the octet rule. Some chemists prefer to minimize formal charges and will write formulas like this. We believe that it will be simpler for you to follow the rule—"obey the octet rule whenever possible".

What do we do to make the three S—O bonds equivalent and still obey the octet rule?

We invoke resonance, which means that we fuse or hybridize the three octet structures



The resulting hybrid has three equivalent S—O linkages with bond orders of 4/3.

Now determine what hybrid orbitals are used to form the sigma bonds.

Because we know that the oxygens are at the corners of an equilateral triangle, we know from geometry that the angles between the S—O bonds must be 120°. This angle requires the use of sp^2 hybrids at the sulfur.

If we call the plane of the molecule the xy plane (the z axis is perpendicular to the plane), what atomic orbitals are hybridized at sulfur to produce three sp^2 orbitals?

Because the hybrids must lie in the xy plane, we must mathematically combine an s, a p_x, and a p_y.

What orbital does the sulfur use to form the π bond?

The remaining p orbital—the p_z. Thus, the π bond extends above and below the plane of the molecule.

What orbital does each oxygen use to form the π bond?

The p_z. Only an orbital with the same symmetry as the p_z on the sulfur will overlap with the p_z on the sulfur.

What does the π bond look like in the resonance hybrid?

It is delocalized among the three SO linkages. That is, two π electrons are shared by three linkages. Thus, each linkage has 2/3 of a π electron.

Predict the S—O bond length.

The only bond length given in Appendix 2 is the one for the S═O bond (143 pm). The bond order of 4/3 predicts a bond length shorter than a single bond but not as short as a double bond. However, each resonance contributor has opposite formal charges which cause some bond shortening. We estimate, therefore, that the SO bond length in SO_3 should be close to the double bond length. The experimental value for SO_3 is 143 pm.

In the planar molecule benzene (a model of which is shown in Figure 6.30), all the C—C—C bond angles are 120°, and all the C—C bond lengths are 140 pm. The carbon atoms are obviously sp^2 hybridized, and these hybrids are used to form the three σ bonds

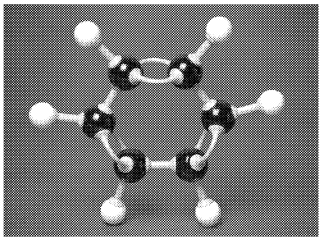
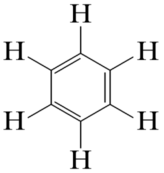
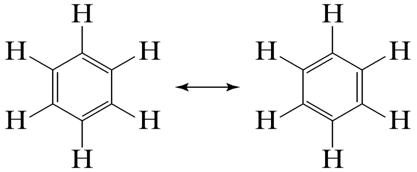


Figure 6.30 A Model of Benzene

at each carbon. Each carbon also has an electron in a *p* orbital perpendicular to the plane of the ring. A suitable electron dot formula for benzene is



This formula would suggest, however, that the C—C linkages are unequal: the three double bonds would be shorter than the three single bonds. The measured equality of the bonds can be accounted for by resonance hybridization of the two structures below:



When these structures are superimposed, a C—C bond order of 1.5 is produced. The length expected for a C—C single bond is 154 pm, whereas the C—C double bond length is 133 pm. The observed value of 140 pm lends credence to the 1.5 bond order and the description of benzene as a resonance hybrid.

The resonance structures above suggest that any π electron in benzene (there are six of them) is delocalized over all six C—C linkages. This is implied by the abbreviated formula for benzene,  where the presence of the carbons and hydrogens is understood.

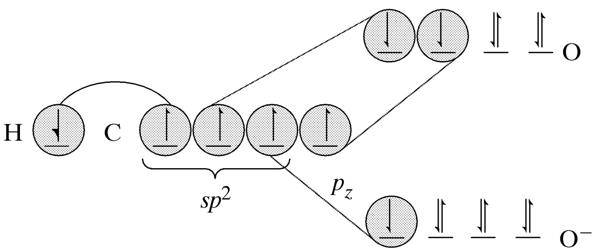
The delocalization of π electrons leads to a lower energy than that expected for a single resonance contributor. This resonance energy is estimated to be 155 kJ/mol for benzene.

Problem 6.5

The formate ion (HCO_2^-) has equivalent C—O bonds with lengths of 126 pm and a bond angle of about 125°. Describe the bonding in this ion.

Solution:

Since the central carbon uses sp^2 hybrid orbitals, the schematics are as follows:



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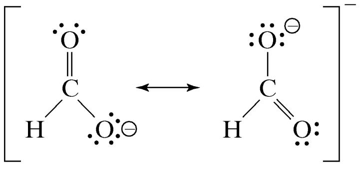
Problem 6.5 *Continued*

Solution: *Continued*

But this description, although it explains the bond angle, does not account for the equal C—O linkages. The formation of a resonance hybrid does, however, produce equal C—O bonds, with bond orders of 1.5. The bond length in formaldehyde, which has a C—O bond order of 2, is 123 pm. A bond order of 1.5 is then not unreasonable, since the corresponding bond length would be expected to be greater than 123 pm.

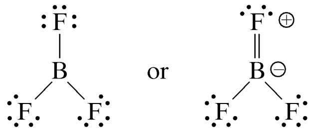


Problem 6.6

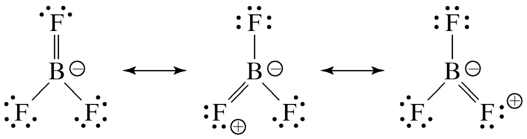
Provide a valence bond description of the bonding in BF_3 that (a) gives each B—F bond some π character, (b) accounts for its 120° bond angles, and (c) produces equivalent B—F bonds.

Solution:

First consider the following electron dot formulas as descriptions of the bonding in BF_3:



Only the right-hand description, which involves overlap of a filled fluorine p_z orbital with the empty p_z orbital on boron, gives π character to a B—F bond. However, this description predicts a shorter bond length for one of the bonds. In order to obtain three equivalent bonds, we must hybridize the following three descriptions:



The bond order of each B—F bond in the resonance hybrid can be obtained by adding up the bonds for a given B—F linkage and then dividing by the number of resonance contributors. Thus the bond order for each B—F bond is 4/3.

Check Point 6.2

The nitrite ion has a bond angle of 115°. What orbital is used to describe the lone pair of electrons on the central atom?

Solution:

sp^2 hybrid orbital

◇ ◇ ◇ ◇ ◇

6.6 MOLECULAR ORBITAL MODEL

The basic assumption of the molecular orbital model is that for every electron in a molecule there exists an orbital that is associated to some extent with the entire molecule. Each molecular orbital, just like an atomic orbital, is designated by its energy and the spatial distribution of its electron density. Indeed, the concept of molecular orbitals is completely analogous to the concept of atomic orbitals.

Since the mathematical equations of the wave model cannot be solved exactly for species as complex as molecules, the energies and electron density distributions of molecular orbitals are obtained by an approximate mathematical method—the combination of atomic orbitals. This process is very similar to hybridization, except that the orbitals involved in the combination are on *different* atoms.

Consider the mathematical construction of the two lowest-energy molecular orbitals for the H_2 molecule. These molecular orbitals are formed by addition and subtraction of the lowest-energy atomic orbitals, the 1*s* orbitals. The electron density of two separated 1*s* atomic orbitals as a function of the distance between the two nuclei (represented by the letters A and B) are shown in Figure 6.31. When the orbitals are allowed to overlap and are added, the electron density between the nuclei increases, as in part b. When the orbitals are subtracted, the electron density is decreased in the region midway between the nuclei (part c).

The buildup of electron density between the nuclei when the 1*s* orbitals are added leads to a lowering of the potential energy relative to the isolated atoms. The molecular orbital formed by the addition of these atomic orbitals is therefore a **bonding orbital** and is usually called the σ1*s* orbital. The term σ (sigma) refers to the concentration of electron density along the internuclear axis; the 1*s* denotes the atomic orbitals from which the molecular orbital was constructed.

Since the molecular orbital that results from the subtraction of the 1*s* atomic orbitals has no electron density in the plane midway between the nuclei, there is no decrease in potential energy when electrons occupy this orbital. In fact, there is an *increase* in energy; this orbital is therefore properly described as **antibonding**. The designation for the orbital is σ^*1s, where the asterisk denotes antibonding.

The energies of the two molecular orbitals relative to the energies of the atomic orbitals are illustrated in Figure 6.32. Note that the bonding orbital is lower in energy than the atomic orbitals, while the opposite is true for the antibonding orbital. The extent to which the energy of the molecular orbital is raised or lowered relative to its constituent atomic orbitals depends on the energies of the atomic orbitals and how effectively they overlap. It is also useful to note that the number of molecular orbitals obtained from a combination of atomic orbitals is the same as the number of atomic orbitals; thus, two molecular orbitals are obtained from two 1*s* atomic orbitals.

These two orbitals certainly suffice for a description of the ground state (lowest energy level) of H_2. The hydrogen molecule contains two electrons, and the aufbau

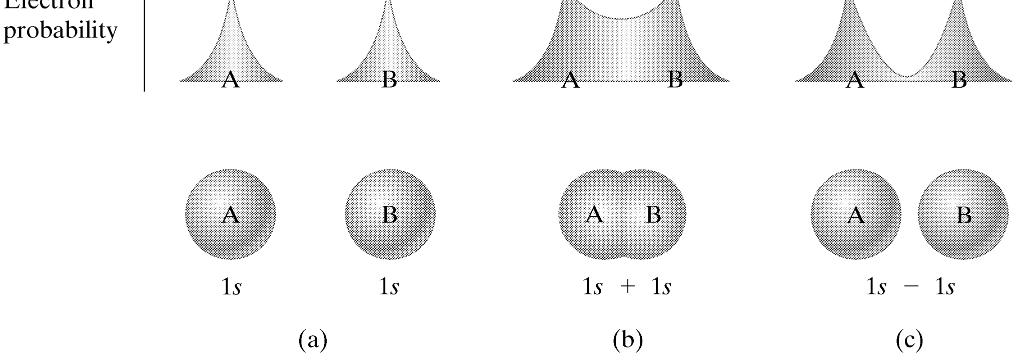


Figure 6.31 Addition and subtraction of two 1*s* orbitals.

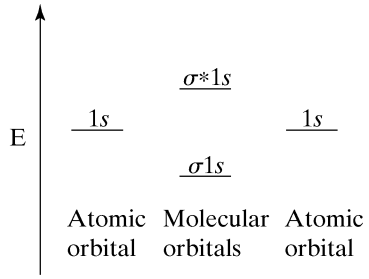


Figure 6.32 The relative energies of the $\sigma 1s$ and σ^*s molecular orbitals.

principle and the Pauli exclusion principle dictate, just as for filling atomic orbitals, that the two electrons occupy the lowest-energy $\sigma 1s$ orbital.

More orbitals are needed to describe the molecular configurations of diatomic molecules with a greater number of electrons, such as O_2. These orbitals are constructed from the other atomic orbitals—2*s*, 2*p*, and so on. For example, $\sigma 2s$ and σ^*2s molecular orbitals are obtained from the addition and subtraction, respectively, of two 2*s* atomic orbitals. Addition and subtraction of two $2p_x$ orbitals (where the *x*-axis is the internuclear axis) produces the $\sigma 2p$ and σ^*2p molecular orbitals. Combination of the p_z orbitals results in π molecular orbitals, since electron density is produced above and below the internuclear line. The p_y orbitals result in π molecular orbitals that have their maximum density areas rotated 90° relative to the $\pi 2p_z$ orbitals. Thus, six molecular orbitals result when three p orbitals on one atom combine with three *p* orbitals on the other atom.

The diagram in Figure 6.33 shows the relative energies and electron density patterns of the 10 lowest-energy molecular orbitals for homonuclear diatomic molecules and ions. Higher-energy orbitals could be formed by combination of the 3*s*, 3*p*, . . . , orbitals, but the molecular orbitals given here are sufficient for a description of diatomic species containing up to 20 electrons.

We are now in a position to write the electron configurations for some simple molecules. We have already seen that the H_2 molecule has two electrons in the σ1s orbital. In keeping with the convention for writing atomic electron configurations, we can denote this molecular configuration as $(\sigma 1s)^2$. This molecule, therefore, has two bonding electrons and consequently a bond order of 1.

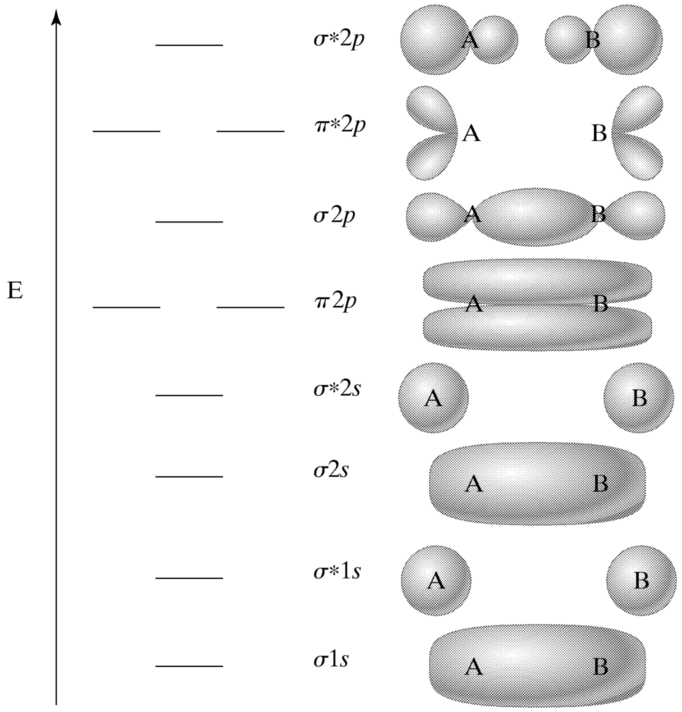


Figure 6.33 Energies and electron density patterns for the molecular orbitals of diatomic molecules.

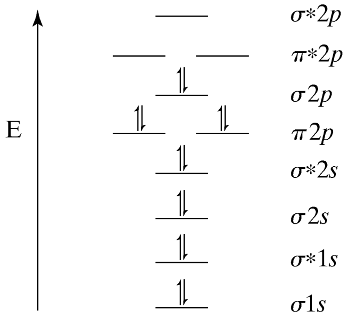


Figure 6.34 The electron configuration of N_2.

The helium diatomic molecule (He_2) would be expected to have its four electrons in the lowest-energy orbitals, and following the Pauli principle we can write the configuration as $(\sigma 1s)^2(\sigma^* 1s)^2$. This molecule would contain two bonding electrons and two antibonding electrons. If we assume that the antibonding electrons exactly cancel the binding effect of the bonding electrons, the bond order in this molecule would be zero. This prediction of instability is borne out by the nonexistence of a stable species of He_2. We will, in general, assume that in molecular orbital theory the bond order for any linkage is given by $\frac{1}{2} \times$ (number of bonding electrons minus number of antibonding electrons).

The nitrogen molecule has a total of 14 electrons, which are distributed among the seven orbitals of lowest energy, as shown in Figure 6.34. The electron configuration for diatomic nitrogen is written as

$$N_2\ (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_y)^2(\pi 2p_z)^2(\sigma 2p_x)^2$$

Since there are 10 bonding electrons and four antibonding electrons, the N_2 bond order is $(10 - 4)/2 = 3$, which is the same as the bond order obtained by the valence bond model.

The diatomic oxygen molecule has two more electrons than N_2; these electrons, according to Hund's Rule, must enter the π^*2p orbitals singly, as shown below. The electron configuration for O_2 is shown in Figure 6.35.

$$O_2\ (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_y)^2(\pi 2p_z)^2(\sigma 2p_x)^2(\pi^* 2p_y)^1(\pi^* 2p_z)^1$$

Because of the single occupancy of the π^*2p orbitals, there are nine electrons in O_2 with one spin quantum number, say $+\frac{1}{2}$, and only seven electrons with the other spin; that is, the spins of two electrons are not "paired." Since any moving charge, such as a spinning electron, has an associated magnetic field, a species with *unpaired* electrons will be attracted to a magnetic field. A compound of this type is said to be **paramagnetic**. An important result of the molecular orbital description of O_2 is the prediction that O_2 is paramagnetic. The valence bond description of O_2, in contrast, predicts no unpaired electrons.

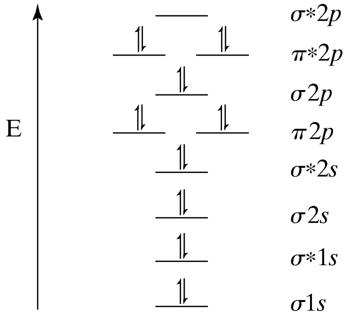


Figure 6.35 The molecular orbital description of O_2.

Since O_2 is indeed paramagnetic, this was considered one of the early triumphs of molecular orbital theory. Both theories, however, predict a bond order of 2.

The species O_2^+ has one less electron than O_2 and thus has only one electron in a π^* orbital. The bond order is therefore $(10 - 5)/2 = 2.5$. The superoxide ion (O_2^-) has one electron more than O_2, and since this electron must also enter a π^* orbital, the bond order is $(10 - 7)/2 = 1.5$. The peroxide ion (O_2^{2-}) with 18 electrons, has a filled π^* level, and consequently a bond order of 1. Clearly, molecular orbital theory accounts very naturally for fractional bond orders. The bond lengths of O_2^+, O_2, O_2^-, and O_2^{2-} are 117 pm, 121 pm, 128 pm, and 149 pm, respectively, in agreement with our bond order-bond length generalization.

Diatomic fluorine is isoelectronic with O_2^{2-} and therefore also has a bond order of 1. The two additional electrons necessary for the Ne_2 molecule would occupy the σ^*2p orbital, thereby producing a bond order of zero. This species is, in fact, unknown.

The energy-level diagram for molecular orbitals (Figure 6.33) can also be used to describe the electron configuration of simple heteronuclear (different nuclei) diatomic molecules or ions. The odd-electron molecule of nitrogen oxide has a bond length of 115 pm, which lies between that of N_2, 110 pm, and that of O_2, 121 pm. The molecule is isoelectronic with O_2^+ and therefore has a bond order of 2.5, in accord with its bond length.

The major difference, then, between the molecular orbital model and the valence bond model is that each electron in a molecular orbital description is assumed to be associated to some extent with every atom of the molecule, whereas in the valence bond model some electrons are localized about specific nuclei. Without sophisticated calculations, the molecular orbital model is difficult to apply to complicated molecules.

Problem 6.7

Predict whether the molecule C_2 will be stable.

Solution:

Using the energy-level diagram in Figure 7.34 we add a total of 12 electrons and obtain the configuration

$$C_2\ (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_y)^2(\pi 2p_z)^2$$

which leads to a bond order of 2. We therefore predict that the molecular species C_2 should have some stability. This does not necessarily mean that C_2 can be prepared, because other species may be even more stable or the rate of formation in a particular reaction may be unfavorable. C_2 has been observed in the gas phase.

Methodology 6.3

In this methodology we will perform the kind of "experiments" that theoretical chemists do—we will construct the molecular orbital diagram of methane, CH_4.

We begin by assuming that only the valence shell orbitals of carbon and hydrogen need to be considered; in other words, the 1*s* electrons of carbon are tightly held and are not likely to be involved in bonding. This means that we must somehow mathematically combine (add and subtract) the carbon 2*s* and three 2*p* orbitals with the four hydrogen 1*s* orbitals. Let us begin by drawing the tetrahedral structure of methane at the corners of a cube. Can you see how a tetrahedron can be obtained from a cube?

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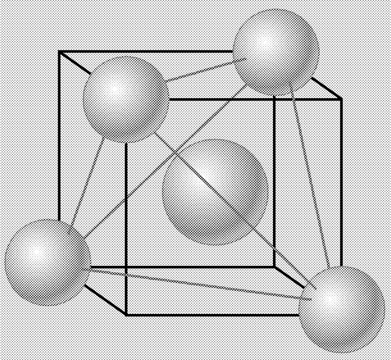
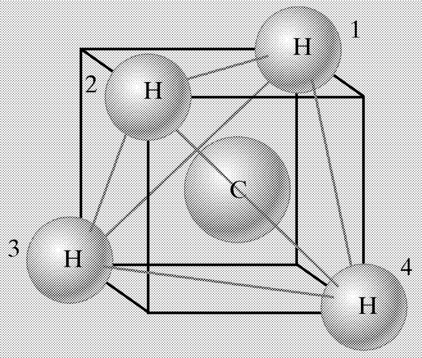
Methodology 6.3 Continued

Here we show each of the hydrogen atoms at appropriate corners of a cube and a carbon atom at the center of the cube. The tetrahedron is drawn in light gray



Now let us assume that each of the spheres in the diagram above represents not the whole atom, but instead just an *s* orbital. In the case of the hydrogens, the spheres represent 1*s* orbitals; in the case of the carbon it represents a 2*s* orbital. Remembering that *s* orbitals have a positive sign everywhere, can you imagine how we can add these orbitals to generate a molecular orbital that will have electron density between the carbon and hydrogens

First, let us number the orbitals.

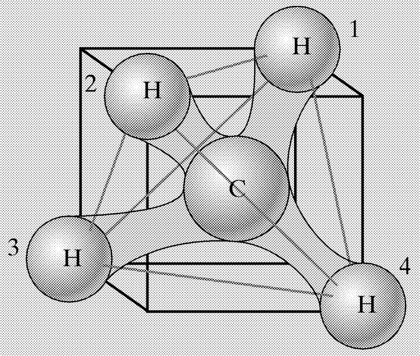


If we call the carbon 2*s* orbital C(2*s*) and the hydrogen 1*s* orbital H(1*s*) we can form one molecular orbital by just adding all of the orbitals:

$$MO_1 = C(2s) + H_1(1s) + H_2(1s) + H_3(1s) + H_4(1s)$$

This molecular orbital produces electron density between the carbon and hydrogens because the orbitals overlap. For example, for carbon and one hydrogen the orbitals reinforce to produce electron density between the nuclei.

Show what the overlap of the carbon with the four hydrogen orbitals might look like.



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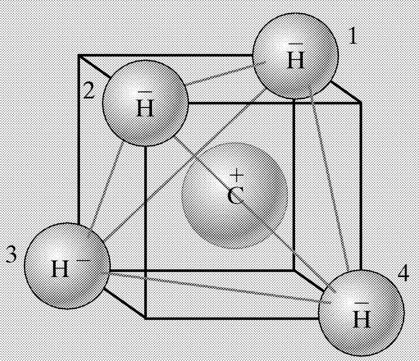
Methodology 6.3 Continued

Be very careful not to confuse this with a model of the bonding in methane. The diagram above is just one of the molecular orbitals of methane and only two electrons can occupy the space indicated by the shaded areas between the hydrogens and the carbon.

We can also generate a molecular orbital that does not provide electron density between the carbon and hydrogens. In this molecular orbital the hydrogen 1s orbitals do not reinforce the carbon $2p$ orbital, and no electron density will appear in the region between the nuclei when the orbital is populated with two electrons. Try to figure out what combination of orbitals will generate this antibonding molecular orbital.

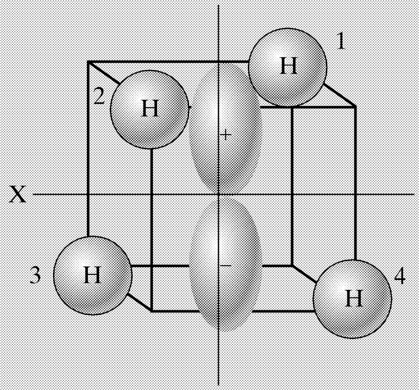
$$MO_2 = C(2s) - H_1(1s) - H_2(1s) - H_3(1s) - H_4(1s)$$

This orbital can be pictured as



Notice that because we subtract the hydrogen orbitals, we change their signs, and consequently the hydrogen wave function does not reinforce the carbon 2*s* wave function. This orbital does not result in bonding; in fact, when an electron occupies this orbital MO_2 it actually detracts from the stability of the molecule.

Now let us examine the interaction of the carbon p_z orbital with the hydrogen orbitals.



Construct a molecular orbital that will result in the build-up of electron density between the carbon and all of the hydrogens.

$$MO_3 = C(2p_z) + H_1(1s) + H_2(1s) - H_3(1s) - H_4(1s)$$

Notice that hydrogen 3 and hydrogen 4 are subtracted so that the sign of the orbital wave function changes and allows overlap between the lower lobe of the carbon $2p_z$ and the 1*s* orbitals on hydrogens 3 and 4.

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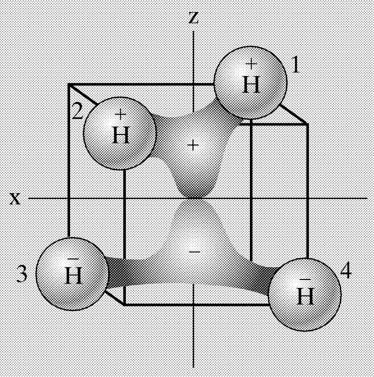
Methodology 6.3 Continued



Now modify this bonding molecular orbital to prevent overlap of the wave functions.

$$MO_4 = C(2p_z) - H_1(1s) - H_2(1s) + H_3(1s) + H_4(1s)$$

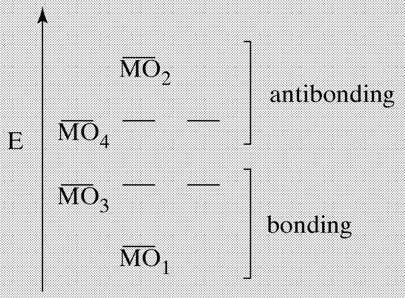
> This operation simply changes the sign of each of the hydrogen orbitals so that H_1 and H_2 are negative while H_3 and H_4 are positive. There then can be no overlap with the carbon p_z and an antibonding molecular orbital results.

We have only considered the carbon p_z orbital, but what about the carbon p_x and p_y orbitals?

> They will overlap in similar ways with the hydrogen orbitals to generate bonding and antibonding molecular orbitals.

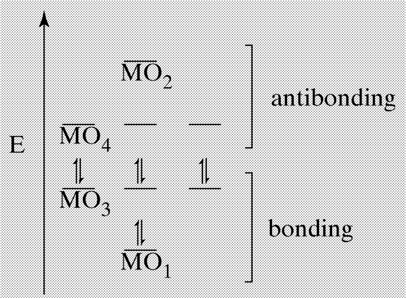
Can you guess what the energies of the eight molecular orbitals that result from the above operations will be?

> It is not easy to predict the relative energies, except that we know that the antibonding molecular orbitals are higher in energy than the bonding molecular orbitals and the 2*p* orbitals are higher in energy than the 2*s* orbital. Moreover, there seems to be no fundamental difference between the three bonding molecular orbitals that result from interaction of the three 2*p* orbitals on carbon with the hydrogen orbitals (except orientation in space). Here is the energy level diagram with the four molecular orbitals that we have created.



> Notice that there are a total of eight molecular orbitals, four of which are bonding and four of which are antibonding. There are two sets of degenerate orbitals. MO_3 belongs to one set and MO_4, its antibonding counterpart, belongs to the other set.

We must now populate these orbitals with the correct number of valence electrons for methane. Count up the electrons and add them to this diagram.



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Methodology 6.3 Continued

There are a total of eight valence electrons for CH_4 and these go into the lowest energy orbitals, according to the Pauli Principle and Hund's Rule.

How many bonding electrons are there?

Eight

Since there are four C—H bonds (from the standpoint of the valence bond and Lewis electron dot model), would it be fair to say that the molecular orbital model predicts that each of these bonds should have a bond order of one?

Yes. Eight electrons divided by four bonds is two electrons per bond; a bond order of one for each C—H bond.

Is it correct to associate the orbital MO_3, for example, with a particular C—H bond?

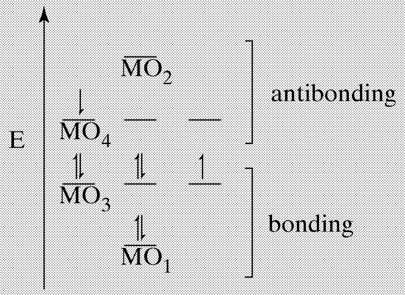
No. MO_3, as we have seen, has electron density distributed over all of the areas between the carbons and hydrogens. So MO_3 is associated with the whole molecule.

Does that mean that the molecular orbital model does not provide the same picture of bonding that is present with the valence bond model?

The molecular orbital model is analogous to the atomic orbital model. Orbitals are created that extend over the entire molecule. After these orbitals are populated by the correct number of electrons, one can obtain some idea of the bond order, the relative potential energy of the molecule, etc. To some extent it is reasonable to characterize the molecular orbital model as a delocalized model and the valence bond model as a localized bond model. In other words, it is much easier to "picture" a molecule using the valence bond or electron dot models.

How is the stability of methane affected by excitation of an electron?

The diagram below shows an excited state of methane



Is the molecule less stable in its excited state?

Yes, because an electron has entered an antibonding orbital and therefore the total stability of the molecule has decreased.

Can the valence bond model be used to describe the excited states of molecules?

Not in the simple, nonmathematical form that we have used. This is one of the disadvantages relative to the molecular orbital model.

CHAPTER SUMMARY

In Chapter 5, we studied one of the two major types of compounds—ionic compounds. The properties of these compounds are accounted for by the ionic model, in which atoms lose and gain electrons to form ions. These ions are held together in a crystal lattice by electrostatic attractions.

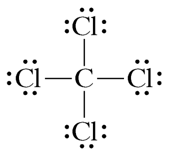
In this chapter we have discussed the second major type of compound, in which atoms are bound together to form molecules. The bonds between the atoms, called covalent bonds, are the result of shared electron density.

To adequately describe the covalent bond, any model must account for certain measurable molecular properties, including bond length, bond angle, bond energy, and bond polarity. You should learn the meaning of these important terms and understand their relationships to the three different but related bonding models: the Lewis model, the valence bond model, and the molecular orbital model.

The Lewis model, one of the earliest covalent bonding models, was developed before the advent of wave mechanics, but it remains extremely useful today. Because of its relative simplicity, the Lewis model is a good beginning point in your study of the nature of the covalent bond.

Basically, the Lewis model is founded on the same premise on which our discussion of the ionic model was based: the inert-gas rule, which states that atoms achieve stability by obtaining the electron structure of the inert gases. To illustrate, consider the compound CCl_4. The electron configuration of the carbon atom and the chlorine atom are $1s^22s^22p^2$ and $1s^22s^22p^63s^23p^5$, respectively. If these atoms were to combine to form an ionic compound, the C atom would have to lose four electrons to obtain the inert-gas configuration, forming a C^{4+} ion. These electrons would be gained by four Cl atoms, forming four Cl^- ions. Since a prohibitively large amount of energy is necessary to remove four electrons from a C atom (review the section on ionization energy in Chapter 3), four Cl^- ions do not form and CCl_4 is not an ionic compound.

On the other hand, let's assume that the C atom shares its four valence electrons—one with each of the four Cl atoms—and that each of the four Cl atoms *shares* one of its valence electrons with the C atom. Then, although no electrons have actually been lost or gained, each of the five atoms has, in a sense, obtained the inert-gas configuration. Each one of the four Cl atoms is bound to the C atom by sharing of a pair of electrons. According to the Lewis model, this shared electron pair is a **covalent bond**, and the resulting molecule can be depicted as



Note that only the valence electrons are shown in this **electron dot formula** and that each of the atoms has eight of these electrons. Also note that the total number of electrons shown in the electron dot formula is equal to the sum of the valence electrons of the individual atoms. (For an ion, the total number of electrons shown must be equal to the sum of the valence electrons *plus* the number of electrons necessary to produce the charge on the ion.) You should learn to write molecular and ionic electron dot formulas quickly and accurately, which can be accomplished only through extensive practice.

The **valence bond model** retains the electron-pair bond concept from the Lewis model, but it uses the principles of wave mechanics to describe this concept in terms of atomic orbitals. Thus, in this model a covalent bond is formed when an orbital of one atom overlaps an orbital of another atom, which can occur only if the spins of the two bonding electrons are paired.

You should become familiar with the terminology employed in the valence bond model and with the concepts of bond order, hybridization of atomic orbitals, and resonance. You should also be able to give the valence bond descriptions of a large variety of compounds in terms of both the overlap of atomic orbitals and the shape and direction of hybrid bonding orbitals necessary to account for bond angles, bond lengths, and bond energies.

Of the three bonding models, the **molecular orbital model** is the most mathematical and the most difficult to understand. A detailed treatment of this model is beyond the scope of an introductory course. However, you should understand the basic concepts of the origin of molecular orbitals and be able to describe simple diatomic molecules and ions in terms of those orbitals. This will require memorization of the relative energies of the molecular orbitals presented in Figure 6.33.

Another important topic treated in this chapter—and one that should be emphasized because it is essential to the study of subsequent chapters—is the concept of **bond polarity**. The two types of chemical bonds we have discussed—ionic bonds and covalent bonds—are, in a sense, idealized extremes. The bond between two atoms of widely different electronegativities is an ionic bond formed by the loss and gain of electrons, adequately described by our ionic model. Conversely, the bond formed between two identical atoms is a "true" covalent bond in that the electrons forming the bond are shared equally between the two atoms. But in between these two extremes, the vast majority of chemical bonds are formed between elements whose electronegativities are different, but not widely different. These bonds are described as having **ionic character** and are called **polar bonds**. You should be able to predict the qualitative polarity of bonds from the difference in electronegativities of the atoms in the bond.

TERMS

Some important terms presented in this chapter are as follows:

Bond length The distance between the centers of two adjacent atoms in a molecule.

Bond angle The angle formed by any two adjacent bonds in a molecule.

Bond energy The amount of energy required to "break" a chemical bond. For example, the bond energy of HCl is the energy required to carry out the process $HCl \rightarrow H + Cl$ in the gaseous state. Bond energy is most commonly expressed in kJ/mol.

Bond polarity A measure of the unequal sharing of electron density between bonded atoms, so that one end of the bond is negative with respect to the other end. The greater the difference between the electronegativities of the two atoms, the more polar the bond.

Polar molecule A molecule in which the electron density is not distributed symmetrically; the molecule has a positive end and a negative end. Any **diatomic** molecule with a polar bond must also be a polar molecule. However, not all **polyatomic** molecules with polar bonds are polar molecules; the shape of the molecule also determines polarity. Polar molecules are also called **dipoles**.

Dipole moment A measure of the polarity of a molecule. Mathematically, a dipole moment is defined as the product of the amount of unequally distributed charge in the molecule and the distance between the unequal charges. The greater the polarity of the molecule, the higher the dipole moment.

Octet rule The statement that an atom gains stability by obtaining the inert-gas configuration, which consists of eight valence electrons. (In the case of the hydrogen atom, however, two valence electrons form an inert-gas configuration.)

Electron dot formula or Lewis formula A depiction of a molecule or an ion in which the valence electrons of all the atoms are indicated by dots; a pair of electrons shared by two atoms is usually represented by a dash.

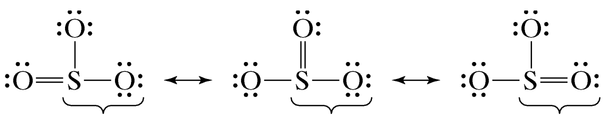
Structural formula A diagram that indicates which atoms are attached to one another in a molecule. Dotted lines are sometimes used to portray the attachments or linkages.

Sigma (σ) bond A bond in which the buildup of electron density (orbital overlap) occurs on the **bond axis** (an imaginary line connecting the nuclei of the two atoms).

Pi (π) bond A bond formed by the overlap of orbitals above and below the bond axis. Since a π bond involves less overlap and is therefore weaker than a σ bond, it rarely forms between atoms unless accompanied by a σ bond.

Bond order One-half the number of electrons involved in the bonding between two atoms. In the **Lewis model**, bond order is the number of pairs of electrons shared by two atoms. In this model a single bond represents a bond order of 1; a double bond represents a bond order of 2; and a triple bond represents a bond order of 3. In the **valence bond model**, a σ bond represents a bond order of 1, a σ bond and a π bond represent a bond order of 2, and a σ bond and two π bonds represent a bond order of 3.

In cases where the molecule is best depicted as the hybrid of a number of resonance forms, the bond order of a given bond is obtained as follows: Add the single, double, and triple bonds shown between the pairs of atoms in question in all the resonance forms; then divide this sum by the number of resonance forms. For example, SO_3 can be described as the hybrid of three resonance forms:



$$\mathrm{O{=}\underbrace{\overset{\overset{\displaystyle O}{|}}{S}{-}O}} \longleftrightarrow \mathrm{O{-}\underbrace{\overset{\overset{\displaystyle O}{\|}}{S}{-}O}} \longleftrightarrow \mathrm{O{-}\underbrace{\overset{\overset{\displaystyle O}{|}}{S}{=}O}}$$

To obtain the bond order for the particular bond indicated by the brace, add the 2 single bonds and the 1 double bond to obtain 4, and then divide 4 by the number of resonance forms (3). Thus, the bond order is $\frac{4}{3}$, Note that the bond order of each of the three bonds in this example is the same: $\frac{4}{3}$.

According to the **molecular orbital model**, the bond order is one-half the number obtained by subtracting the number of antibonding electrons from the number of bonding electrons.

(**NOTE**: The greater the bond order, the higher the bond energy and the smaller the bond length.)

Isoelectronic Having the same number of electrons (examples are N_2 and C_2H_2; O_2 and C_2H_4).

Hybrid orbitals Orbitals formed by the combination of atomic orbitals of a given atom. The number of hybrid orbitals is equal to the number of atomic orbitals combined to make the hybrids. Thus, hybridization of one *s* orbital and one *p* orbital results in two *sp* hybrid orbitals; hybridization of one *s* orbital and two *p* orbitals results in three sp^2 hybrid orbitals; and so on. This concept is part of the valence bond theory, postulated to account for molecular shape.

Resonance A theory devised to provide a more adequate description of molecular bonding using the valence bond model. The properties of many molecules cannot be satisfactorily characterized in a single valence bond description. By assuming that the structure of the molecule is a **hybrid** of a number of individual valence bond descriptions, we can more accurately describe the real molecule. (Each one of these individual structures is called a **resonance form** or a **resonance contributor**.) Resonance is a delocalization, or a "spreading out," of electrons.

Resonance energy The difference between the energy expected for a given resonance form and the actual energy of the real molecule. Resonance usually results in a decrease in energy.

Formal charge A device used in connection with electron dot formulas to represent the distribution of electrons in a qualitative way. The formal charge for any given atom is determined by adding the number of the atom's nonbonded electrons to one-half the number of its shared electrons and then subtracting this sum from the number of valence electrons in the neutral atom.

Molecular orbitals Orbitals formed from the combination of atomic orbitals and associated to some extent with the entire molecule. According to the molecular orbital theory, every electron in a molecule has an associated molecular orbital. If the energy of the molecular orbital is lower than that of the atomic orbitals from which it was formed, it is called a **bonding orbital**. If the energy is higher than that of the corresponding atomic orbitals, the molecular orbital is an **antibonding orbital**.

Paramagnetism The attraction of some substances to a magnetic field. A substance is paramagnetic if it contains one or more unpaired electrons (that is, more electrons of one spin than of the opposite spin).

PROBLEMS

1. Write the molecular formula for each of the following compounds:
(a) arsenic trichloride
(b) boron triiodide
(c) diphosphorus pentoxide
(d) hydrogen selenide
(e) xenon hexafluoride
(f) germanium tetrachloride
(g) zirconium tetrafluoride
(h) antimony pentafluoride
(i) bromine trifluoride
(j) dichlorine oxide

2. Name the following compounds:
(a) NO (b) N_2O (c) N_2O_4
(d) NO_2 (e) PCl_5 (f) SF_6
(g) SO_3 (h) P_2O_5 (i) $SiBr_4$
(j) OF_2 (k) Cl_2O (l) SnI_4

3. Which compound in each of the following pairs has the greater amount of ionic character in its bonds?
(a) LiBr and $BeBr_2$ (b) BF_3 and NF_3
(c) LiF and LiI (d) CF_4 and CI_4
(e) SiO_2 and SiS_2 (f) CCl_4 and $SnCl_4$
(g) F_2 and IF

4. Write suitable electron dot formulas for the following ions:
(a) carbonate (b) chlorate
(c) sulfate (d) perchlorate
(e) hydroxide (f) nitrate
(g) sulfite (h) ammonium
(i) phosphate

5. Write suitable electron dot formulas for the following molecules:
(a) carbon dioxide (b) tin tetrachloride
(c) carbon monoxide (d) methanol
(e) water (f) dimethyl ether

6. Write electron dot formulas, including appropriate resonance forms, for the following:
(a) carbonate (b) borate (BO_3^{-3})
(c) sulfate (d) hydrogen carbonate
(e) nitrate (f) ethyne
(g) propanone (h) 1,3-butadiene
(i) acetic acid (j) iodine pentafluoride
(k) tin tetrachloride

7. Write suitable electron dot formulas for the following species:
(a) boron tribromide (b) sulfur tetrafluoride
(c) arsenic pentafluoride (d) CH_3^+
(e) CH_3^- (f) NO

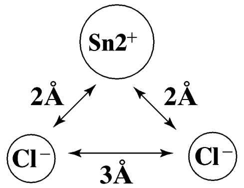
8. For which species in Problem 6 is the octet rule violated?

9. Write suitable electron dot formulas for the following acids:
(a) acetic acid (b) nitrous acid
(c) sulfuric acid (d) perchloric acid
(e) phosphoric acid (f) chlorous acid

10. Which ions in Problem 4 are isoelectronic?

11. Write suitable electron dot formulas for each of the following species:
(a) H_3O^+ (b) NCO^-
(c) OF_2 (d) SiF_6^-
(e) HCN (f) SO_3
(g) $GeCl_4$ (h) XeF_4

12. For $SnCl_2$:
a. First, assume that it is covalent and give an electron dot formula, the geometry, and hybridization for an $SnCl_2$ molecule.
b. Next, assume that it is ionic. Calculate the potential energy for a *mole* of ions arranged in a triangle as follows:



13. The following questions deal with a compound containing only nitrogen and hydrogen.
a. The percentage composition of this compound is 93.33% N and 6.67% H. The molecular weight is 30.0. Calculate the empirical and molecular formulas for this compound.
b. Write all the reasonable structural formulas that this compound might have and show that the electron-dot formulas for each of the structures obey octet rule.
c. Write appropriate electron-dot formulas for each of the structures given in b.
d. How many different compounds are represented by the structural formulas given in b.
e. The compound in question has a nitrogen-nitrogen bond length corresponding to an effective bond order of 2. Which of the structures given in b above is the structure of the compound?

14. For each of the following, write all of the resonance forms that obey the octet rule (indicating formal charges) and determine the bond order for each bond:
(a) CO_3^{-2} (b) SO_2 (c) SO_3^{-2}

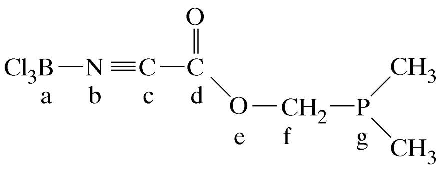
15. The bond lengths of the following species (or their derivatives) are often used as standards for determining approximate bond orders of other species.

SPECIES	STANDARD FOR BOND	LENGTH OF BOND (pm)
CH_3CH_3	$C-C$	154
$H_2C=CH_2$	$C=C$	134
$HC\equiv CH$	$C\equiv C$	120
CH_3OH	$C-O$	143
H_2CO	$C=O$	123
CO	$C\equiv O$	113
CH_3NH_2	$C-N$	147
$H_2C=NH$	$C=N$	129
CN^-	$C\equiv N$	115
H_2NOH	$N-O$	146
HNO	$N=O$	121
NO^+	$N\equiv O$	106
H_2NNH_2	$N-N$	145
$HN=NH$	$N=N$	125
N_2	$N\equiv N$	110
$HOOH$	$O-O$	148
O_2	$O=O$	121

Rationalize the following bond length orders:

$C-C > C-N > C-O$
$C=C > C=N > C=O$
$C-C > C=C > C\equiv C$

16. Provide the following information for the molecule



a. The formal charge on boron (a).
b. The formal charge on nitrogen (b).
c. The bond angle around nitrogen (b).
d. The hybridization at carbon (d).
e. The number of lone pairs on oxygen (e).
f. The hybridization at phosphorus (g).

17. For binary compounds, it can be shown that dividing the total number of valence electrons in a molecule by eight gives the number of sigma bonds to the central atom. Any remainder is equal to the number of nonbonding electrons residing on the central atom. Why is it that this approach is not valid for binary hydrogen compounds?

18. a. Give appropriate electron dot formulas for nitromethane, CH_3NO_2.
b. Given that the NO single bond length is 1.40 Å and the NO double bond length is 1.21 Å, predict the NO bond length in nitromethane. Explain.
c. Give the valence bond description of nitromethane in the diagram. Label every orbital.

19. The $C\equiv O$ bond is stronger than the $N\equiv N$ bond, but carbon monoxide is more reactive than diatomic nitrogen. Explain.

20. Attempts have been made to prepare the species SO_4 and NH_4. Write electron dot formulas for each species and discuss the probable stability of each.

21. Provide a valence bond description, complete with appropriate electron-dot formulas, for each of the following. Each description must be consistent with the data supplied.

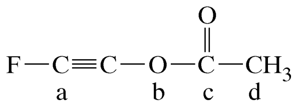
1. SO_2: both SO bonds are 1.48 Å long; bond angle = 120°.
2. SO_3: all SO bonds are 1.43 Å long; bond angle = 120°. Can you rationalize the fact that the bond length in SO_2 and SO_3 are the same?
3. NO_2^+: both bonds 1.15 Å; bond angle = 180°. (NO bond length in HNO is 1.21 Å.)
4. NO_2: both bonds 1.19 Å; bond angle = 134°. (See length in NO_2^+.)
5. NCO^-: NC and CO bond lengths = 1.18 Å; bond angle 180°. (Bond length in HCN = 1.16 Å, in $(CH_3)_2C=NOH$ = 1.29 Å, in CO_2 = 1.16 Å.)
6. NCCN (cyanogen): CC bond length = 1.38. (CC bond length in ethane = 1.54 Å; in ethene = 1.33 Å.)

22. For each of the following give appropriate electron-dot formulas (including formal charges), the shape, hybridization and bond angles.

a. PO_3^{3-} b. BO_3^{3-} c. SO_3

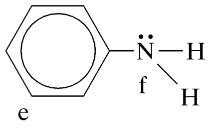
23. For the following molecules give both the bond angle and hybridization at every indicated (lettered) atom.

a.

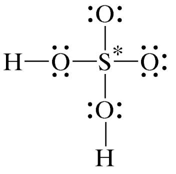


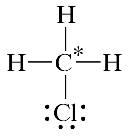
$F-\underset{a}{C}\equiv C-\underset{b}{O}-\underset{c}{\overset{\overset{O}{\|}}{C}}-\underset{d}{CH_3}$

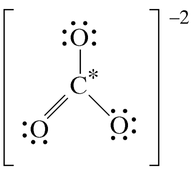
b.

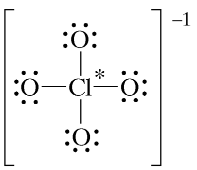


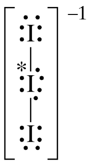
24. Give the formal charge on the starred element in each of the following:

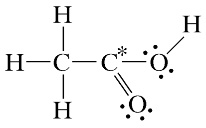












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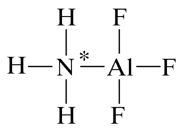
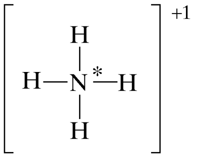
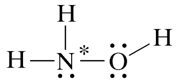
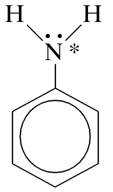
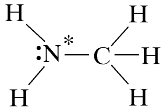










25. a. Give appropriate electron-dot formulas for nitromethane, CH_3NO_2.
b. Given that the NO single bond length is 1.40 Å and the NO double bond length is 1.21 Å, predict the NO bond length in nitromethane. Explain.
c. Give the valence bond description of nitromethane. Label every orbital.

26. Provide a valence bond description for each of the following compounds. Where appropriate, include a diagram showing overlap of orbitals, hybridization, and resonance.

(a) SO_2	(b) SO_3	(c) CO_2
(d) ClNO	(e) H_2Se	(f) H_2CCO
(g) BCl_3	(h) HN_3	(i) O_2NCl

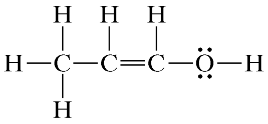
27. Name the following and write appropriate electron dot formulas for and give the shapes of the anions.
a. Ag_2SO_3 b. $Fe(NO_2)_2$ c. $Cd(ClO_3)_2$ d. $Ba(OH)_2$

28. Following the instructions in Problem 26, provide a valence bond description for each of the following ions:

(a) CO_3^{2-}	(b) I_3^-	(c) N_3^-
(d) NO_2^-	(e) HCO_2^-	(f) BO_3^{3-}

29. Write an electron-dot formula for the cyanamide ion (CN_2^{2-}). What common molecule is isoelectronic with this ion? What would you predict as the shape of the ion?

30. The Lewis dot structure for 1-propen-1-ol is given below.



Give the hybridization of the atomic orbitals on the following atoms:
a. C_1
b. C_3
c O
Specify which orbitals overlap in the formation of each of the following bonds:
d. the sigma bond between O and H
e. the sigma bond between C_2 and C_3
f. the pi bond between C_1 and C_2

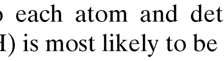
31. For each compound give the geometry, hybridization, and indicate whether or not it has a dipole moment.

a. BCl_3	b. $BrCl_3$	c. SiF_4
d. PCl_5	e. SF_6	f. XeF_2

32. a. In the species—NOBr, NO_2Br, $NOBr_3$—the nitrogen is the central atom. For each species give electron-dot formula(s), molecular geometry, hybridization and NO bond order.
b. Which molecule has the shortest NO bond?

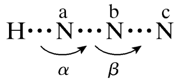
33. The electronic structure of hydrazoic acid, HN_3, can be represented as a resonance hybrid of the two resonance structure (I and II) shown below:

I



II

Refer to the following structural formula for hydrazoic acid and answer the questions.



a. Which linkage is shorter, $N^{a}\cdots N^{b}$ or $N^{b}\cdots N^{c}$?
b. Which angle is larger, α or β?
c. Predict the value of α.
d. In resonance structure II what orbital is used to house the nonbonded pair of electrons on N^c?
e. What is the hybridization at N^b?

34. The NO bond length in O_2NCl (the nitrogen is the central atom) is 1.20 Å. The NCl bond length is 1.84 Å. The N=O double bond reference length is 1.21 Å, and the N—Cl single bond reference length is 1.75 Å.
a. Based on the information above, write appropriate electron-dot formulas for this molecule.
b. Predict the geometry of this molecule.
c. Predict the hybridization at nitrogen.
d. Explain the NO bond length.

35. Both ICN and SCN^- are linear species. Give valence bond descriptions for each that are consistent with their shape.

36. The nitro group in nitrobenzene ($C_6H_5NO_2$) has equal nitrogen-oxygen bond lengths. Account for this fact with suitable resonance structures.

37. Write three resonance structures for the NCO^- ion, assign formal charges to each atom and determine which acid (HNCO or NCOH) is most likely to be formed when H^+ is added to NCO^-

38. Write three resonance structures for the molecule COS (carbon is the central atom). The CO bond length in the molecules CO_2, COS, and COSe is 116 pm in all three. What resonance structure is most likely for all of the molecules?

39. The OO bond length in dioxygen difluoride is 122 pm. The OO bond length in H_2O_2 is 148 pm. Explain the difference.

40. In C_3O_2 the oxygen atoms are terminal atoms. The molecule is symmetric. Write an electron dot formula for the molecule.

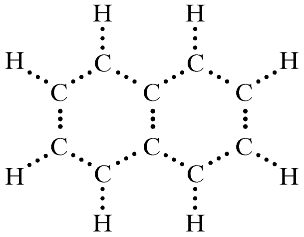
41. The nitrogen-nitrogen bond length in N_2O_4 is 175 pm, which is considerably greater than the nitrogen-nitrogen single-bond length of 145 pm found for hydrazine (H_2NNH_2). Explain, using appropriate electron dot formulas.

42. The nitrogen-oxygen bond length for the nitronium ion (NO_2^+) is 110 pm; for nitrogen dioxide, it is 119 pm; and for the nitrite ion, it is 124 pm. Use the valence bond model to rationalize these bond lengths.

43. The following bond lengths have been reported for cyanogen (NCCN): C—N, 115 pm, and C—C, 138 pm. Compare these with the bond lengths given in Problem 15 and then write electron dot formulas for cyanogen that will rationalize the data.

44. Isocyanic acid (HNCO) has an H—N—C bond angle of 128°, an N—C bond length of 129 pm, a C—O bond length of 117 pm, and an N—H bond length of 99 pm. The NCO^- ion reportedly has an N—C bond length of 121 pm and a C—O bond length of 113 pm. Use appropriate resonance structures to rationalize these data.

45. The compound naphthalene, sometimes used as a moth repellent, has the structure



Draw three resonance structures for this compound. How would the resonance energy of naphthalene compare with that of benzene?

46. Contrast the Lewis and valence bond models in terms of (a) their theoretical bases and (b) the way in which they rationalize molecular geometry.

47. Describe the bonding in the following species using the molecular orbital model. Determine the bond order and predict the stability of each species.

(a) He_2 (b) Li_2 (c) Be_2 (d) N_2
(e) O_2 (f) O_2^+ (g) O_2^- (h) O_2^{2-}
(i) NO (j) NO^+ (k) F_2

48. Rationalize the following bond lengths, based on your description in Problem 47.

O_2^-	128 pm	NO	115 pm
O_2	121 pm	NO^+	106 pm
O_2^+	117 pm	N_2	110 pm

49. Use the molecular orbital model to describe the bonding in the F_2^- ion.

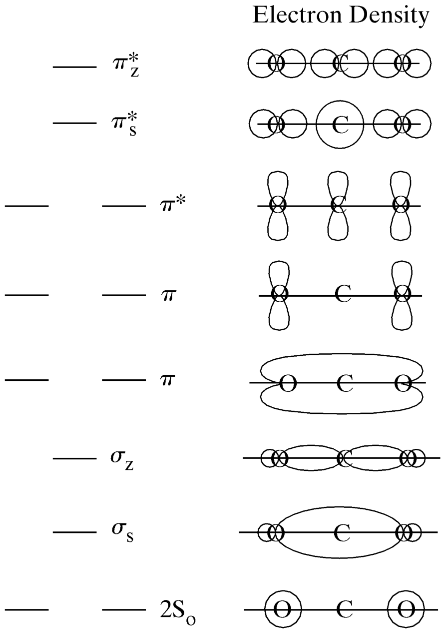
a. Give the MO diagram for the ion.
b. Determine the bond order and any other pertinent characteristic of the ion.
c. Would the addition of an electron to F_2 to get F_2^- be a favorable reaction?

50. The cyanide ion, CN^-, is more stable than the neutral CN molecule.

a. Rationalize the relative stabilities with molecular orbital theory.
b. Rationalize the relative stabilities with valence bond theory.

51. Describe the bonding in NO using the Lewis model, the valence bond model, and the molecular orbital model. Make each description as consistent as possible with the fact that the bond length in NO is 115 pm. Carefully evaluate the success of each of the models in this case.

52. Given below are the molecular orbital energy levels for the *valence* electrons of CO_2 and approximate electron density diagrams for each set of orbitals.



The determination of bond order for polyatomic molecules (from molecular orbital theory) is not quite as simple as for diatomic molecules. The definition of bond order is the same (number of bonding electrons-number of antibonding electrons) but there are frequently also nonbonding electrons—electrons that are essentially localized on one atom and do not contribute to, nor detract from, bonding between atoms. Another difficulty is that one must be careful to divide the total bond order (as defined above) between the proper number of bonds.

a. Four *orbitals* on the diagram above are nonbonding orbitals. By examining the electron density diagrams decide which orbitals are nonbonding and label them nb.
b. Determine the bond order of each C—O bond.
c. What is the major difference between the electron density diagrams of the bonding and antibonding orbitals? Why are the antibonding orbitals antibonding?

The bonding in carbon dioxide can also be described by the valence bond method.

d. Write the box (line) diagram of the electron configuration for carbon.
e. Now promote an *s* electron to an empty *p* orbital and hybridize an *s* and *p* orbital. Give the box diagram for this configuration.

f. Show the box diagram of the electron configuration of an oxygen atom.
g. Now allow the oxygen p_z orbitals (z is the internuclear axis) to overlap with the carbon *sp* hybrids. These are the sigma bonds. The π bond between C and O is formed by overlap of an oxygen *p* orbital with a carbon *p* orbital. Draw a picture of the bonding in CO_2 according to this model.
h. In what orbitals are the oxygen lone-pairs?
i. Focus your attention on the π-bonds in CO_2 and decide how the MO "picture" differs from the valence bond.

53. Indicate the difference between the terms in each of the following pairs:
(a) atomic orbital and molecular orbital
(b) bond length and bond order
(c) ionic compound and covalent compound
(d) valence bond model and molecular orbital model
(e) resonance hybrid and electron dot structure
(f) sigma bond and pi bond
(g) hybrid orbitals and atomic orbitals

54. Multiple-choice questions

1. Which of the following compounds is *least* likely to be ionic?
   a. K_2S b. P_2S_3 c. Sb_2S_3 d. SnS
2. Which of the following has the *shortest* bond length?
   a. N_2 b. O_2 c. F_2 d. Cl_2
3. Which of the following is *not* isoelectronic with the others?
   a. N_2 b. O_2^+ c. CO d. CN_2
4. The bond order in NO predicted by molecular orbital theory is
   a. 1 b. 1.5 c. 2 d. 2.5
5. In which of the following compounds do the bonds have the *most* covalent character?
   a. $AlCl_3$ b. $SiCl_4$ c. $SrCl_2$ d. $SnCl_4$
6. Which one of the following molecules is paramagnetic?
   a. CO_2 b. NO_2 c. SO_2 d. SO_3
7. According to the molecular orbital model, the bond order in OF^- is
   a. 1 b. 1.5 c. 2 d. 2.5
8. For which of the following can the *most* resonance forms be written?
   a. ClO_3^- b. NO_3^- c. ClO_4^- d. SO_4^{2-}
9. In which of the following are the oxygen nuclei *closest* together?
   a. O_2 b. O^{2-} c. O_2^-
   d. the oxygen nuclei are the same distance apart in all
10. In which one of the following compounds is the octet rule *not* obeyed?
    a. SCl_2 b. $AsCl_3$ c. SiF_4 d. TeF_4
11. Which one of the following molecules has no π bond?
    a. CO_2 b. SO_2 c. OF_2 d. CO
12. Which of the following compounds contains the *strongest* carbon-oxygen bond?
    a. CO b. CO_2 c. CH_3OH d. CH_3OCH_3

7

The Structures of Molecules

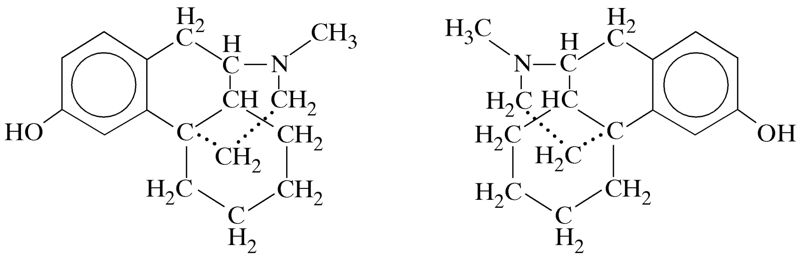
While the nature of the atoms and the type of bonding present in a compound are the major determinants of its chemical and physical properties, the three-dimensional geometry of molecules is of prime importance in a covalent compound. The marked difference in physiological properties of the two drugs levorphan and dextrophan is just one example of the dramatic influence of structure on chemical behavior. The only difference between the two compounds is that their structures are mirror images of each other (Figure 7.1), and yet levorphan is more strongly analgesic and addictive than morphine, whereas dextrophan is neither addictive nor an analgesic.

As we progress through this chapter, we will first discuss a simple method for the prediction of the geometry around a single atom and then proceed to examine some more subtle features of the three-dimensional structure of molecules. Eventually, you should be able to draw and visualize molecules like the ones above in three-dimensional perspective. You will also learn more about the consequences of geometrical differences and how the chemist determines the geometry of molecules.

7.1 THE GEOMETRY OF MOLECULES

In the previous chapter, the concept of hybridization was used to **rationalize** molecular geometry. Because of the importance of the structure of molecules, it is desirable to have at hand a method to predict geometries rather than rationalize them. Over the past several decades, chemists have developed such a method, which is based on the hypothesis that a molecule will adopt the shape that minimizes the electrostatic repulsions between electrons.

Since electrons are negatively charged and therefore repel one another, it is certainly reasonable to assume that their electron clouds will be as far apart as possible. Furthermore, wave mechanics reveals that the close approach of electrons of opposite spin is more likely than the close approach of electrons of the same spin. Thus, electrons of opposite spin will tend to group in pairs, and a molecule will adopt a geometry that minimizes repulsions between these pairs. This is the basis for the **valence shell electron pair repulsion model** (VSEPR) for the prediction of the geometry of molecules.



Levorphan

Dextrophan

Figure 7.1 The structures of levorphan and dextrophan.

In order to predict this geometry for a given molecule, we first need to know how many pairs of electrons are in the valence shell of each atom. This can be determined most simply from the electron dot formula for the molecule. Not all of the electron pairs shown in the electron dot formula are considered, however. For example, a pi-bond is directed along a sigma bond and therefore we assume that

the geometry about a given atom is determined by the number of sigma-bonded and nonbonded pairs of electrons at that atom.

As a first example, consider beryllium chloride. Two plausible electron dot formulas are:

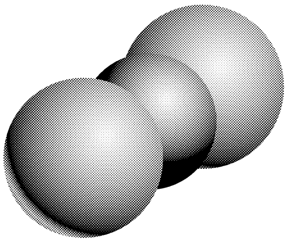
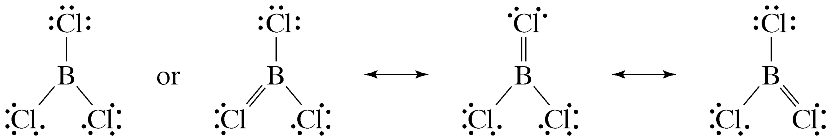


Figure 7.2 Computer Model of $BeCl_2$.

Both show two sigma-bonded pairs but no nonbonded pairs about the central beryllium atom. Hence, the two electron pairs must be positioned about beryllium in a way that will minimize the repulsions between them. Clearly, this can be accomplished by placing them on opposite sides of the beryllium on a straight line, leading to a prediction that the molecule is **linear** with a bond angle of 180°. The experimentally determined structure of gaseous $BeCl_2$ is indeed linear. A computer-generated view of $BeCl_2$ is shown in Figure 7.2.

The electron dot formula for boron trichloride can be written as

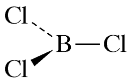


In any one resonance form, there are three sigma-bonded electron pairs, and by the application of simple geometry it can be shown that the separation of the three pairs is maximized if these pairs point toward the corners of an equilateral triangle. The bond angle should therefore be 120°, and the molecular shape can be characterized as **trigonal planar** (see Figure 7.3).

Problem 7.1

Draw BCl_3 in three-dimensional perspective. Since this will be your first attempt at depicting geometry on a two-dimensional surface you will need to know about a couple of conventions: a) Use a wedge to show a bond sticking out of the surface toward you. b) Use a dotted line to show a bond extending behind the plane of the surface (away from you). c) Use a solid line to indicate bonds in the plane of the surface. d) Position wedges, dotted lines, and solid lines at angles that will give the best representation of the geometry of the molecule.

Solution:



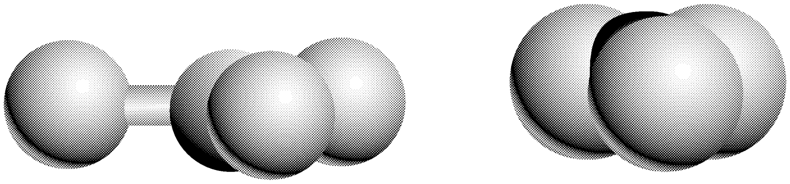
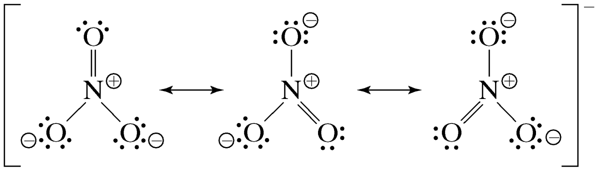


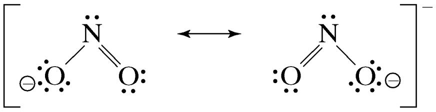
Figure 7.3 Computer Models of BCl_3. A ball-and-stick model is shown on the left and a space-filling model on the right.

The nitrate ion can be described as a resonance hybrid of three electron dot formulas:



Each formula shows three sigma-bonded pairs of electrons, so the shape of this ion is also trigonal planar.

A third example of a species with three electron pairs directed toward the corners of a triangle is the nitrite ion:



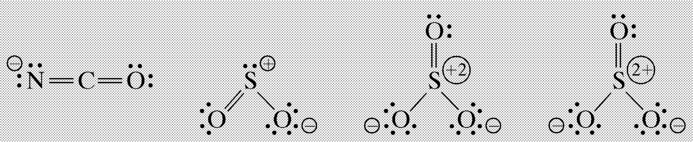
One of the pairs is a nonbonded pair, however, and since the shape of a molecule or ion is determined by the positions of the **atoms**, this ion is described simply as **angular** or **bent**.

Methodology 7.1

Describe the geometry of each of the following species: OCN^-, SO_2, and SO_3.

The first step in using the VSEPR theory is to write a correct electron-dot formula for the species.

One resonance structure for each of the species is shown below.



In the second step of the procedure we determine the number of sigma bonds and lone electron pairs.

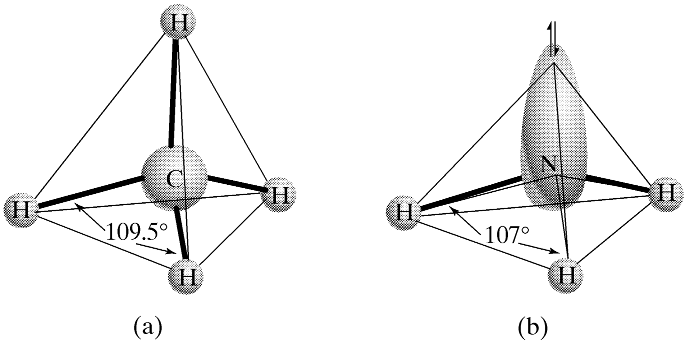
The central carbon of the cyanate ion has two sigma bonds surrounding it; the central sulfur of SO_2 has two sigma bonds and one lone pair; the central sulfur of SO_3 has three sigma bonds surrounding it.

Now we must determine how to arrange n pairs of electrons (the sum of the number of sigma bonds and the number of lone pairs of electrons) around a central atom in order to minimize the repulsions between them. What geometries do we use to minimize the repulsions between two and three pairs of electrons ($n = 2$ and $n = 3$)?

For $n = 2$ we direct the pairs to the opposite ends of a straight line. For $n = 3$, the repulsions are minimized when the pairs are directed to the corners of an equilateral triangle.

The final step is to describe the position of the atoms in the molecules.

The two electron pairs in OCN^- must be directed toward the opposite ends of a straight line, thereby making OCN^- a **linear** species. Both SO_2 and SO_3 have three electron pairs, whose repulsions can be minimized by locating them at the corners of an equilateral triangle. However, in SO_2 there are only two atoms at the corners of the triangle and this molecule is therefore described as **bent**. SO_3, on the other hand, has atoms at all three corners of the triangle and is described as **trigonal planar**.



(a) (b)

Figure 7.4 Molecular geometries of (a) methane, (b) ammonia.

The repulsions among four electron pairs are minimized if they are directed toward the corners of a regular tetrahedron. Methane has four sigma-bonded pairs and is therefore a **tetrahedral** molecule (Figure 7.4a). Ammonia has three sigma-bonded pairs and one nonbonded pair of electrons about its central nitrogen atom. Although these four electron pairs are tetrahedrally disposed about the central atom, the arrangement of the atoms in ammonia is described as **pyramidal** (Figure 7.4b). Another example of a molecule whose central atom is tetrahedrally surrounded by electron pairs is water. Since the hydrogen atoms are attached to only two of the pairs, the shape of the molecule is denoted as **bent** (Figure 7.5 shows molecular models of H_2O, NH_3, and CH_4).

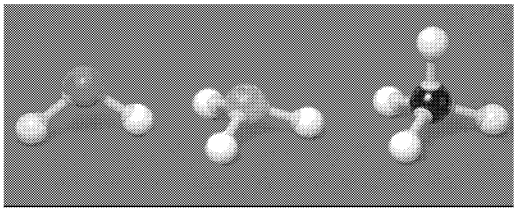


Figure 7.5 Molecular models of H_2O, NH_3, and CH_4.

Empirically, it has been found that most compounds of the type AB_5 with five bonded and no nonbonded pairs of electrons about the central atom have a **trigonal bipyramidal** structure (Figure 7.6). This configuration, shown in Figure 7.7 for phosphorus pentachloride (the ball-and-stick model on the right is a computer-generated representation of PCl_5) has bond angles of 90° between the bonds in the equatorial plane and the bonds on the axial positions and 120° between the bonds in the equatorial plane.

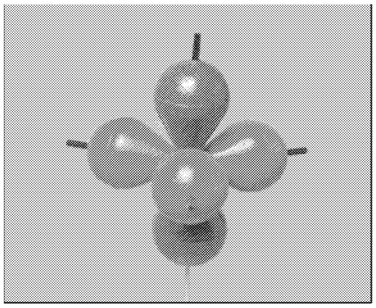


Figure 7.6 The Trigonal Bipyramidal Arrangement of Five Electron Pairs. The light gray areas represent pairs of electrons in the equatorial plane, while the dark gray areas are the axial positions.

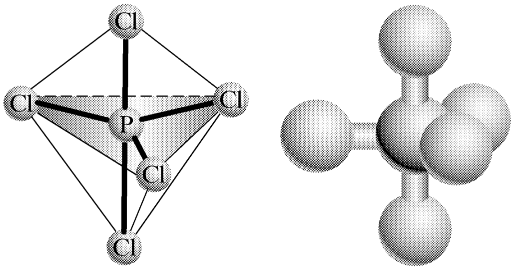


Figure 7.7 Representations of PCl_5.

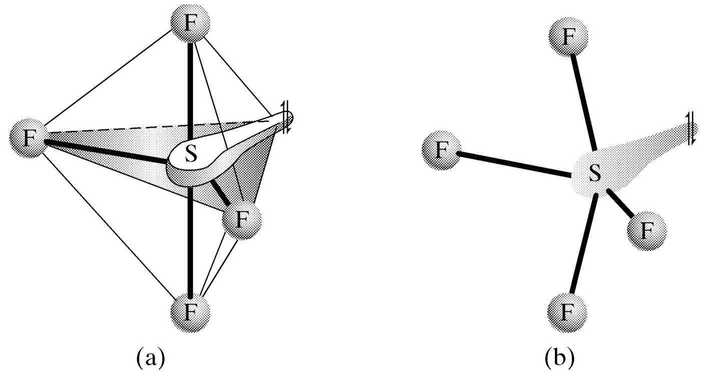


Figure 7.8 The geometry of SF_4: (a) An idealized geometry, and (b) The actual geometry.

It has also been found that when one or more of the five pairs of electrons are nonbonded pairs, these nonbonded pairs are positioned on the equatorial plane of the trigonal bipyramid. Sulfur tetrafluoride, therefore, has the shape given in Figure 7.8. Actually, the structure of SF_4 is not quite that shown in part (a). Instead, the angle between the axial fluorines is somewhat less than 180°; that is, they "lean" toward the other fluorines, as shown in part (b). This distortion of the trigonal bipyramid can be explained in terms of the repulsions between the electron pairs. Because bonded pairs are attracted to two nuclei rather than one, the electron density of these pairs is less "spread out" than the electron density of nonbonded pairs (see Figure 7.9). Therefore two bonded pairs do not repel each other as strongly as a nonbonded pair and a bonded pair. For the same reason, the repulsion between two nonbonded pairs is greater than that between a nonbonded pair and a bonded pair.

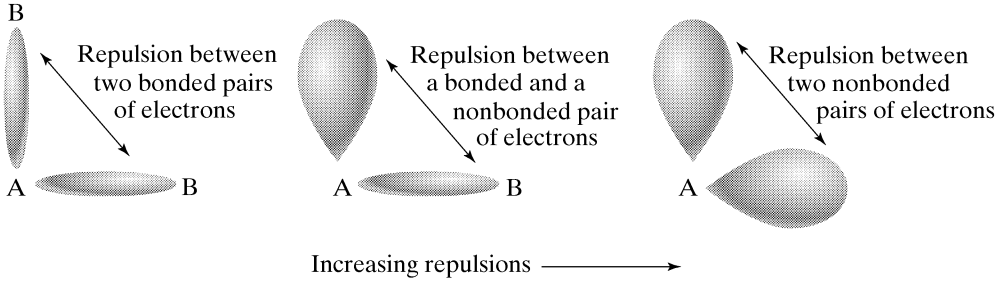


Figure 7.9 The relative repulsions of bonded and nonbonded electron pairs.

Chlorine trifluoride is an example of a molecule with five electron pairs, two of which are nonbonding, about the central atom. Both nonbonded pairs reside in the equatorial plane, giving the molecule a T-shape (Figure 7.10). The actual bond angle of 87°, slightly less than 90°, can again be rationalized by nonbonded-bonded electron repulsions.

The repulsions among six pairs of electrons can be minimized by placing them at the apexes of an octahedron (Figure 7.11). In the ion SiF_6^{2-}, for example, the silicon is sur-

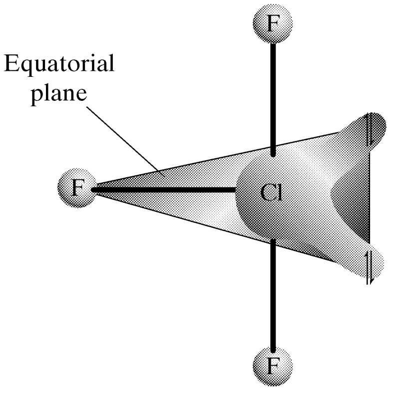


Figure 7.10 The structure of ClF_3.

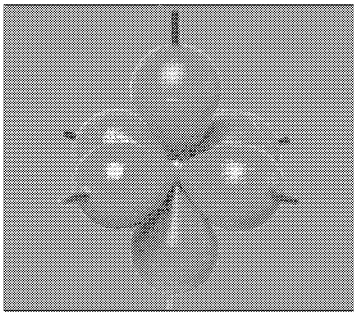


Figure 7.11 The octahedral arrangement of six electron pairs.

rounded by an octahedron of fluorines and thus the shape of the ion is designated as octahedral , with bond angles of 90° (Figure 7.12).

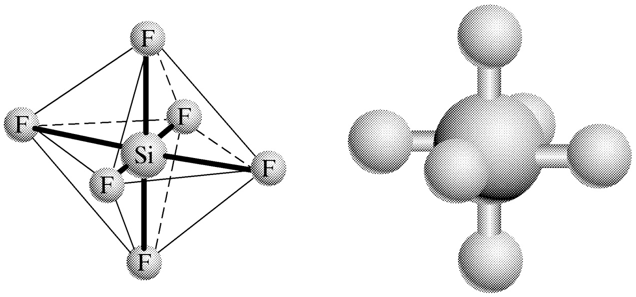
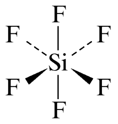


Figure 7.12 The octrahedral shape of SiF_6^{2-}

Problem 7.2

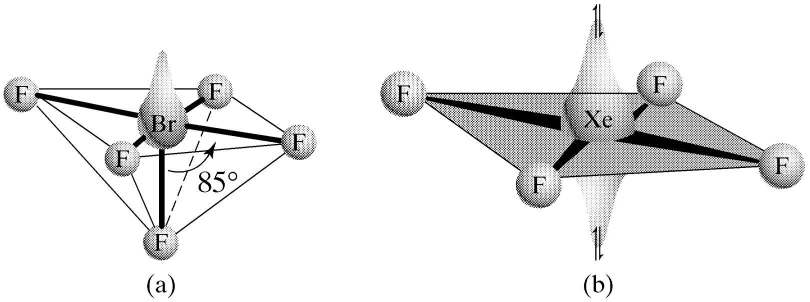
Draw a three-dimensional perspective of SiF_6^{2-}.

Solution:



When one of the six pairs of electrons is nonbonding, the structure of the molecule can be described as a **square pyramid**. Bromine pentafluoride is an example of such a molecule; its structure is shown in Figure 7.13. Again, the deviation of the bond angle from 90° can be attributed to greater repulsions between the lone pair and the Br—F bonds than between adjacent Br—F bonds.

Xenon tetrafluoride also has six pairs of electrons about the central atom, but two of these are nonbonded pairs. To minimize the repulsions between these two pairs, they are positioned as far apart as possible. As shown in Figure 7.13(b), this results in a **square planar** geometry for XeF_4.



(a)

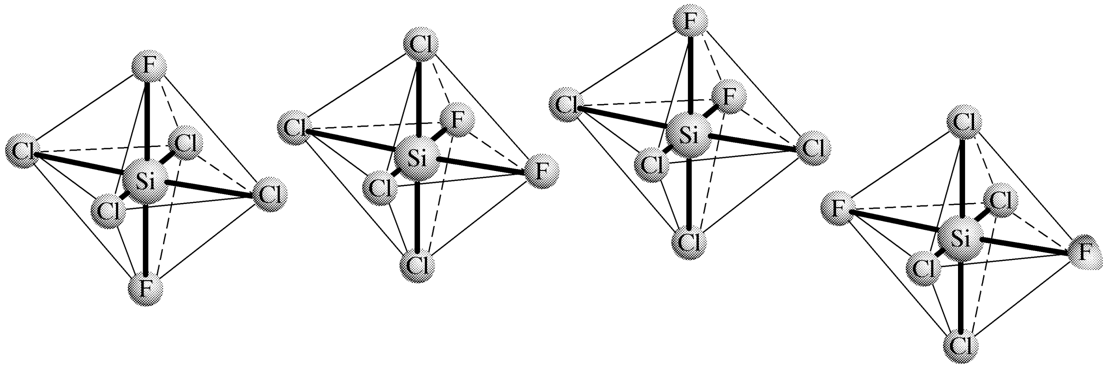
(b)

Figure 7.13 (a) The square pyramidal structure of BrF_5, and (b) the square planar structure of XeF_4.

Now that we have examined the molecular structure of several types of compounds using our predictive approach, let us briefly review the principles of this approach: The geometry of a molecule or ion is determined by repulsions between the sigma and nonbonded electron pairs about the central atom, and the shape adopted is the one that minimizes these repulsions. Since the strength of the repulsions varies among bonded and nonbonded electron pairs (nonbonded-nonbonded > nonbonded-bonded > bonded-bonded), this factor must be considered in the prediction of molecular shapes. Table 7.1 provides a summary of molecular geometry and the corresponding hybridization.

Visualization 7.1

In the ion $SiCl_4F_2^{2-}$ there are several different ways to position the fluorines in an octahedral structure. Among the structures shown below, only two are different. Decide which structures are the same.



(a) (b) (c) (d)

Solution:

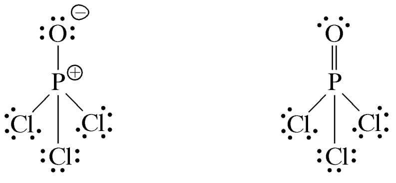
Structures (a) and (d) are the same; (b) and (c) are the same

Problem 7.3

Predict the shape of $OPCl_3$.

Solution:

Two acceptable electron dot formulas for this compound are illustrated here as I and II.



I II

Continued on next page

TABLE 7.1 Summary of the Geometry of AB_n Species

NUMBER OF SIGMA BONDING AND NONBONDING ELECTRON PAIRS ABOUT CENTRAL ATOM	NUMBER OF NONBONDING PAIRS	EXAMPLES	SHAPE	HYBRIDIZATION	BOND ANGLE
2	0	$BeCl_2(g)$ CO_2, $HgCl_2$, N_3^-	linear	*sp*	180°
3	0	BCl_3, CO_3^{2-}, NO_3^-	trigonal planar	sp^2	120°
3	1	NO_2^-	bent	sp^2	120°
4	0	CH_4, BF_4^- SO_4^{2-}	tetrahedral	sp^3	109.5°
4	1	NH_3, H_3O^+	pyramidal	sp^3	107.3°
4	2	H_2O, SCl_2	bent	sp^3	104.5 & 101.0°
5	0	PCl_5, $AsCl_5$	trigonal bipyramidal	sp^3d	90°, 120°
5	1	SF_4, $TeCl_4$	see-saw	sp^3d	90°, 120°
5	2	BrF_3	T-shaped	sp^3d	90°
5	3	I_3^-	linear	sp^3d	180°
6	0	SiF_6^{2-}	octahedral	sp^3d^2	90°
6	1	BrF_5	square pyramidal	sp^3d^2	90°
6	2	ICl_4^-, XeF_4	square planar	sp^3d^2	90°

Problem 7.3 *Continued*

Solution: *Continued*

Both formulas show four sigma-bonded electron pairs and no nonbonded pairs about the central atom. In order to minimize repulsions, these pairs must be directed toward the corners of a tetrahedron. The molecule could be described as tetrahedral, although it cannot have the shape of a regular tetrahedron because there are two different kinds of atoms (and therefore two different bond lengths) surrounding the central atom.

The bond angles would be predicted to be approximately 109° and the hybridization is sp^3.-

Check Point 7.1

What is the geometry of the chlorate ion?

Solution:

pyramidal

◇ ◇ ◇ ◇ ◇

Methodology 7.2

Explain the fact that BF_3 does not have a dipole moment, whereas both NF_3 and ClF_3 do.

What determines whether a molecule has a dipole moment?

> The magnitude of a molecule's dipole moment depends on (a) the difference in electronegativities between the atoms within the molecule and (b) the geometry of the molecule.

What does the difference in electronegativities between the atoms in a bond indicate?

> This difference tells us whether (and how much) the electron density in the bond between the atoms is unequally distributed. If there is a difference in electronegativities, the bond will have a bond moment; that is, an unequal distribution of electron density.

Which bond—the B—F, the N—F, or the Cl—F bond—has the greatest bond moment?

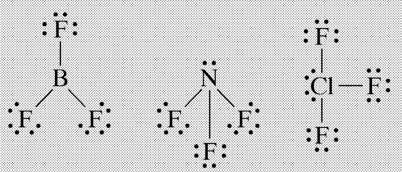
> Since the electronegativity difference is greater between boron and fluorine than between nitrogen and fluorine or between chlorine and fluorine, the B—F bonds in BF_3 are almost certainly more polar (have a greater bond moment) than the N—F bonds in NF_3 or the Cl—F bonds in ClF_3.

If the bond moment for the B—F bonds is greater than the moments for the bonds in the other molecules, why is the dipole moment for BF_3 zero?

> The dipole moment for the molecule depends upon the orientation of the bond moments. In fact, the dipole moment can be obtained by vector addition of the bond moments. The fact that BF_3 has no dipole moment, whereas NF_3 and ClF_3 do, can therefore be attributed to a difference in geometries.

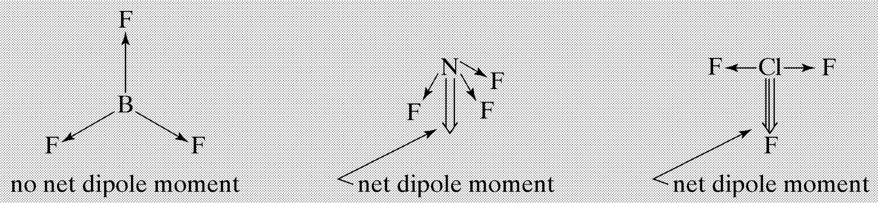
Apparently, then, the structures of these three molecules must be different. What are the structures?

> Examination of electron dot formulas for the three molecules shows that BF_3 has no nonbonded electron pairs, NF_3 has one, and ClF_3 has two. Boron trifluoride is therefore a trigonal planar molecule with120° bond angles; nitrogen trifluoride has its electron pairs directed toward the corners of a tetrahedron and is a pyramidal molecule; chlorine trifluoride has its five electron pairs directed towards the corners of a trigonal bipyramid and is a T-shaped molecule.



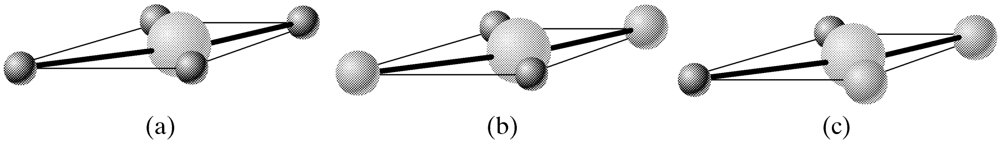
How can I determine that the bond moments in a trigonal planar structure cancel and therefore result in a zero dipole moment?

> It may be useful to imagine that you have an expensive vase sitting in the center of a table with three ropes attached to it. Each rope is directed toward a corner of an equilateral triangle. You now find two friends and each of you pull on one of the ropes with exactly the same force. In other words, the force you exert on your rope is analogous to the bond moment of the B—F bond. Now you must ask: Will the vase move? You can probably imagine that because of the symmetry of the arrangement of the ropes and the fact that you and your two friends are pulling with equal forces, that the vase, in fact, will not move. If you apply the same reasoning to ClF_3, you will discover that the vase will move toward the person that has no one directly across from her. The effect of shape on the dipole moment of each molecule is summarized below:



Visualization 7.2

The following diagrams show the structures of $XeCl_4$ and $XeCl_2F_2$. Predict which has a dipole moment.



Solution:

(a) and (b) have zero dipole moments. In (c) the Xe—F and Xe—Cl bond moments do not cancel, and, consequently, the molecule has a dipole moment.

Problem 7.4

The dipole moments for PCl_3 and PCl_5 are 2.5 and 0 D. Explain.

Solution:

Although the P—Cl bond is polar, in the high symmetry molecule PCl_5, which has five sigma bonds and therefore a trigonal bipyramidal shape, the P—Cl bond moments cancel. For pyramidal PCl_3, on the other hand, the moments add in, as previously described in Methodology 7.2 for NF_3.

7.2 THE DYNAMICS OF MOLECULAR GEOMETRY

Our previous discussion of structure and bonding may have produced the impression that molecules are rather rigid, static objects containing atoms held at fixed positions within the molecule. Experimental evidence suggests, however, that the atoms within molecules, and the molecules themselves, are in constant motion. These motions can be divided into the following categories: translational motion of the entire molecule, rotation of the molecule, vibration of atoms within the molecule, and rotations of atoms and groups within the molecule.

When a molecular substance is in either the liquid or gaseous state, each molecule is free to move throughout the entire volume of the substance. This motion is termed **translation** and is essentially a random, straight-line motion. When the substance is in the solid state, the molecules are fixed in their lattice positions (they do vibrate about these positions, however) and thus there is no net translational movement.

While a molecule in the liquid or gaseous states is translating through space, it also undergoes a tumbling motion. The atoms within a molecule are also in continual vibratory motion.

It has also been shown experimentally that within polyatomic molecules there is rotation of groups that are attached by single bonds. This rotation of groups is a consequence of the cylindrical symmetry of sigma bonds. That is, the distribution of electron density of a sigma bond is not affected by the orientation of attached atoms, and therefore rotation of groups does not affect the energy of the bond.

As an example of more complex rotations, consider 1-propanol. Three of the many possible conformations of the molecule are presented in Figure 7.14 (Note that the word **conformations** is used to denote spatial orientations resulting from rotation about single bonds.)

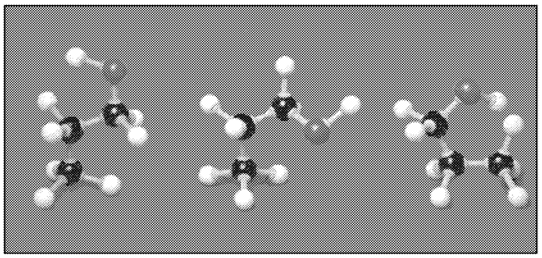


Figure 7.14 Several conformations of 1-propanol.

Now let us examine the possibility of rotation about double bonds. For example, do the CH_2 groups of ethene* rotate relative to each other? The valence bond description of ethene depicts the formation of the pi bond via overlap of p_z orbitals on the carbon atoms. If one CH_2 group were to rotate 90° relative to the other (Figure 7.15), the p_z orbitals would be perpendicular rather than parallel, and their electron densities would no longer overlap. Thus, rotation of the CH_2 groups necessarily destroys the pi bond and is therefore energetically unfavorable. At room temperature, then, groups do not rotate about double bonds. But when sufficient energy (through heating or absorption of a photon) is available to break the pi bond, this type of rotation is possible.

7.3 ISOMERISM

The word **isomerism** is derived from the Greek word **isomeres**, meaning "of equal parts." In chemistry the word is used to designate two or more compounds that contain the same (equal) atoms but differ in the arrangement of these atoms. The arrangement of atoms can differ in (a) the way in which they are linked together, or (b) their spatial orientation. Correspondingly, there are two principal types of isomers: **Structural isomers** have the same molecular formula but different structural formulas, whereas **stereoisomers** have the same structural formula but different three-dimensional arrangements of the atoms.

Structural Isomers

As an illustration of structural isomerism, consider the seven compounds that have the molecular formula $C_4H_{10}O$. Their structural formulas are given in Table 7.2. Within this set of **structural isomers**, the alcohols are sometimes said to be **functional group isomers** of the ethers; that is, the alcohols have the same molecular formula as the ethers but a different functional group (see Methodology 7.3). Also, the compounds 1-butanol and 2-methyl-1-propanol are sometimes called **chain isomers** because they have the same molecular formula and functional group but different branching on the alkyl chain. Finally, the

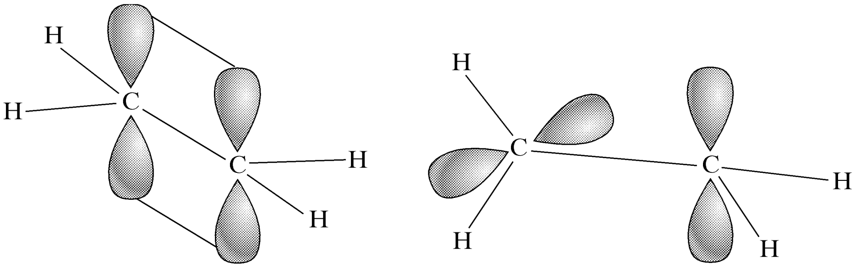


Figure 7.15 Overlap and rotation of the p_z orbitals in ethene

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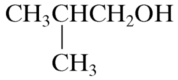
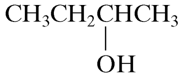
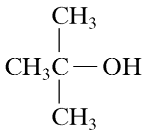
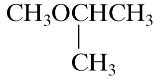
* Ethene has the formula $H_2C{=}CH_2$ and is the simplest alkene. The alkenes are one member of the family of organic compounds called the hydrocarbons. The hydrocarbons contain skeletons made up of carbon-carbon bonds. The simplest type of hydrocarbon is the alkane family, which contains only carbon-carbon single bonds. For example, $H_2C{-}CH_2$ is ethane. The alkenes contain at least one carbon-carbon double bond. Ethene is the simplest alkene. All of the atoms lie in the same plane. See the Descriptive Booklet on The Nomenclature of Organic Compounds in the electronic version of this text.

TABLE 7.2 Structural Isomers with the Molecular Formula $C_4H_{10}O$

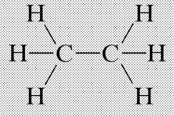
$CH_3CH_2CH_2CH_2OH$	1-butanol
 $CH_3\underset{\begin{array}{c}\vert\\CH_3\end{array}}{C}HCH_2OH$	2-methyl-1-propanol
 $CH_3CH_2\underset{\begin{array}{c}\vert\\OH\end{array}}{C}HCH_3$	2-butanol
 $CH_3\overset{\begin{array}{c}CH_3\\\vert\end{array}}{\underset{\begin{array}{c}\vert\\CH_3\end{array}}{C}}—OH$	2-methyl-2-propanol
$CH_3CH_2OCH_2CH_3$	ethyl ether
$CH_3OCH_2CH_2CH_3$	methyl *n*-propyl ether
 $CH_3O\underset{\begin{array}{c}\vert\\CH_3\end{array}}{C}HCH_3$	methyl isopropyl ether

compounds 1-butanol and 2-butanol are sometimes referred to as **position isomers** because they differ only in the position of the —OH group. The methyl ethers in the table are also position isomers.

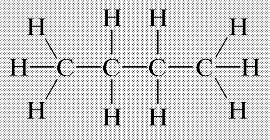
Methodology 7.3

Give the structural formulas for the structural isomers of butanal.

First, let us briefly discuss the structures of organic compounds. All organic compounds contain carbon and hydrogen and usually also elements such as oxygen and nitrogen. The simplest type of organic compound is the hydrocarbon which contains carbons linked together by single, double, or triple bonds. The alkanes contain only C—C single bonds. For example:



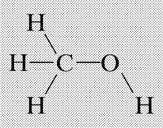
is ethane, and



is butane. Compounds with at least one C=C bond are alkenes. It is important to recognize that in these structures, each carbon has four bonds. In general, in organic compounds, each carbon has four bonds, each oxygen has two bonds, each nitrogen has three bonds, and each hydrogen and halogen has one bond.

When the hydrocarbons contain certain types of groups (functional groups), their reactivity is quite different. Some of the most important functional groups are:

(1) Alcohols, which have an OH group, for example, methanol:



which is also written as CH_3OH.

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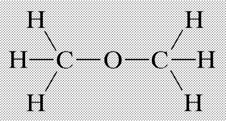
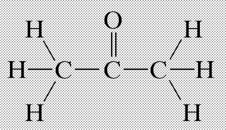
Methodology 7.3 Continued

(2) Ethers which have two carbons attached to an oxygen, as in dimethyl ether



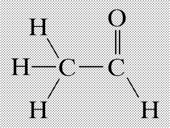
Dimethyl ether contains two methyl groups and is also written as CH_3OCH_3.

(3) Ketones, which contain the carbonyl group C=O and two carbons, both attached to the carbon of the carbonyl group. For example, the simplest ketone is propanone (or dimethyl ketone):



and is also written as CH_3COCH_3.

(4) Aldehydes, which contain the carbonyl group and at least one hydrogen attached to the carbon of the carbonyl group. For example,



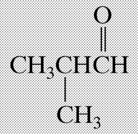
is called ethanal or acetaldehyde.

Butanal contains four carbons and is an aldehyde (Notice that the ending of the name provides a hint about the functional groups: alcohols are alkanols, ketones are alkanones, aldehydes are akanals.) Write the structural formula and molecular formula for butanal.

$\mathrm{CH_3CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}$ C_4H_8O

Can you think of a structural isomer of butanal that has the same functional group?

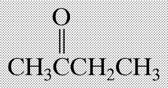
This is always a good way to start a problem like this; that is, start with compounds that contain the same functional group but have a different carbon skeleton (branching) or different placement of substituents. In the case of butanal, there is only one compound that is also an aldehyde and is a structural isomer—2-methylpropanal:



$\mathrm{CH_3}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}$

Can you think of a structural isomer with a different functional group, but one that contains a carbonyl group?

Butanal has only one oxygen, so our structural isomers can also have only one oxygen. The only other functional group with one carbonyl is the ketone. The only ketone with four carbons is butanone.



$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CH_3}$

Can you think of compounds that have functional groups that do not contain a carbonyl? These compounds must have four carbons, eight hydrogens, and one oxygen.

Other functional groups that contain oxygen but do not contain a C=O are alcohols and ethers. It is important to realize that when you switch from a doubly bonded oxygen to a

Continued on next page

Methodology 7.3 Continued

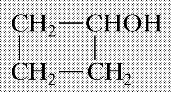
singly bonded oxygen you are adding two more hydrogens. Thus, two hydrogens must be removed from somewhere in the remainder of the molecule in order to maintain the same number of hydrogens.

How can I remove two hydrogens from the rest of the molecule?

There are two ways to remove two hydrogens: a) by introducing a C=C bond in the carbon skeleton, or, b) by making a ring out of the skeleton. An example of a structural isomer with the alcohol functional group and a C=C bond is 1-hydroxy-2-butene:

$$CH_3CH{=}CHCH_2OH$$

An example of a cyclic compound with the alcohol functional group is cyclobutanol:

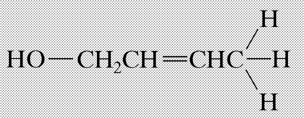


Are these the only structural isomers of butanal?

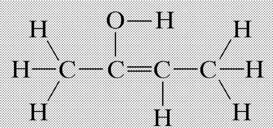
No, remember that we have not formed any ethers, for example 1-methoxy-1-propene (note that the CH_3O group is called the methoxy group):

$$CH_3CH{=}CHOCH_3$$

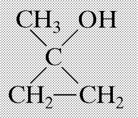
We can also change the position of the OH, for example, in the alcohols. Thus, 2-hydroxy-1-butene, 3-hydroxy-1-butene, and 4-hydroxy-1-butene are all structural isomers of butanal. We can also change the position of other parts of the molecule; for example, the double bond in the unsaturated alcohols. Thus, 1-hydroxy-2-butene and 2-hydroxy-2-butene are both structural isomers.

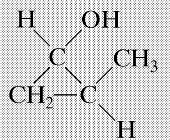


and



Some other structural isomers of butanal are 1-methyl-1-cyclopropanol, 2-methyl-1-cyclopropanol, and ethyl vinyl ether (note that the CH=CH2 group is called vinyl).

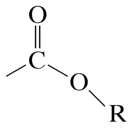




$$CH_3CH_2OCH{=}CH_2$$

Problem 7.5

Give the structural formulas of at least three structural isomers of methyl acetate ($CH_3CO_2CH_3$). This compound contains the



functional group (R stands for some group like methyl (CH_3), ethyl (CH_3CH_2–), propyl ($CH_3CH_2CH_2$–), and butyl ($CH_3CH_2CH_2CH_2$–) which is the ester functional group. The

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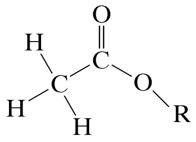
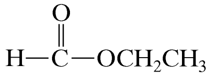
Problem 7.5 *Continued*

carboxylic acid group is very similar except that it has a hydrogen in place of the R group. For example, acetic acid (or ethanoic acid) is

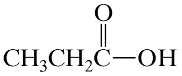


Solution:

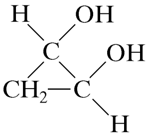
Ethyl formate, propanoic acid, 1,2-dihydroxycyclopropane



$$H{-}\overset{\overset{\large O}{\|}}{C}{-}OCH_2CH_3$$



$$CH_3CH_2\overset{\overset{\large O}{\|}}{C}{-}OH$$



Stereoisomers

There are also several types of stereoisomerism. We know that the three-dimensional orientation of atoms is influenced by rotation about single bonds and lack of rotation about double bonds. While rotation about single bonds produces different conformations of atoms, and one conformation may be more stable than another, the rotation is so rapid at room temperature that these **conformational isomers** cannot be isolated. Two conformations are shown in Figure 7.16 for 1,2-dichloroethane. The first conformation (left-hand side) is the more stable of the two but rapid rotation prevents its isolation at room temperature.

Geometric Isomerism. The absence of rotation about double bonds at room temperature results in a second type of stereoisomers, known as **geometrical isomers**. As an example, the structural formula of 2-butene is $CH_3CH{=}CHCH_3$, but there are two compounds with this formula. One compound, called *cis*-2-butene, has both methyl groups on the same side of the double bond (remember that the carbon skeleton is planar, since the middle carbons are sp^2 hybridized); the other compound, called *trans*-2-butene, has the methyl groups on opposite sides of the double bond. The *cis-trans*

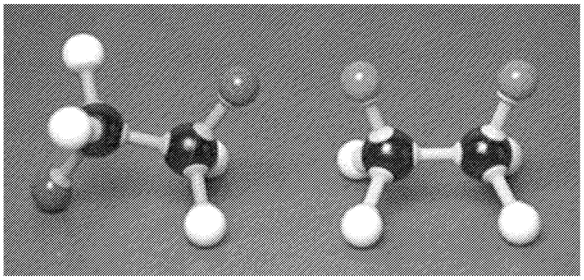
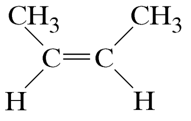
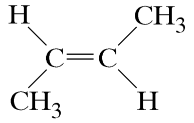


Figure 7.16 Two conformations for 1,2-dichloroethane.

nomenclature is derived from the Latin words *cis*, meaning "on this side," and *trans*, meaning "across."



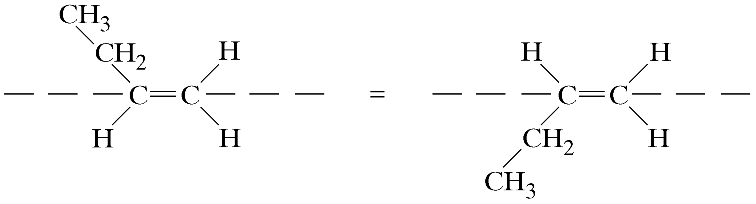
cis-2-butene



trans-2-butene

These two compounds, like all geometrical isomers, have different physical and chemical properties. For example, *cis*-2-butene has a boiling point of 1.0 °C, while the boiling point of *trans*-2-butene is 2.5 °C.

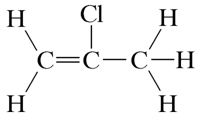
The presence of a double bond is not a sufficient condition for geometrical isomerism. While two compounds have the structural formula of 2-butene, there is only one compound with the structural formula of 1-butene, $CH_3CH_2CH{=}CH_2$. As shown below, shifting the ethyl group from one side of the double bond to the other does not produce a different compound, since this shift can be accomplished by rotating the structure 180° about the C=C axis (dashed line).



Likewise, rotation about the C=C bond in 1,1-dichloroethene produces the same compound; rotation about the C=C bond in 1,2-dichloroethene produces a different compound. These geometrical isomers of 1,2-dichloroethene are not superimposable* nor can they be interconverted† at room temperature. Thus, a necessary condition for geometrical isomerism in alkenes is the presence of two *different* groups attached to each of the double-bonded atoms (Figure 7.17).

Problem 7.6

Give the name of a structural isomer of 2-chloro-1-propene



that exhibits geometrical isomerism.

Solution:

1-chloro-1-propene

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* It is important to be clear about the meaning of superimposable. The molecule that results from rotation about the C=C bond is identical to the original molecule; that is, all of the atoms would be matched up. On the other hand, the geometrical isomers of 1,2-dichloroethene can not be superimposed. In order to be clear about this, you should obtain a model kit, make the models, and try to superimpose them.

† This is one of many words or phrases that contain one of the two prefixes—inter or intra. "Inter" means between two things, while "intra" means within one thing. For example, intercollegiate sports are those played between two colleges, whereas intramural sports are those played within the walls of one institution. The term interconverted means converted between two forms.

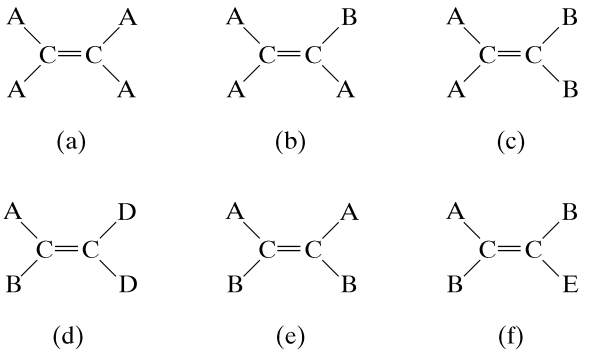
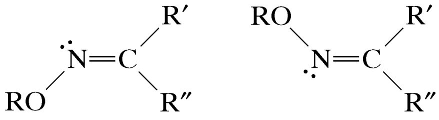


Figure 7.17 Some possible structures of alkenes; only structures (e) and (f) exhibit geometrical isomerism.

Geometrical isomerism is not restricted to alkenes. Many compounds containing a nitrogen-nitrogen or carbon-nitrogen double bond, for example, are found to exhibit geometrical isomerism. In the geometrical isomers below, the lone pair of electrons on each nitrogen functions as the other "group" in the configuration.

cis *trans*

Oximes have the general formula RON=CR′R″ and can exist as isomers when R′ and R″ are different groups.



A fascinating example of the presence of geometrical isomerism in biological processes is provided by the visual pigment, rhodopsin, found in the retina of the eye. Rhodopsin consists of an alkene attached to a protein. The alkene, called retinal, can exist as a number of geometrical isomers. When it is firmly attached to the protein, it exists in the form shown in Figure 7.18. This form is referred to as 11-*cis*-retinal because all the hydrogen and methyl groups attached to the alkene chain are *trans* to one another except for those at the number 11 and 12 carbons. When light strikes the eye, sufficient energy is imparted to the 11-*cis* isomer to produce a rotation about the number 11-number 12 carbon-carbon double bond. This rotation is, in effect, a rotation of the entire group shown in the tinted portion of the figure and results in the all-*trans* isomer (Figure 7.19). It is this isomerization and accompanying changes in the attachment to the protein that allow the perception of light by the eye.

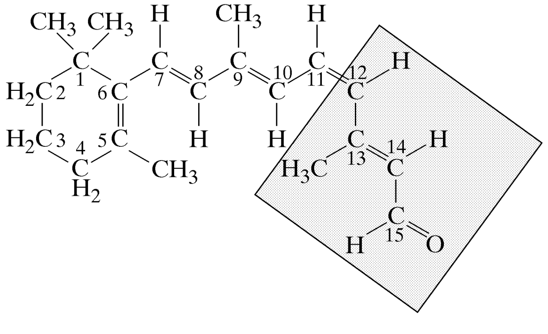


Figure 7.18 11-*cis*-retinal.

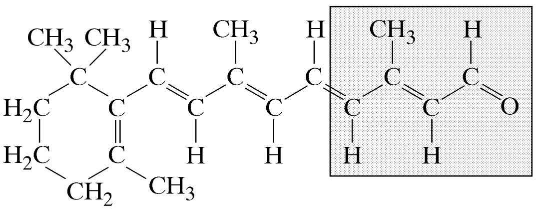
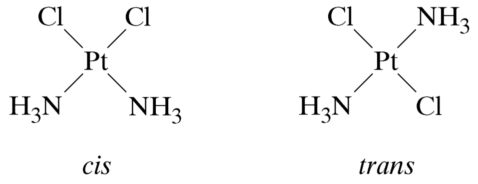
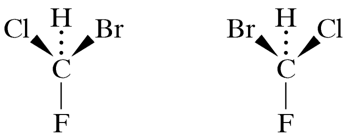


Figure 7.19 All *trans*-retinal.

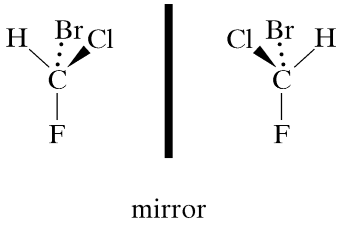
Geometrical isomerism can also occur in compounds that do not contain double bonds, such as in the square planar platinum compound $Pt(NH_3)_2Cl_2$. In this compound, the chlorine atoms can be either adjacent to each other (*cis*) or across from each other (*trans*). The *cis* isomer of this compound has the commercial name *cis* platin and has been found to be a powerful anti-tumor agent. The *trans* isomer shows little anti-tumor activity.



Optical Isomerism. A third type of stereoisomerism occurs with compounds that are nonsuperimposable mirror images. In bromochlorofluoromethane, for example, there are two possible arrangements of the three halogens about a fixed C—H bond, as shown below.

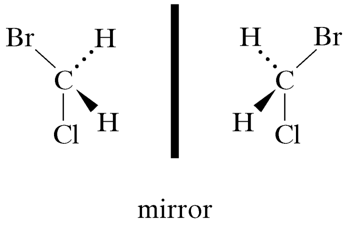


If the image of one configuration is reflected in a mirror, the image seen is that of the other configuration.



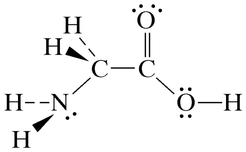
Since these two configurations cannot by any manner of rotation be made superimposable, they are not identical configurations.

The two analogous configurations of bromochloromethane, on the other hand, are superimposable and thus are identical. Thus, a sufficient condition for nonsuperimposable mirror images is the presence of *four different* groups attached to a carbon atom.



Problem 7.7

The simplest amino acid, glycine, has the formula $H_2NCH_2CO_2H$. Draw this molecule in three-dimensional perspective and then decide if it exhibits optical isomerism.



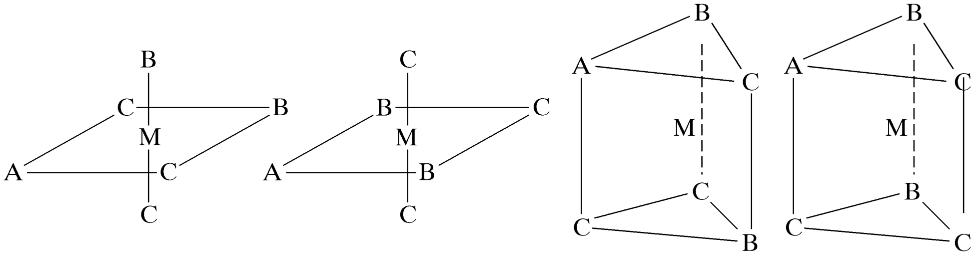
Solution:

It does not exhibit optical isomerism because the mirror image is superimposable on the original image. No atom has four different groups around it.

Experimentally, it has been observed that all except one of the physical properties of nonsuperimposable mirror images are identical. The one exception is the effect of the two configurations on plane-polarized light. As discussed in Chapter 3, light consists of electromagnetic waves, and these waves vibrate in all possible orientations along the path of the light beam (Figure 7.20). If a beam of light is passed through an appropriate filter, all of the oscillations except those confined to one plane are removed. The resulting electromagnetic

Visualization 7.3

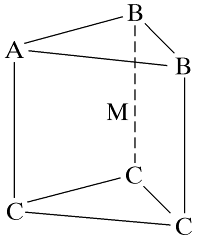
Before the octahedral structure was established for many molecules and ions that have a central atom surrounded with six groups, it was believed that molecules and ions could also adopt a prismatic structure. Examine closely the following structures for a compound of the type MAB_2C_3, where M is the central atom and A, B, and C surround the M atom. Which of these structures have nonsuperimposable mirror images?



(a) (b) (c) (d)

Solution:

All but (b) have nonsuperimposable mirror images. Can you draw a prismatic structure that does not have nonsuperimposable mirror images?



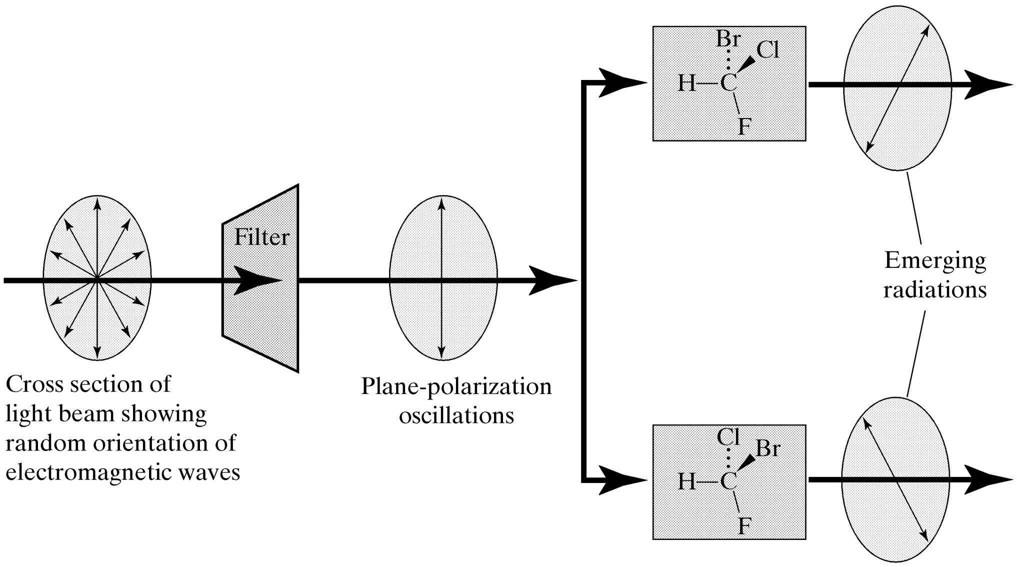
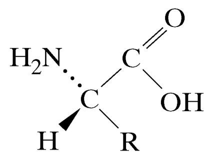
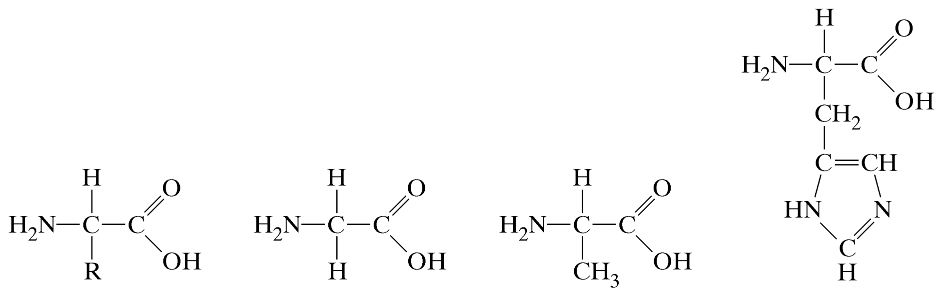


Figure 7.20 The interaction of nonsuperimposable mirror images with plane-polarized light.

radiation is plane-polarized light. When this light is passed through a substance whose molecules have one of the two configurations, the plane of the emerging radiation is rotated relative to the plane of the entering radiation. The same behavior is observed for the mirror image, except that the plane is rotated in the opposite direction (but by the same amount). For this reason, nonsuperimposable mirror images are termed **optical isomers**, or **enantiomers** (from the Greek *enantios*, "opposite"; *mer*, "form"). The isomers are usually distinguished by the designations *levo* (Latin: *laevus*, "left") and *dextro* (Latin: *dexter*, "right"), depending on the direction in which they rotate light. The property of nonsuperimposability on a mirror image is also referred to as **chirality** (Greek: *cheir*, "pertaining to the hand").

A biologically important example of optical isomerism is provided by the constituents of proteins, the amino acids. The general formula for the amino acids is given in Figure 7.21. All of the amino acids except the simplest one, glycine, in which R═H, have four different groups attached to the central carbon and can therefore exist in one or both of the two optically active configurations. But because of some peculiarity of chemical evolution, all the naturally occurring amino acids have the same configuration:



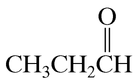


(a) General formula (b) Glycine (c) Alanine (d) Histidine

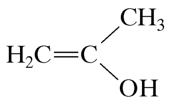
Figure 7.21 Some amino acids.

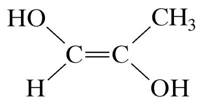
Problem 7.8

Determine which of the following compounds are structural isomers and which exhibit stereoisomerism:

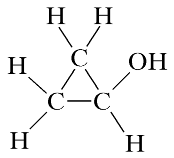
(a) 

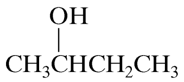
$CH_3CH_2\overset{O}{\overset{\|}{C}}H$

(b) 

(c) 

(d) $CH_3CH_2CH_2OH$

(e) 

(f) 

$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3$

Solution:

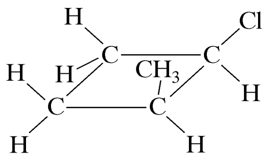
Compounds (a), (b), (c), and (e) all have the same molecular formula (C_3H_6O) but different structural formulas. Within this set of structural isomers, (a) is an aldehyde and (b), (c), and (e) are alcohols; thus (a) is a functional group isomer of (b), (c), and (e). Because the —OH group appears at a different carbon on the C═C—C chain of compounds (b) and (c), these are position isomers.

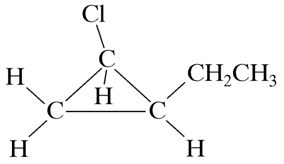
Compounds (c) and (f) exhibit stereoisomerism. Compound (c) can exist as *cis-trans* geometric isomers because of the two different groups attached to each carbon of the double bond. Compound (f) has a nonsuperimposable mirror image because of the four different groups attached to the second carbon and therefore exhibits optical isomerism.

Problem 7.9

Draw two cyclic structural isomers of 1-chloro-1-pentene ($CH_3CH_2CH_2CH{=}CClH$) that exhibit geometric isomerism.

Solution:





7.4 SPECTROSCOPY: ABSORPTION OF RADIANT ENERGY

Much of the information we possess about the structure of molecules comes from the manner in which they interact with electromagnetic radiation. When electromagnetic vibrations (a form of energy) impinge on matter, certain vibrations are selectively absorbed. Which specific vibrations a given substance will absorb is determined by the particular structure and thus the particular energies of that substance. Two different compounds, then, will absorb different frequencies of radiation, and each compound has its own unique **absorption spectrum**. The measurement of these spectra is called **absorption spectroscopy**.

Let us begin our discussion by examining the various types of energy that a molecule (or ion) possesses. **Nuclear energy**—energy associated with the composition of the molecule's nucleus—accounts for nearly all of the total energy of the molecule. The remainder of the energy may be divided into the following categories: **electronic energy**, or the energy of the molecule attributable to its electron distribution; **vibrational energy**, resulting from the vibratory motions of the atoms within the molecule; **rotational energy**, associated with the rotation of the molecule about its center of mass; and **translational energy**, the energy possessed by the molecule because of its translational (linear) motion.

Each of these four types of energy is quantized; that is, if the molecule loses or gains energy in any of these categories, the energy transfer must occur in the form of definite energy packets, called **quanta**. The quanta associated with changes in translational energy are so small that for practical purposes translational energy may be considered continuous, and translational energy changes are directly related to the absolute temperature. However, changes in electronic, vibrational, and rotational energy involve quanta of magnitudes that correspond to frequencies within the electromagnetic spectrum. Thus, these three energies of a molecule may be raised above the ground state (the lowest energy state of the molecule) by the absorption of electromagnetic vibrations. But since a molecule can absorb only those frequencies of radiation that correspond to energy transitions possible for that particular molecule, each different substance has its own unique absorption spectrum.

The quanta involved in electronic energy transitions are quite large compared with those for vibrational or rotational transitions, with the rotational quanta being the smallest. This relationship is illustrated schematically below, where ΔE_{rot}, ΔE_{vib}, and ΔE_{elect} represent transitions from the ground state to the next higher rotational, vibrational, and electronic states, respectively. Because of the difference in magnitude of these three types of energy transitions, each of the three absorbs energy from a different portion of the electromagnetic spectrum.

Electronic Spectra

Transitions in electronic energy are usually of such magnitude that they correspond to frequencies of radiant energy in the ultraviolet and visible portions of the electromagnetic spectrum. Therefore, molecules absorb specific, characteristic wavelengths from this spectral region.

Suppose we had a source of ultraviolet radiation of a single wavelength—say, 200 nm*—and we allowed that radiation to pass through a thin layer of some substance. (Radiation of a single wavelength is referred to as **monochromatic**.) Further, assume that we had some means of measuring the intensity of the beam both before it entered the substance and after it had passed through it. We could then determine the percentage of the radiation transmitted by the substance or, alternatively, the percentage absorbed by it. Now, after making this measurement, suppose we repeat the process using a monochromatic beam of wavelength 201 nm, then 202 nm, and so on through a large number of beams of progressively increasing wavelengths. If we then plot the percent transmission (or absorption) against wavelength, as shown in Figure 7.22, we would obtain the absorption spectrum of the substance. (Since the portion of the electromagnetic spectrum employed is in the ultraviolet region, this plot may also be referred to as an **ultraviolet spectrum**.) Note that our hypothetical compound transmits completely (shows no absorption) at wavelengths below approximately 250 nm and above 350 nm, and that it has an absorption maximum at about 290 nm. Therefore, the energy of radiation with a wavelength of 290 nm corresponds to an electronic energy transition of the compound.

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* Different regions of electromagnetic radiation usually have their own characteristic nomenclature for expressing the frequency or wavelength of the light. In the ultraviolet and visible regions, nanometers, nm (1×10^{-9} m), are used to express wavelength. In the infrared, wavelength is described in microns (m, 1 × 1026 m) and a special term—cm^{-1}—is used to express frequency.

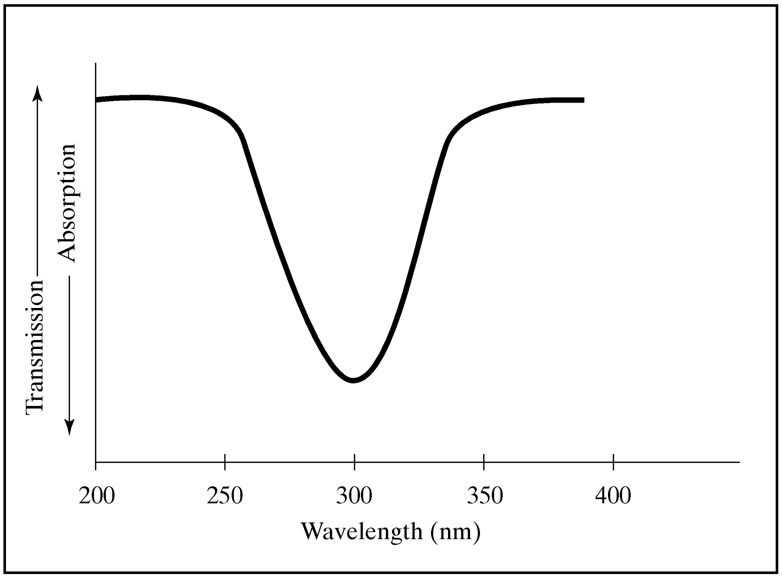


Figure 7.22 An ultraviolet absorption spectrum.

The ultraviolet spectra of several compounds, measured by an instrument known as a **spectrophotometer**, are shown in Figure 7.23. Note that the absorptions in these spectra occur as broad bands rather than as sharp lines. This observation raises the following question: Since an electronic transition is quantized, and therefore only radiation with a particular frequency can be absorbed, why does an absorption peak not appear as a single line at a specific wavelength? The answer is to be found in a consideration of the energy-level diagram shown above. Within each electronic energy level there are many vibrational and rotational levels, and transitions can occur from several vibrational and

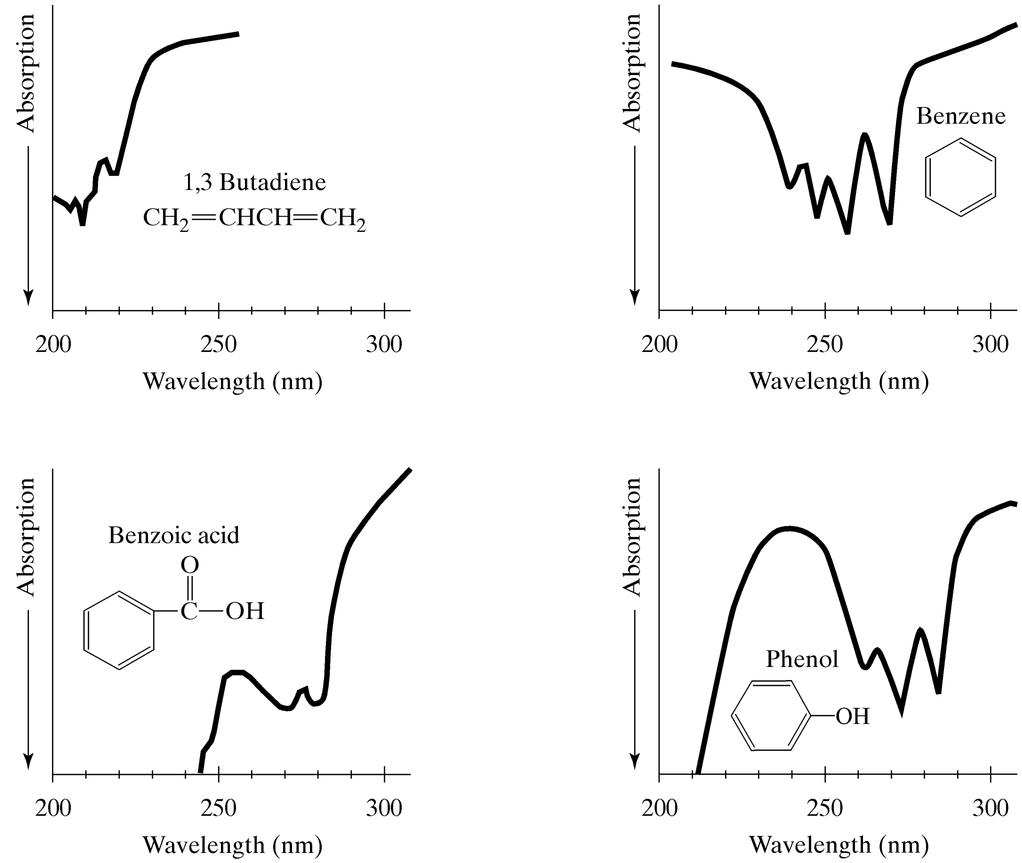


Figure 7.23 Some ultraviolet absorption spectra.

rotational levels of the electronic ground state to a number of the vibrational or rotational levels of the excited electronic state. Thus, an absorption peak really consists of many absorption lines, so closely spaced that it is beyond the power of the spectrophotometer to resolve them, and they appear as one continuous, smooth band.

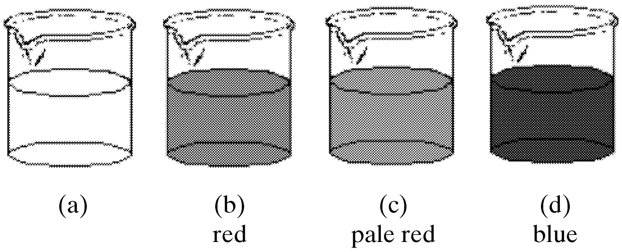
Color. Another important aspect of the electronic spectrum of a substance is its relationship to the color of that substance. The color that an object appears to be is determined by the wavelengths of light that travel from the object to the retina of the eye. In general, when light falls on an object, some of it may be absorbed by the object, some may be transmitted through it, and some may be reflected from it. If the object in question is opaque, then essentially no light is transmitted; it is either absorbed or reflected. In the case of translucent objects (including solutions), light is either absorbed or transmitted, with essentially none being reflected. The light that travels from the object to the eye, then, is light that has been either reflected or transmitted by the object; in other words, it is white light minus whatever has been absorbed by the object.

Substances whose electronic spectra consist of absorption bands entirely within the ultraviolet region are without color—they appear white in the solid state, and their solutions are colorless—for they reflect or transmit to the eye all wavelengths of the visible spectrum with equal intensity. On the other hand, a substance that absorbs radiation in the visible region of the spectrum is colored; the light that reaches the eye does not contain all wavelengths of white light in equal intensity. Thus, the color of an object is determined by those wavelength bands that are not absorbed. A solution containing permanganate ion is purple because that ion shows an absorption band in the region of 500–600 nm (the green-yellow region); that is, the green portion of the spectrum is absorbed, and the combination of the red and blue regions that are transmitted results in the purple color. Similarly, a red dye transmits the longer wavelengths of the visible spectrum (red) and absorbs the shorter wavelengths (violet, blue, green, and so on).

If the object being viewed is illuminated by light containing wavelengths of only part of the visible spectrum, its color may be different from that when viewed in white light. For example, consider a piece of cloth patterned with red polka dots on a blue background. In white light, the dots reflect the red portion of the spectrum and the background reflects the blue portion. If this same cloth is viewed in a room illuminated with blue light, the pattern will appear as black polka dots on a blue background. Since the light striking the cloth does not contain the red wavelengths, these wavelengths cannot be reflected, and the dots appear black.

Visualization 7.4

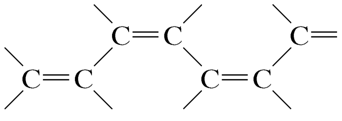
Which beaker will absorb the greatest amount of blue light?



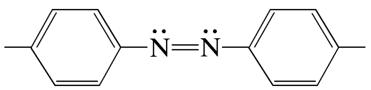
Solution:

Beaker (b) because it contains the most intense red solution. Beaker (a) will transmit all of the blue light because it is colorless; beaker (d) will transmit all of the light because it is blue and contains, therefore, no molecules that can absorb blue light. Beaker (b) and (c) appear to be red in white light because they absorb the blue region of the visible spectrum and reflect back to our eyes the red part of the spectrum.

Thus, the kinds of compounds we would expect to be colored are those whose structures permit electronic transitions of relatively low energy—low enough to correspond to frequencies in the visible portion of the electromagnetic spectrum. In general, more closely-space energy levels are found in molecules that have extended pi bonding (alternating multiple bonds); that is to say, in structures such as



This extended pi bonding results in delocalization of the pi electrons, making it "easier" for an electron to move to an unoccupied orbital of higher energy, since less energy is required for the transition. (Delocalization of electrons in a molecule has the same effect on the electronic energy levels as increasing the length of the line for a particle confined to a line: An increase in the length results in more closely spaced energy levels.) An illustration of the relationship between extended pi bonding and color is provided by the class of compounds known as azo dyes. This is an extensive group of yellow, orange, and red compounds, many of which contain the following structure within their molecules:



Another type of bonding condition that permits low-energy electronic transitions exists in compounds of the transition elements, for the transition metals form many highly colored ions, while most ions of the representative elements are colorless.

Cu^{2+}	blue	Na^{+}	colorless
Ni^{2+}	green	Ba^{2+}	colorless

Vibrational Spectra

We have already established that the quanta involved in changes in vibrational energy are considerably smaller than those involved in electronic energy changes. Therefore, vibrational spectra result from absorption of radiant energy of lower frequencies (longer wavelengths) than in the case of electronic spectra. Transitions in vibrational energy are caused by photons with wavelengths in the infrared portion of the spectrum, between approximately 1 μ and 100 μ. (In the infrared spectrum, it is customary to express wavelengths in terms of **microns**, μ, rather than nanometers; 1 μ = 1000 nm.)

Using instrumentation somewhat similar to that used for measuring electronic spectra, vibrational spectra can be recorded as the amount of infrared radiation transmitted (or absorbed) versus wavelength, or, as is commonly the case, versus cm^{-1} (the reciprocal of the wavelength expressed in centimeters, usually referred to as wavenumber). In most practical applications of infrared spectra, measurement is limited to the spectral region between 2.5 μ and 15 μ. As in electronic spectra, the absorptions in vibrational spectra appear as bands rather than lines, because a single vibrational energy change is accompanied by a number of rotational energy changes.

The vibrations that give rise to infrared absorption are of two kinds: stretching and bending. A **stretching vibration** occurs between two atoms along the bond that connects them and is analogous to two balls attached to a coiled spring that is alternately compressed and extended. Note that since the distance between the two atoms is continuously changing because of this vibration, a "bond length" is really an average value. In a diatomic molecule the stretching vibration can take only one form, but in a triatomic molecule there are two **stretching modes**: a symmetrical stretch, in which both bonds are being shortened or lengthened at the same time, and an asymmetrical stretch, in which one bond is shortened while the other is lengthened.

A **bending vibration** involves a change in bond angle. Thus, reported bond angles, like bond lengths, are only average values.

In order for a molecular vibration to result in absorption of infrared radiation, it must cause a rhythmical change in the dipole moment of the molecule. A change in the distribution of charge within the molecule is necessary for interaction between the molecule and the oscillating field of the infrared radiation. Thus, in a molecule such as CO_2, the asymmetrical stretch gives rise to an absorption band, but the symmetrical stretch does not, since it causes no change in the dipole moment.

Using the analogy between atoms connected by a bond and balls connected by a spring, we may apply Hooke's law of simple harmonic oscillators:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where ν is the vibrational frequency, k is the **force constant**, a measure of the stiffness of the spring or the strength of the bond, and μ is the **reduced mass**—the product of the masses of the balls (or atoms) divided by the sum of the masses. It is clear from this relationship that for each mode of vibration, the vibrational frequency (and therefore the wavelength of radiation absorbed) is determined by the strength of the bond between atoms and the masses of those atoms. Thus, a given bond, such as C—H, O—H, or C═O, has approximately the same stretching frequency in different molecules. Moreover, the bending frequencies are nearly the same for any given group of atoms (for example, $-CH_3$, $-\overset{\overset{\displaystyle O}{\|}}{C}-H$, or $-NH_2$) in different molecules. While the vibrational frequencies of a given bond or given group of atoms are not precisely the same in all molecules because of the effect of environment (neighboring groups or atoms) within the molecule, rather narrow frequency ranges can be assigned. These assigned frequency ranges, a few of which are listed in Table 7.3, are of great practical value as an aid in deducing the structure of a molecule from its infrared spectrum.

Furthermore, since every compound has a characteristic infrared spectrum, different from that of every other compound, the infrared spectrum serves as a kind of "fingerprint" from which positive identification can be made. Spectra of a few simple compounds are shown in Figure 7.24.

Rotational Spectra

Since differences between rotational energy levels are very small, rotational transitions involve quanta of relatively little energy and absorb radiation in the far infrared and microwave portions of the electromagnetic spectrum.

TABLE 7.3 Some Characteristic Infrared Absorption Bands

GROUP	VIBRATION	WAVENUMBER (cm^{-1})	WAVELENGTH (μ)
O—H	Stretching	3700–3200	2.70–3.15
N—H	Stretching	3500–3300	2.86–3.03
C—H	Stretching	3300–2700	3.03–3.70
C═O	Stretching	1900–1640	5.45–6.10
C═C	Stretching	1700–1580	5.90–6.40
N—H	Bending	1650–1490	6.10–6.70
C—H	Bending	1475–1300	6.90–7.70
O—H	Bending	1450–1200	6.85–8.40
C—O	Stretching	1300–900	7.70–11.2

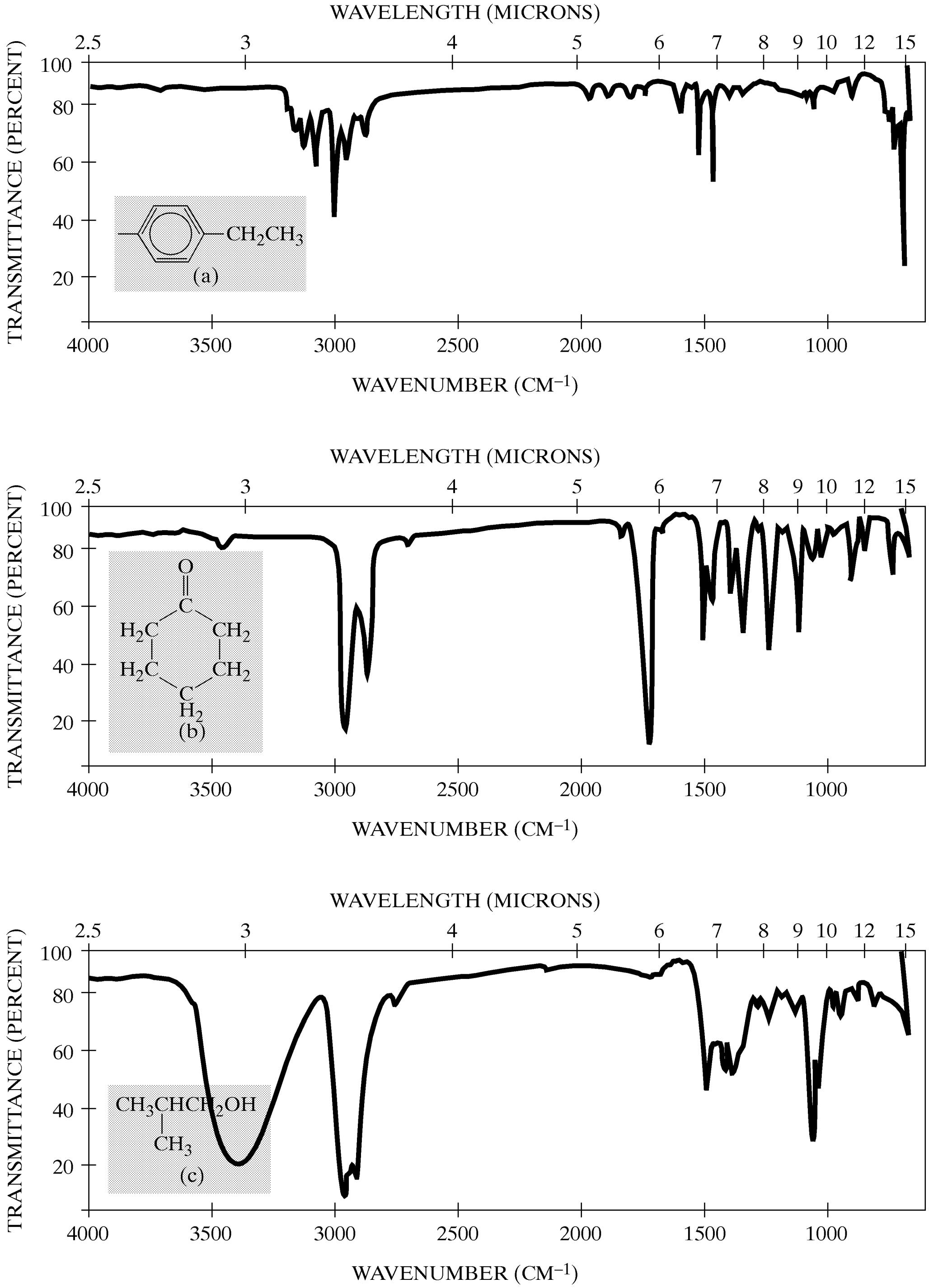


Figure 7.24 Some infrared spectra.

In order for a molecule to give rise to a rotational spectrum, it must have a dipole moment. Thus, molecules such as H_2, N_2, and CO_2 show no absorptions corresponding to changes in rotational energy, while HCl, CO, and similar polar molecules yield definite spectra in this region.

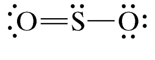
Rotational spectra, which consist of evenly spaced lines, do not have anywhere near the applicability of electronic or vibrational spectra. Their primary usefulness has been in the determination of bond lengths in rather simple molecules, which involves measurement of the spectral line spacings and a rather complex mathematical application of wave mechanics.

CHAPTER SUMMARY

We have concluded our study of the composition and structure of compounds by considering four important molecular phenomena:

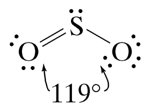
1. Molecules have specific geometrical shapes.
2. Molecules are in motion, and so are the atoms within them.
3. Some molecules exhibit isomerism.
4. Molecules absorb radiant energy.

In the previous chapter the valence bond model was used to **rationalize** the shape of a molecule, whereas the VSEPR model presented in this chapter was designed for the **prediction** of shape. This predictive model is based on the simple idea that pairs of valence electrons in each atom of a molecule should be arranged so as to minimize the repulsions between them. Since a π bond is directed along a σ bond, only the sigma-bonded and nonbonded pairs of electrons need be considered. To illustrate the procedure to be followed in making these predictions, consider the simple molecule SO_2. First, we write the electron dot formula for SO_2 (being sure that it obeys the octet rule, if possible):



The hybridization at the central atom is determined by adding the number of σ bonds attached to that atom to the number of nonbonded electron pairs (lone pairs) on the atom. In the case of SO_2, we have one lone pair and two σ bonds, or a total of three pairs of electrons. The separation of these three electron clouds is maximized (the repulsions between them are minimized) if the three orbitals point toward the corners of an equilateral triangle. In the language of the valence bond model, we say that there are three sp^2 hybrid orbitals pointing toward the corners of an equilateral triangle.

If the lone pair of electrons on the sulfur atom were bonded to another atom, as in SO_3, for example, then all four atoms would lie in a plane, with S in the center and one of the three oxygen atoms at each corner of an equilateral triangle. The bond angles would be 120°. However, one of the orbitals in SO_2 is nonbonding, which means in a sense, one of the corners of the triangle is missing. The result is a **bent** molecule with the bond angle of 120°. Finally, we must assume that the nonbonded pair of electrons exerts a somewhat greater repulsion on the bonded electron pairs than these bonded pairs exert on each other. Thus, the two O atoms are "squeezed together" slightly, making the bond angle a little less than 120° (the actual measured bond angle is 119°):



By following the procedure and the reasoning used in this illustration, you should be able to predict the shape and the approximate bond angles of a large number of molecules with hybridizations of sp, sp^2, sp^3, sp^3d, and sp^3d^2. (Other types of hybridization exist, but they are relatively rare.) Table 7.1 lists a number of compounds and ions—both with and without nonbonding electron pairs—that have various hybridizations. Be sure that you can determine the correct shapes of all of the species in the table; then practice predicting the shapes of other simple molecules and ions.

Once you are able to determine the shape of a molecule, you will be able to predict whether or not the molecule is polar. Recall from Chapter 6 that a bond is polar if it joins together two atoms with different electronegativities. If a molecule contains one or more polar bonds and if its shape does not permit these bond dipole moments to cancel one another, then the molecule is polar and possesses a dipole moment. Thus, CH_4 has no dipole moment because it is tetrahedral, but NH_3 does have a dipole moment because it is pyramidal. Similarly, $BeCl_2$ is not polar because it is linear, but SCl_2 is polar because it is bent (its bond angles are approximately 109°). For further practice in making predictions of this type, determine whether or not the molecules listed in Table 7.1 have dipole moments.

The study of models and textbook diagrams of molecules may create the impression that the molecule is a rigid body composed of stationary atomic spheres and stick-like bonds. However, it is important to understand the motions that take place within molecules. Bond angles are only average angles, and bond lengths are average lengths.

Another topic that was discussed in this chapter is **isomerism**. There are two major types of isomers: **structural isomers** and **stereoisomers**. Structural isomers can be divided into three separate categories: functional group, chain, and position isomers. Stereoisomers are either geometrical or optical. You should understand the structural factors that produce the different types of isomerism. “Ball-and-stick” molecular models, which can be purchased, or molecular modeling computer programs are a useful aid for visualizing the structures of stereoisomers.

The final topic presented in the chapter is the absorption of radiant energy by compounds. You will need to understand the electromagnetic spectrum as well as the various kinds of molecular and ionic energy. Increases in different types of energy by the absorption of electromagnetic vibrations result in electronic, vibrational, and rotational spectra. These spectra are related to molecular structure and therefore are important tools in chemical investigation.

TERMS

Some important terms presented in this chapter are as follows:

Isomerism The occurrence of two or more compounds that contain the same atoms but different arrangements of those atoms.

Structural isomers Compounds that have the same molecular formula but different structural formulas.

Functional group isomers Structural isomers that contain different functional groups. The chemical and physical properties of functional group isomers usually differ greatly. (Examples are methyl acetate and propionic acid; methyl ether and ethyl alcohol.)

Chain isomers Structural isomers that differ only in the branching of their carbon chains. Chain isomers usually have very similar chemical properties but somewhat different physical properties. (*n*-Butane and isobutane are examples of chain isomers.)

Position isomers Structural isomers that differ in the position of a functional group. Position isomers exhibit somewhat different chemical and physical properties. (Examples are 1-butanol and 2-butanol; *o*-dichlorobenzene and *p*-dichlorobenzene.)

Stereoisomers Two or more compounds that have the same structural formula but different configurations (spatial arrangements of atoms).

Geometrical isomers Stereoisomers that consist of two different configurations, resulting from the absence of rotation about a double bond. The two isomers are distinguished from each other by the prefixes *cis* and *trans*. Geometrical isomers usually have somewhat different physical and chemical properties.

Optical isomers Stereoisomers whose configurations are nonsuperimposable mirror images of each other. Optical isomers are identical, except in their ability to rotate the plane of polarized light. They are distinguished by the designations *levo* and *dextro*, depending on the direction in which they rotate the plane. Optical isomers are also referred to as **enantiomers**.

Nuclear energy The energy of a molecule or an ion that is associated with the composition of the atomic nucleus of the molecule. Nuclear energy accounts for almost all of the energy of the molecule.

Electronic energy The energy a molecule or an ion possesses by virtue of the distribution of its electrons.

Vibrational energy The energy of a molecule or an ion that results from the vibratory motions of the atoms within the molecule.

Rotational energy The energy associated with the rotation of a molecule about its center of mass.

Translational energy The energy a molecule possesses because of its linear (translational) motion.

Absorption spectrum A recording or a plot of a compound's absorption of radiant energy of various wavelengths. If the wavelength region is the ultraviolet and visible, the absorption peaks are due to transitions in electronic energy and the spectrum is called an **electronic spectrum**. A **vibrational spectrum** is the result of vibrational energy transitions, which represent absorptions in the near infrared region. **Rotational spectra** occur in the far infrared and the microwave regions, where absorptions correspond to transitions in rotational energy.

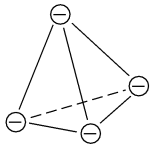
Hooke's law A mathematical relationship that describes the frequency of vibration of a simple harmonic oscillator:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

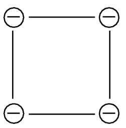
where ν is the vibrational frequency, k is the force constant, and μ is the reduced mass. This relationship can be applied qualitatively to the vibration of atoms within a molecule.

PROBLEMS

1. Calculate the potential energy of four electrons located at the apices of a tetrahedron with distances of 2.0 Å.



2. Calculate the potential energy of four electrons located at the corners of a square with edges of 2.0 Å.



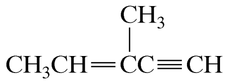
Compare the value obtained with the value obtained for the tetrahedron in Problem 1. Which configuration of electrons is more stable?

3. If the repulsions between four pairs of electrons were minimized by a square planar geometry what would be the structure (give the geometry and bond angles) of each of the following:

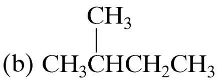
(a) NH_4^+ (b) NH_3 (c) H_2O

4. If the repulsions between four pairs of electrons were minimized by a square planar geometry what would be the lowest energy geometry of ethane?

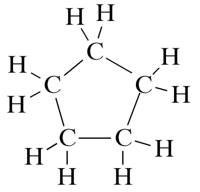
5. Which of the following compounds (a) are structural isomers, (b) exhibit geometrical isomerism, (c) exhibit optical isomerism?

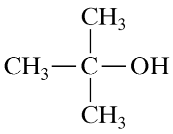
(a) 

$CH_3CH{=}\overset{\overset{CH_3}{|}}{C}C{\equiv}CH$

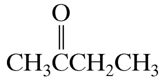
(b) 

$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

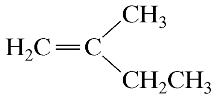
(c) 

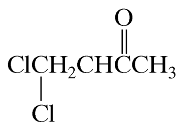
(d) 

$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH$

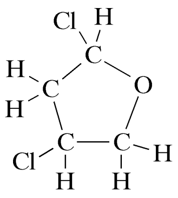
(e) 

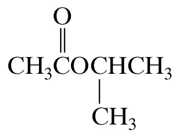
$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$

(f) 

(g) 

$ClCH_2\underset{\underset{Cl}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_3$

(h) 

(i) 

$CH_3\overset{\overset{O}{\|}}{C}O\underset{\underset{CH_3}{|}}{C}HCH_3$

6. Account for the difference in bond angles between members of the following pairs:
(a) $NH_3(107°)$, $NO_3^-(120°)$ (b) NH_3, $PH_3(94°)$
(c) $NF_3(102°)$, $BF_3(120°)$ (d) NF_3, $ClF_3(87°)$
(e) NF_3, NH_3

7. Predict the shape of the species and hybridization at the central atom for each of the following:
(a) $HgCl_2$ (b) $Si(CH_3)_4$ (c) IF_5
(d) SF_4 (e) PF_3 (f) BF_4^-
(g) NO_2^- (h) $B(CH_3)_3$ (i) NO_3^-
(j) $SnCl_2$ (k) SnF_6^{2-} (l) SO_4^{2-}
(m) ICl_4^- (n) ClF_3 (o) SO_3^{2-}
(p) I_3^- (q) ClO_2^- (r) XeF_4
(s) H_3O^+ (t) NH_2^- (u) NH_4^+
(v) ClO_3^-

8. The following species all have the generic formula AB_3: BF_3, CO_3^{2-}, NO_3^-, OH_3^+, NF_3, ClF_3.
a. Which are isoelectronic?
b. Which are isoelectronic with regard to valence electrons?
c. Which have the same geometry?

9. The following species have the generic formula AB_2: H_2O, CO_2, NO_2^+, NO_2^-, SCl_2
a. Which have the same number of valence electrons?
b. Which have the same geometry?

10. For each of the following species give the number of lone pairs at the central atom:
(a) CO_2 (b) NO_2^- (c) SO_3
(d) SO_4^{2-} (e) SF_4 (f) ClF_3
(g) I_3^- (h) $SnCl_6^{2-}$ (i) PCl_3
(j) PCl_5

11. Use the dipole moment generator in the notebook of the electronic versions of the text to calculate the dipole moments of the following:
a. PF_3 b. PCl_3 c. PBr_3 d. NF_3

12. Given that the repulsion between lone pairs is greater than that between lone pairs and bonded pairs, why is I_3^-, which has three lone pairs at the central atom, not bent?

13. It has been suggested that liquid bromine trifluoride (BrF_3), a highly conductive substance, is better represented as BrF_2^+ and BrF_4^- ions. For each ion, draw an electron-dot formula and give the hybridization of the central atom. Then describe the shape of each ion.

14. The percentage composition of a compound containing only carbon and hydrogen is 85.6% C and 14.4% H. The molecular weight is 56.
(a) Calculate the empirical and molecular formulas for this compound.
(b) Write all the reasonable structural formulas that this compound might have and show that the electron dot formula for each obeys the octet rule.
(c) How many different compounds are represented by these structural formulas?

15. The reaction of fluorine with xenon in a closed nickel container produced a crystalline compound. Analysis showed that 0.295 g of xenon had reacted with 0.173 g of fluorine and that the compound had a molecular weight of 207. Calculate the empirical and molecular formulas of the compound. Then write an electron dot formula for the compound and predict its molecular shape.

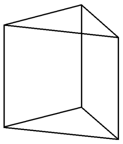
16. Each of the compounds below has a central atom attached to three, four, five, or six groups. Determine the shape of each and then decide which molecules exhibit geometrical isomerism and which exhibit optical isomerism.
(a) BBr_2Cl (b) $As(CH_3)ClH$
(c) $Pt(NH_3)_2Cl_2$ (square planar) (d) PF_2Cl_3
(e) $SClF_5$

17. Draw all of the possible structural isomers and stereoisomers for compounds with the following molecular formulas:
(a) $C_2H_2Cl_2$ (b) C_4H_7Cl
(c) C_5H_{10} (d) C_4H_9Cl

18. Does 2-butyne ($CH_3C{\equiv}C{-}CH_3$) exhibit geometric isomerism?

19. Write structural formulas for structural isomers of acetaldehyde (CH_3CHO):

20. An alternative geometry (to octahedral) for atoms with six pairs of electrons is prismatic, as shown below (the top and bottom of the prism are equilateral triangles).



(a) Predict the number of geometric isomers for a compound with a prismatic geometry and the formula $SnFCl_5^{2-}$ (Sn is at the center of the prism).
(b) Predict the number of geometric isomers for a compound with a prismatic geometry and the formula $MABC_4$ (M is at the center of the prism). Do any of these have nonsuperimposable mirror images?

21. For the octahedral compound MA_2B_4 give all the possible geometric isomers, indicate which exhibit optical isomerism, and which have a dipole moment.

22. (a) For the compound SCl_3F_3, the sulfur is the central atom. Determine whether this compound exhibits geometrical isomerism and, if so, clearly represent these isomers with drawings.
(b) Do any of these geometrical isomers exhibit optical isomerism?

23. Distinguish carefully between:
(a) structural isomers and stereoisomers
(b) molecular formula and structural formula
(c) geometrical isomers and optical isomers
(d) translation and rotation

24. For each of the following molecular formulas, draw all possible structural isomers and name them:
(a) $C_2H_4Cl_2$ (b) C_3H_7Cl (c) $C_3H_6Br_2$

25. An aqueous solution of permanganate ion is purple when viewed in white light. What would be the color of this solution in a room illuminated only by blue light? red light? green light?

26. Why are some substances colored and others are not?

27. What is the color of a substance that strongly absorbs wavelengths between 500 and 800 nm?

28. As indicated in Table 7.3, the infrared absorption due to a C—H stretching vibration occurs in the region 3300–2700 cm^{-1}; the C=O stretching vibration occurs at 1900–1640 cm^{-1}; and the C—O stretching vibration occurs at 1300-900 cm^{-1}. Carefully account for the order for the energy of these absorptions: C—H > C—O and C=O > C—O.

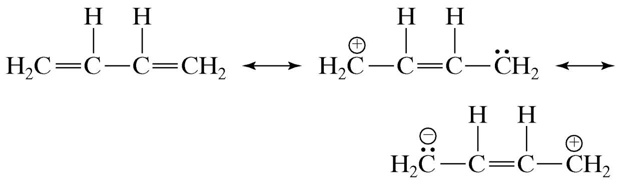
29. A substance is believed to be either acetone or methanol. The infrared spectrum of the compound shows absorptions at 3.0, 3.4, 3.5, 7.0, and 9.7 μ. Identify the substance.

30. A liquid has a molecular weight of 86 and an elemental composition of 69.8% C, 11.6% H, and 18.6% O. Its infrared spectrum contains no absorptions above 2950 cm^{-1} and none between 2500 cm^{-1} and 1500 cm^{-1}. Determine a possible structural formula for the compound.

31. A compound with a percentage composition of 63.2% C, 12.3% H, and 24.5% N has a molecular weight of 57 and exists as geometrical isomers. The absorption due to the carbon-nitrogen linkage appears at about 1680 cm^{-1} (the C—N single bond gives rise to absorption in the region 1000–1200 cm^{-1}). Determine the molecular formula of the compound and then draw all possible structural formulas. From the data given, determine the structural formula for this compound.

32. Account for the fact that heavy water (water in which both the hydrogens are $^{2}_{1}H$) has its O—H stretching vibration at a lower frequency than that of ordinary water.

33. Alkenes that contain carbon-carbon double bonds at alternate carbons (for example, 1,3-butadiene) behave as though the π electrons are partially delocalized over the entire molecule. In the valence bond model, this delocalization would be represented by resonance structures such as



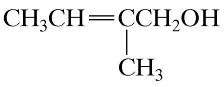
$$H_2C{=}\overset{H}{\overset{|}{C}}{-}\overset{H}{\overset{|}{C}}{=}CH_2 \longleftrightarrow H_2\overset{\oplus}{C}{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}\ddot{C}H_2 \longleftrightarrow H_2\overset{\ominus}{\ddot{C}}{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}\overset{\oplus}{C}H_2$$

If it is assumed that each π electron has as its domain the entire length of the molecule, the energy of molecular orbitals for the π electrons can be calculated from the equation derived in Chapter 5 for the energy of an electron confined to a line.

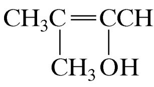
Using an effective length of 0.6 nm for a molecule of 1,3-butadiene, calculate the energies of the four lowest-energy π-molecular orbitals. Indicate which orbitals are occupied by the four π electrons and then calculate the energy required for a transition from the occupied orbital of highest energy to the unoccupied orbital of lowest energy. What is the wavelength of the radiation required for this transition? What region of the electromagnetic spectrum is this radiation in? Is 1,3-butadiene colored according to this description?

34. Circle the most correct answer:

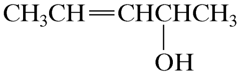
1. Which of the following is a polar molecule?
   (a) CO_2 (b) SO_2
   (c) SO_3 (d) none of the above
2. Which of the following has four stereoisomers?

a 

$CH_3CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_2OH$

b 

$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}{=}\underset{\underset{\displaystyle OH}{|}}{C}CH_3$

c 

$CH_3CH{=}CH\underset{\underset{\displaystyle OH}{|}}{C}HCH_3$

d $HOCH_2CH{=}CHCH_2CH_3$

3. Which of the following is not planar?
   (a) BCl_3 (b) ClF_3
   (c) PCl_3 (d) XeF_4
4. Which of the following has the *smallest* bond angles?
   (a) CO_2 (b) SO_2
   (c) SO_3 (d) SO_4^{2-}
5. Which of the following has the *largest* dipole moment?
   (a) CS_2 (b) $AsCl_3$
   (c) SO_3 (d) BF_3
6. For which *one* of the following are position isomers possible?
   (a) C_2H_5Cl (b) CH_2Cl_2
   (c) CH_3NH_2 (d) $C_2H_4Cl_2$
7. Which of the following compounds is a structural isomer of one or more of the other compounds and also exhibits geometrical isomerism?
   (a) $H_2C{=}CHCH_2CH_2CH_3$
   (b) $CH_3CH{=}CHCH_2CH_3$
   (c) $H_2C{=}CHCH{=}CHCH_3$
   (d $(CH_3)_2C{=}CHCH_3$
8. Which of the following is *not* tetrahedral in shape?
   (a) CH_4 (b) SO_4^{2-}
   (c) BCl_4^- (d) ICl_4^-
9. Which of the following has the *highest* dipole moment?
   (a) HF (b) H_2O
   (c) NH_3 (d) CH_4
10. For which compound are geometrical isomers possible?
    (a) $BrCH_2CH_2Br$ (b) $CH_2{=}CBr_2$
    (c) $BrCH{=}CHBr$ (d) $BrCH_2CHBrCH_3$
11. If a solution strongly absorbs all of the visible wavelengths except those around 600 nm, the color of the solution will be
    (a) blue (b) green
    (c) orange (d) red
12. Absorption of light in the ultraviolet region corresponds to transitions in
    (a) nuclear energy (b) electronic energy
    (c) vibrational energy (d) rotational energy

8 Solids and Liquids

Our study of the structure of matter to this point has dealt primarily with matter on the submicroscopic level. We have examined the structure of the basic particles of matter: atoms, ions, and molecules. Now let us consider how these "building blocks" of matter are held together to form macroscopic specimens—matter in bulk.

In examining the structure of matter in bulk, two basic properties of the particles must be considered. First, the particles are in motion and therefore possess kinetic energy. The magnitude of their kinetic energy—and therefore their velocity—is dependent on temperature: the higher the temperature, the greater the velocity of the particles. Second, there are attractive forces between the particles of matter that tend to hold them together. In a sense, then, matter possesses these two opposing influences: kinetic energy, which tends to separate the structural units, and attractive forces, which tend to pull them together. It is the precise relationship between these two opposing factors that determines the physical state in which a particular substance exists—solid, liquid, or gas. These three states of matter are portrayed at the molecular level in Figure 8.1.

It is characteristic of gases that they have no definite shape and no definite volume; a gas takes the shape and the volume of the container in which it is confined. Furthermore, the density of a gas is very low and varies greatly with temperature and pressure. These facts suggest that the particles of a gaseous substance are very diffuse, have freedom of motion, and that the forces between them are weak.

Solids, on the other hand, have both definite shapes and definite volumes. Their densities are high and are only slightly affected by temperature and pressure. The structural units of solids, therefore, must be close together, their attractive forces relatively strong, and their motion greatly restricted.

Liquids have characteristics intermediate between gases and solids. A liquid has a definite volume, but its shape is determined by the container. Densities of liquids generally range between those of solids and gases, and although a liquid's density varies more with temperature and pressure than a solid's does, the variation is not nearly so great as it

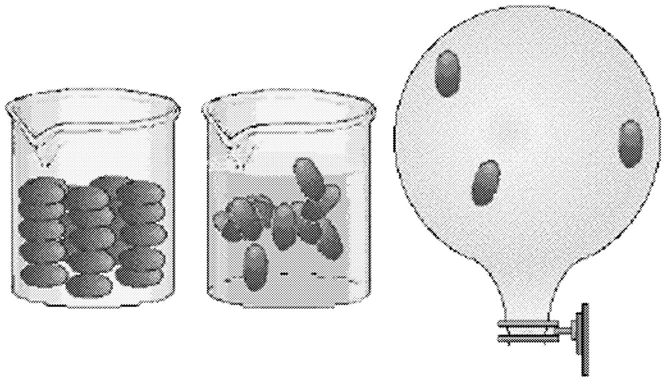


Figure 8.1 The three states of matter.

is in a gas. The particles of a liquid may be thought of as having greater freedom of motion than particles in a solid, but less than those in a gas. The attractive forces in the liquid state are also intermediate between the forces in a solid and those in a gas.

The attractive forces that hold the particles of matter together are all electrical in nature, but they are of several different kinds and of varying strengths. They are described in the following discussions of the various states of matter. The remainder of this chapter deals with solids and liquids; the gaseous state and transitions between states are discussed in Chapter 9.

THE SOLID STATE

Materials that have the general characteristics of the solid state—rigidity, definite volume, and definite shape—are of two structurally different kinds: crystalline solids and amorphous solids. In a **crystalline solid**, the structural units are arranged in a regular, repeating, three-dimensional pattern called the crystalline **lattice**. In an **amorphous solid**, on the other hand, the units are scattered randomly, without any pattern. Amorphous solids—often called **glasses** because ordinary glass is a common example ("hard candy" and solidified tar are other examples)—are structurally more like liquids than like crystalline solids. In fact, they have the properties of extremely viscous liquids and are usually considered as such. Throughout our discussion of matter in bulk, when we employ the term "solid" we will mean "crystalline solid."

8.1 TYPES OF CRYSTALS

There are four basically different types of crystalline solids—ionic, metallic, molecular, and covalent network solids. The distinctions among them are based on both the nature of the structural particles and the forces of attraction involved.

Ionic Crystals

Ionic compounds form crystals in which the units making up the lattice are ions. The forces holding the crystal together are the electrostatic attractions between ions of opposite charge. As illustrated schematically in Figure 8.2, each positive ion is surrounded by negative ions and vice versa. No particular positive ion "belongs" to any particular negative ion; there is no molecule as such. The interionic attractions—sometimes called the *ionic bonds*—are relatively strong, and considerable energy is required to overcome them. Ionic crystals and their forces of attraction have been discussed in detail in Chapter 5.

Metallic Crystals

The properties of metals in the solid state can be accounted for by a rather simple crystal model. The lattice is composed of positive ions, closely packed and embedded in an electron cloud. The ions are derived from neutral atoms by loss of electrons from the unfilled valence shells. These nonlocalized valence electrons constitute the electron cloud (also known as the "sea of electrons," or "electron gas"), which belongs to the entire crystal. The crystal is held together by the attraction between the electron cloud and the positive ions. The strength of this attraction—referred to as the **metallic bond**—depends on the

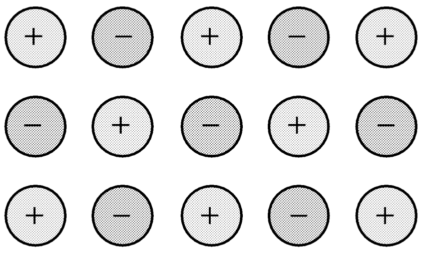


Figure 8.2 The ions in an ionic crystal.

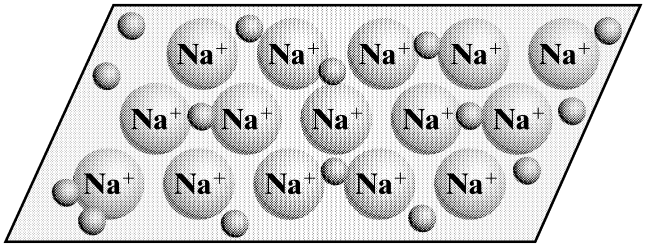


Figure 8.3 The "Sea of Electrons" Model for a Metal

size of the ions and the number of valence electrons "contributed" by each atom, and it therefore varies considerably from metal to metal. The structure of a metallic crystal is illustrated schematically in Figure 8.3, using sodium as an example (the dark spheres are electrons). Since a sodium atom has only one electron in its outermost energy level, each ion in the crystal has a single positive charge. The number of electrons in the electron cloud is equal to the number of ions in the crystal.

While this simple model offers a satisfactory description of most metals, there is evidence that some of the transition metals possess covalent bonding between ions, in addition to the attraction between the ions and the electron cloud.

Molecular Crystals

Substances that exist in the form of molecules crystallize in still another type of crystal: molecular crystals. In this type of crystal, the lattice is composed of individual molecules held together by intermolecular forces. The nature of these forces will be discussed in some detail later in this chapter. For the present, it is sufficient to point out that intermolecular forces are generally very weak—much weaker than the ionic bond and, in most cases, weaker than the metallic bond.

As a simple example of this crystal type, consider the elementary substance iodine. Each iodine molecule consists of two iodine atoms bound together by a strong covalent bond, but the molecules are held to each other in the crystal by weak intermolecular forces (Figure 8.4).

A photograph of a model of solid CCl_4 is shown in Figure 8.5. A CCl_4 molecule is present at each point in the crystal lattice.

Covalent Network Crystals

The fourth type of crystal is the covalent network crystal, in which the lattice is made up of atoms linked to one another by covalent bonds. No separate molecules exist within the crystal; in fact, the entire crystal is a single giant molecule. The classic example of this

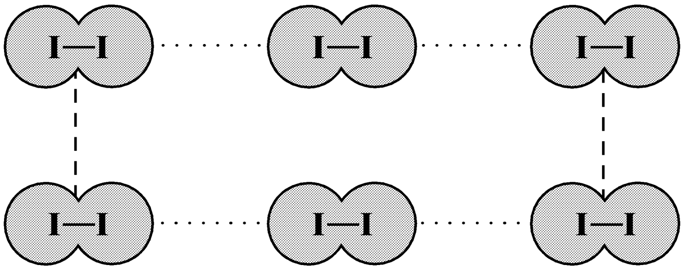


Figure 8.4 The molecules in a molecular crystal held together by weak intermolecular forces.

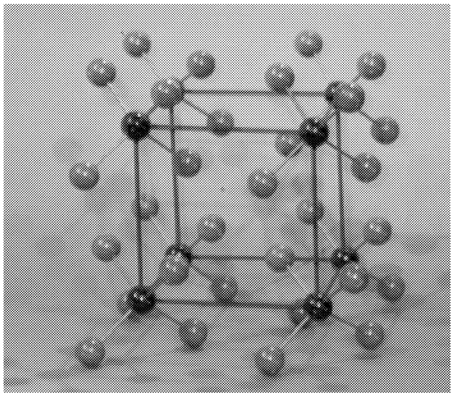


Figure 8.5 A model of the structure of molecular CCl_4.

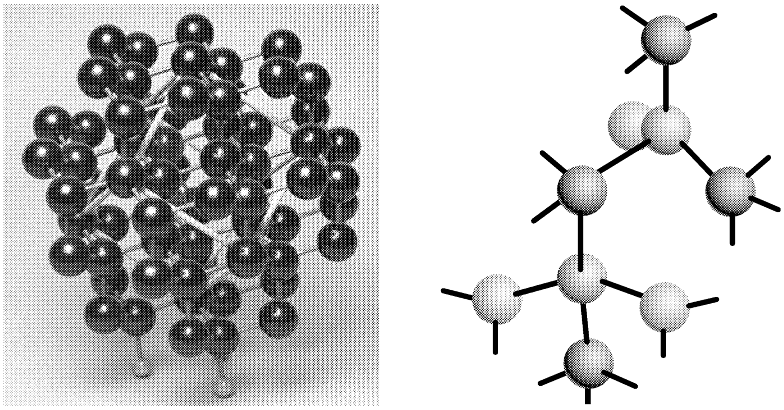


Figure 8.6 The Diamond Structure. A portion of the 3-D network on the right.

type of crystal is diamond, one of the **allotropes** of carbon. Allotropes are two or more different forms of an elementary substance in the same physical state. The existence of these forms, referred to as allotropy, results from a difference in the number of atoms in a molecule (such as in oxygen and ozone), or a difference in crystal form, as in diamond and graphite.

In diamond, each carbon atom is at the center of a tetrahedron and is attached by covalent bonds to four other carbon atoms, which form the corners of that tetrahedron. Each of these four atoms is also the center of a tetrahedron, and is attached to four other carbon atoms, and so on. The result is a three-dimensional covalent network as shown by the model in Figure 8.6. A close-up of the model is shown to the right.

Other examples of covalent network crystals include the elementary substances silicon and germanium, and the extremely abundant compound silicon dioxide (silica). The structure of silica is shown in Figure 8.7. Each silicon atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms, giving a silicon/oxygen ratio of 1 : 2 and therefore a formula of SiO_2.

Graphite, another allotrope of carbon, has a crystal form that is a mixture of molecular and covalent network crystal forms. Each carbon atom is bonded covalently to three other carbon atoms, and each atom has one electron available for pi bonding to the

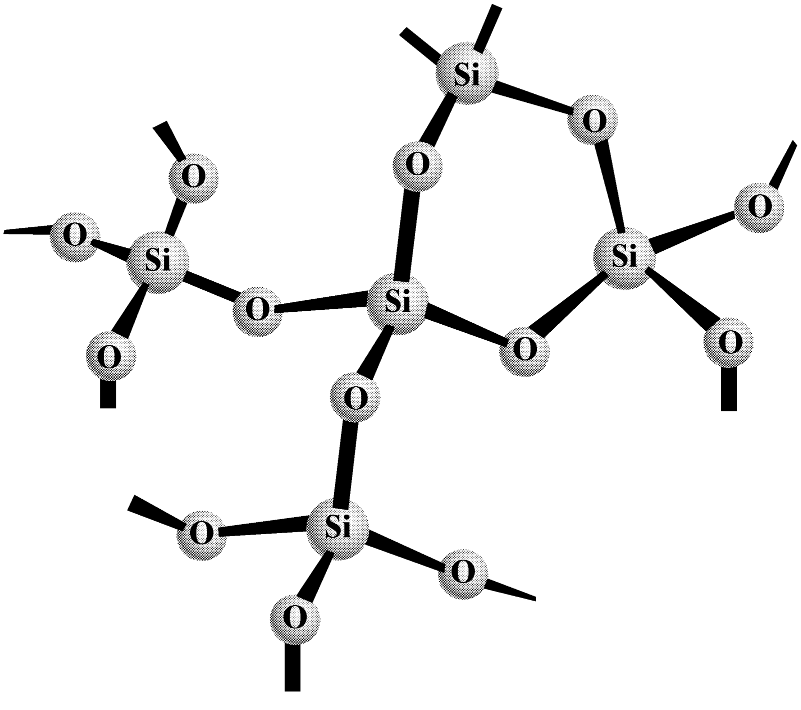


Figure 8.7 The three-dimensional network of covalent bonds in SiO_2.

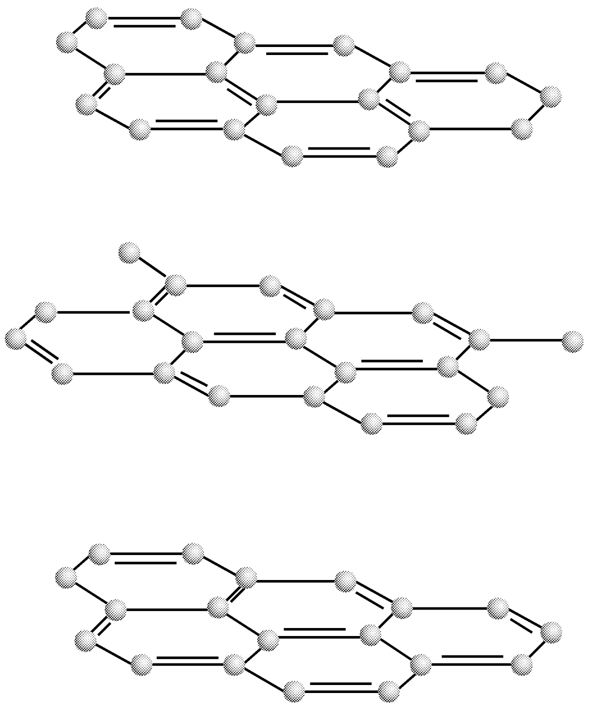


Figure 8.8 The graphite structure.

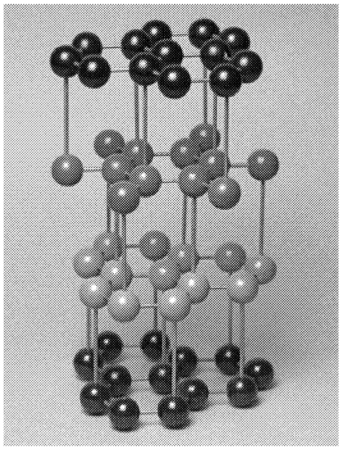


Figure 8.9 A model of the graphite structure.

adjacent carbons. This results in planar sheets of atoms arranged in hexagons. Each of the sheets may be thought of as a giant molecule of indefinite size, held to adjacent sheets by intermolecular forces, as illustrated in Figure 8.8. (The electron-dot formula shown in this figure is only one of many possible resonance forms, and since each group of four carbons shares one pi bond, the bond order for each carbon-carbon linkage is $^{4}/_{3}$. The very weak forces between atoms of different layers permit the sheets to slide over one another, accounting for graphite's unusual lubricating properties.

A photograph of a model of the graphite structure is shown in Figure 8.9, where the vertical rods serve only to maintain separation between the layers; that is, they do not indicate a particular bonding interaction.

8.2 PROPERTIES OF CRYSTALS

Some properties of solids are dependent upon the strength of the attractive forces within the crystal. Because the four different crystal types represent different kinds of forces, certain generalizations can be made regarding those properties.

Melting Point

Recall that the particles of matter are in constant motion. In a crystalline lattice, this motion is greatly restricted and amounts to nothing more than a vibration. This vibratory motion of the particles, which is working against the attractive forces, increases as the temperature is increased. When the temperature becomes sufficiently high, the motion of the particles becomes great enough to overcome the attractive forces holding them in the lattice. The particles then are able to move past one another, the lattice structure breaks down, and the substance passes into the liquid state. This process is called **melting**, and the temperature at which it occurs for a particular substance is that substance's **melting point**. Figure 8.10 shows the melting of a solid over a 2 °C range.

Clearly, the melting point of a solid is related to the strength of the lattice forces. In general, the stronger the attractive forces in the crystal, the greater the kinetic energy of

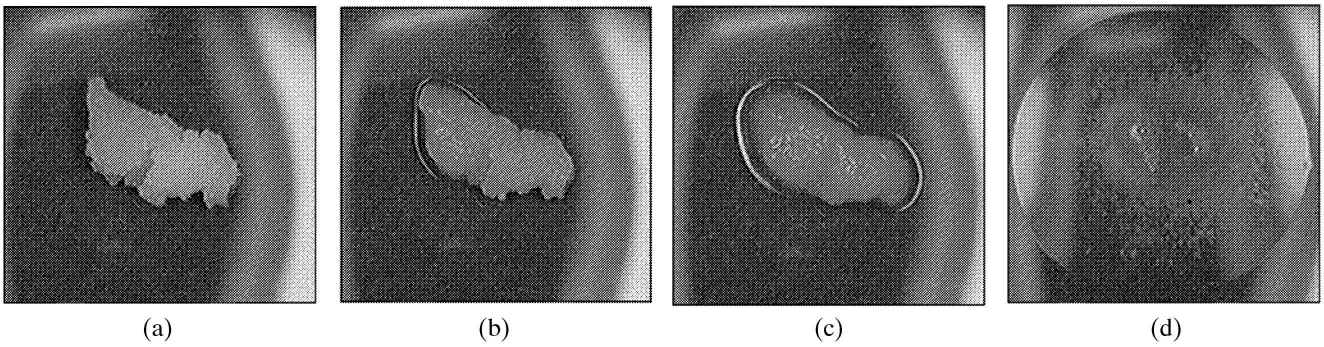


Figure 8.10 **The Melting of a Solid over a 2.0 °C Range.** Melting begins in (a) and ends in (d)

the particles must be in order to overcome those forces, and therefore the higher the melting point.

The covalent bonds in **covalent network crystals** are among the strongest attractive forces found in any of the crystal types. Therefore, crystals of this type have very high melting points. For example, the melting point of diamond is above 4500 °C; SiO_2 melts at around 1600 °C.

At the other extreme are the **molecular crystals**. Because intermolecular forces are weak, molecular crystals have low melting points, rarely over a few hundred degrees. As we shall see, many molecular substances have such low melting points that they exist as liquids, or even gases, at room temperature.

The electrostatic attractions between ions are generally much stronger than intermolecular forces. **Ionic crystals**, as a rule, have melting points higher than those of molecular crystals, but lower than the melting points of covalent network crystals. To illustrate, the melting points of three common ionic compounds are: NaCl, 800 °C; KI, 723 °C; $MgSO_4$, 1185 °C.

Finally, in **metallic crystals** the strengths of the attractive forces apparently vary widely, for the melting points of metals cover a wide range. Some of the structural and coinage metals are high-melting (Fe, 1535 °C; Au, 1063 °C; Ag, 961 °C; Cu, 1083 °C); other metals have moderate melting points (Bi, 271 °C; Pb, 328 °C; Sn, 232 °C); and a few have melting points even lower than those of many molecular crystals (Na, 98 °C; Cs, 28 °C; Ga, 30 °C).

The alkali metals (the elements of Group IA) have particularly low melting points. This fact can be explained with the aid of our metallic crystal model (cations in a "sea" of electrons), because each atom has only one valence electron to contribute to the electron cloud. Thus, the density of the cloud is low and the metallic bond is relatively weak. Comparison of the melting points of the alkali metals with those of the alkaline earth metals shows the latter to be considerably higher (Table 8.1). The alkaline earth metals have two valence electrons to contribute, forming 2+ ions, and the metallic bond is therefore stronger.

TABLE 8.1 Melting Points of the Alkali Metals and the Alkaline Earth Metals

ALKALI METAL	mp (°C)	ALKALINE EARTH METAL	mp (°C)
Li	179	Be	1283
Na	98	Mg	650
K	64	Ca	850
Rb	39	Sr	770
Cs	28	Ba	725

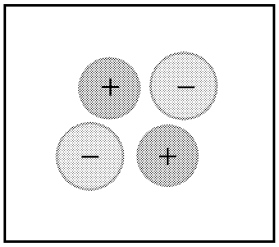
Heat of Fusion

When a crystalline solid is heated, the temperature of the solid gradually rises until the melting point is reached. Once this point is reached, additional heat does not cause a temperature increase. Instead, the solid melts at constant temperature. Only after melting is complete does the temperature begin to rise again. The thermal energy supplied during the melting process is used in bringing about the transition from the solid to the liquid state; it is used to overcome the attractive forces holding the particles (ions, molecules, or atoms) of the crystal together. The energy necessary to bring about melting, or **fusion**, is called the **heat of fusion**. It is often measured in joules per gram or, more conveniently, in kilojoules per mole.

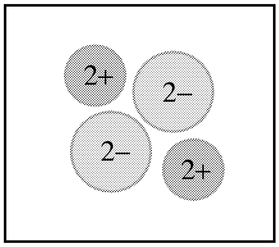
The magnitude of a crystal's heat of fusion is related to the forces holding the crystal together: the stronger the forces, the higher the heat of fusion. Thus, heats of fusion follow a pattern similar to that of melting points, related to the various crystal types. Covalent network crystals generally have very high heats of fusion (for diamond it is estimated to be 598 kJ/mol); ionic crystals have somewhat lower heats of fusion (for NaCl, 28 kJ/mol); and molecular crystals have the lowest (6.0 kJ/mol for ordinary ice). Metals, as might be expected from their melting points, have a range of heats of fusion, from low-melting cesium (2.1 kJ/mol) to very high-melting tungsten (35.2 kJ/mol).

Visualization 8.1

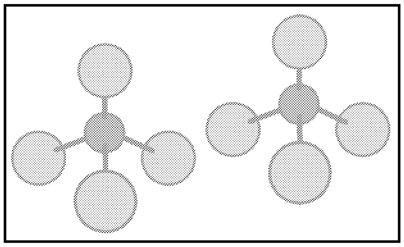
Rank the following substances in the solid state in order of melting point.



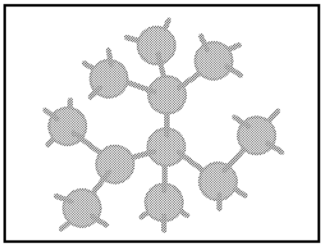
(a)



(b)



(c)



(d)

Solution:

Substance (d) is a covalent network solid and consequently has a very high melting point. Compound (b) is ionic, with 2+ cations and 2− anions. It therefore has a high melting point; that is, the electrostatic interactions between the ions are great and considerable energy is required to "break" those interactions. Compound (a) is also ionic, but has lower charges and, consequently, weaker electrostatic interactions. Compound (c) is molecular, appears to have no dipole moment because of its tetrahedral shape, and therefore has only weak intermolecular forces between the molecules. It has the lowest melting point.

The melting points increase in the order: (c) < (a) < (b) < (d)

Hardness

Another property that varies with crystal type is hardness. The scratching or breaking of a crystal requires the breaking of crystal bonds and disruption of the lattice. Hardness is measured by the Moh hardness scale which arbitrarily goes from 1 (softest) to 10 (hardest). The hardness of a particular crystal is determined by its ability to scratch a crystal of known hardness. Talc, a very soft mineral, is assigned a hardness of 1, while diamond, the hardest naturally-occuring substance, is assigned a hardness of 10.

Covalent network crystals are very hard because of the large number of strong covalent bonds that must be broken. Most ionic crystals are quite hard also, although they show a greater brittleness and tendency to fracture by cleavage than covalent network crystals do. Molecular crystals are usually soft by comparison.

Metals range from very hard to very soft, and they possess a property not found in the other crystal types. Because the electrons in a metallic crystal are highly mobile and provide a uniform distribution of charge, the positions of the positive ions can be changed without destroying the bonding. Therefore, metallic crystals can be deformed rather easily, and metals possess the properties of malleability and ductility (the ability to be hammered into various shapes and to be drawn into wire, respectively).

Vapor Pressure

Vapor pressure as a property will be discussed in detail later in this chapter. For now, suffice it to say that vapor pressure is a measure of the tendency of the structural particles in a solid or a liquid to leave the surface and become a gas. (For liquids, this process is known as **evaporation**; for solids, it is called **sublimation**.) With few exceptions, molecular crystals are the only ones that have an appreciable vapor pressure at room temperature, for only intermolecular forces are weak enough to be so easily overcome.

Electrical Conductivity

In order for a substance to conduct electricity, its structure must permit the motion of electrical charges through it. Of the four basic crystal types, only metallic crystals conduct electricity, since the highly mobile electrons of the electron cloud are able to move without destroying the crystal lattice. When electrons are forced into one end of a metal wire, they displace electrons of the metallic crystal's electron cloud. These displaced electrons take new positions by displacing neighboring electrons, and so on down the wire until electrons are forced out at the opposite end. In the other three crystal types, the electrons are all too tightly bound to permit delocalized motion.

Although ionic crystals are nonconductors, ionic substances in the liquid state will conduct electricity. Thus, for example, solid sodium chloride is a nonconductor, but molten sodium chloride is a conductor. In the liquid state, the electrical charge can be carried by the motion of ions.

Graphite, the structure of which was described earlier (Figure 8.9), is something of an exception in that it is an electrical conductor. This fact can be explained from the graphite structure by the assumption that the pi-bonding electrons are not localized between two carbon atoms (as is implied by the double bonds in Figure 8.9); instead, they are free to move throughout the entire sheet. It is the motion of these electrons that gives rise to electrical conductivity. This view is supported by the observation that the degree of conductivity is rather high in a direction parallel to the sheets but is quite low in a direction perpendicular to them.

Structural features and relative properties of the four crystal types are summarized in Table 8.2.

8.3 INTERMOLECULAR FORCES

Since the majority of all the different substances currently known exist in the form of molecules, the type of attractive forces most frequently encountered is intermolecular forces. In our discussion of molecular crystals, these forces were characterized simply as weak electrical attractions between molecules, and discussion of their origin was deferred. Let us now examine in some detail the nature of these forces.

Dipole-Dipole Attractions

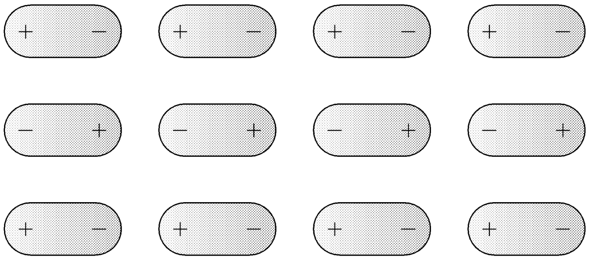
The polarity of covalent bonds and the dipole moment of molecules have been discussed in Chapter 6. Recall that because of unequal sharing of electrons within certain molecular shapes, the electron cloud in some molecules is not distributed symmetrically about the

TABLE 8.2 Structural Features and Relative Properties of Crystal Types

CRYSTAL TYPE	LATTICE	ATTRACTIVE FORCE	MELTING POINT	HEAT OF FUSION	HARDNESS	VAPOR PRESSURE	ELECTRICAL CONDUCTIVITY
Ionic	Positive and negative ions	Electrostatic attraction (ionic bond)	high	high	hard	very low	no
Metallic	Positive ions	Attraction between positive ionsnand electron on cloud (metallic bond)	Ranges from high to low	Ranges from high to low	Ranges from hard to soft	very low	yes
Molecular	Molecules	Intermolecular forces	low	low	soft	relatively high	no
Covalent network	Atoms	Covalent bond	very high	very high	very hard	negligible	no

atoms in the molecule. Thus, even though the molecule as a whole is electrically neutral, there is a charge separation that makes one end of the molecule slightly positive and the other end slightly negative with respect to each other. A molecule in this condition is said to be **polar** and is called a **dipole**.

Because of this charge separation, the negative end of one polar molecule is attracted to the positive end of another, and vice versa. This intermolecular force is called **dipole-dipole attraction**. In the crystalline lattice of a polar molecular substance, the molecules are oriented so as to maximize the effect of dipole-dipole attraction, as illustrated below.



The strength of the dipole-dipole interaction depends on both the dipole moment and the distance between the molecules. When similar molecules are compared, it is generally true that the larger the dipole moment (the more polar the molecule), the stronger the attractive force between the molecules. The strength of the attraction is reflected in various properties of the compound, such as melting point, boiling point, hardness, and heat of vaporization. The dipole moments and melting points of three isoelectronic molecules are compared in Table 8.3.

A special kind of intermolecular force that occurs between certain types of polar molecules is called the **hydrogen bond**. This force, which is stronger than ordinary dipole-dipole attractions, only occurs when a hydrogen atom is attached to a very electronegative atom (usually O, N, or F). This very important type of intermolecular force will be discussed later in the chapter.

TABLE 8.3 The Effect of Polarity on Melting Point

MOLECULE	DIPOLE MOMENT (D)	MELTING POINT (°C)
SiH_4	0	−185
PH_3	0.55	−132.5
H_2S	0.94	−82.9

Van der Waals Forces

Forces of attraction also exist between nonpolar molecules. The nonpolar gases (O_2, N_2, and even the inert gases) can be liquefied; the nonpolar substances Cl_2 and Br_2 are rather easily solidified; and I_2 is a solid at room temperature. Thus, there must be intermolecular forces other than dipole-dipole attractions. The existence of these forces was first suggested by the Dutch physicist Johannes van der Waals and the German-American physicist Fritz London. They are consequently called either **van der Waals forces** or **London dispersion forces**.

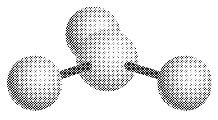
Van der Waals forces, which are present in all matter, are generally weaker than dipole-dipole attractions. Their origin may best be described in terms of a simple monatomic substance such as the inert gas Xe. The electrons within the atoms are not in fixed positions, but form an electron cloud by their constant motion. Although on the average, with time, the electron cloud is symmetrical within the atom, at a given instant there may be more electrons on one side of an atom than the other. The result of this distortion, or polarization, is that for an instant the atom is a **temporary dipole**. A second atom, adjacent to the temporary dipole, will be influenced by it; its electron cloud will be distorted toward the positive end of the first atom. This arrangement is very fleeting since the electrons are in motion, but as the electron density of the first atom moves to the opposite end, the electrons in the second atom will move in the same direction, reversing the polarization. Thus, a kind of fluctuating dipole is set up.

On the average, then, over a finite period of time, the electron clouds of all the atoms are symmetrical, but it is the instantaneous polarizations of the atoms that result in attractions between them. The attractions are weak, to be sure, and even negligible when the molecules are far apart; but when the molecules are close enough, these forces are capable of retaining them in a crystal lattice.

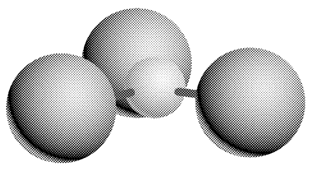
The magnitude of the van der Waals interaction depends on the ionization energy, polarizability, and distance between the molecules. Of these three factors, the easiest to assess is the polarizability, since it generally depends on the number of electrons in the molecule: the greater the number, the greater the polarizability and the stronger the van der Waals forces. Since the number of electrons increases with increasing molecular weight, it follows that the strength of van der Waals forces increases with increasing molecular weight. This relationship is demonstrated by the nonpolar halogen molecules, wherein the melting points and boiling points—both indications of the strength of intermolecular forces—increase steadily as molecular weight increases (Table 8.4).

Visualization 8.2

Rank the following molecules in order of increasing boiling point.



(a)



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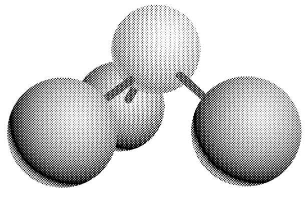


(c)

Continued on next page

Visualization 8.2 *Continued*

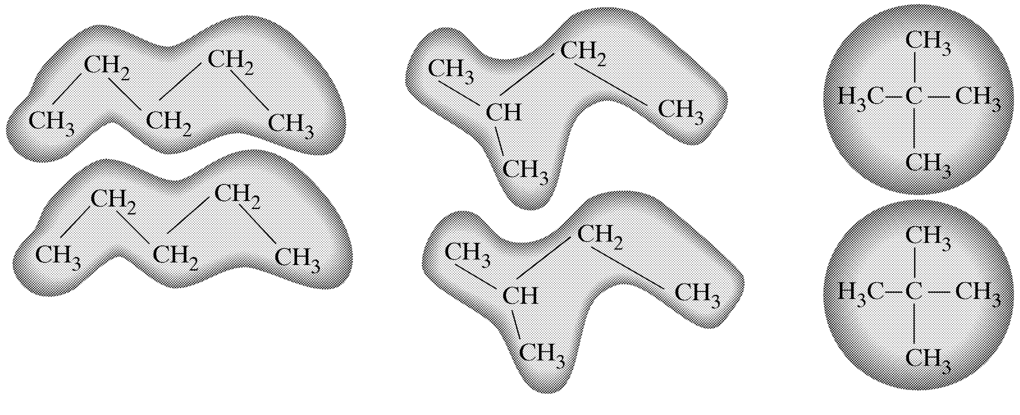
Solution:

Both (a) and (b) are trigonal planar and each molecule has identical terminal atoms. Therefore, neither (a) nor (b) have dipole moments. Although the central atom of (b) is the same as that of (a), the terminal atoms of (b) are larger, presumably have more electrons and, therefore, the van der Waals forces are greater for (b) than those in (a). Molecule (c), on the other hand, is pyramidal and likely has a dipole moment. The central atom is also larger than the central atom in (a) and (b). Thus, (c) not only has a dipole moment and, consequently, dipole-dipole intermolecular forces, but it also has more electrons than either (a) or (b) and, consequently, greater van der Waals forces. The boiling points parallel the strength of the intermolecular forces and vary as (c) > (b) > (a).

TABLE 8.4 The Relationship of Van der Waals Forces to Molecular Weight in the Halogens

HALOGEN	MOL WT	mp (°C)	bp (°C)
F_2	38	−218	−188
Cl_2	71	−101	−34
Br_2	160	−7	59
I_2	254	114	184

Molecular shape is also a factor in determining the strength of van der Waals forces. Other factors being equal, the smaller the distance between molecules, the stronger the van der Waals forces will be. Consider, for example, the three chain isomers of pentane, C_5H_{12} (Figure 8.11). The three molecules have identical molecular weights, yet their different boiling points indicate a difference in the strengths of the intermolecular forces. The straight-chain structure of *n*-pentane permits close approach and intimate contact between molecules, giving rise to the strongest forces and therefore the highest boiling point. The branching in isopentane reduces the contact surface between molecules and leads to weaker forces and a lower boiling point. Finally, the neopentane molecule, being almost spherical, offers the least possibility for close contact and has the weakest van der Waals forces and the lowest boiling point of the three. It is a general rule that in chain isomers, the more branched the chain, the weaker the van der Waals forces.



n-Pentane
(bp 36.1°C)

Isopentane
(bp 27.9°C)

Neopentane
(bp 9.5°C)

Figure 8.11 The effect of shape on distance between molecules and their intermolecular forces.

8.4 CRYSTAL STRUCTURE

Much of our knowledge about the internal structure of crystals is the result of measurements involving the interaction of x-rays with crystals. Since x-rays are high-energy electromagnetic vibrations, a beam of these rays has the same general properties as a beam of light. Some understanding of the interaction of x-rays with a crystal lattice can be gained by comparing it with the phenomenon of **diffraction** of light through a grating.

If two waves come together so that their maximum amplitudes coincide at the same point at the same time (that is, both the crests and troughs coincide), they are said to be **in phase**, and they reinforce each other. This reinforcement results in a wave with greater amplitude but with the same wavelength as the original two waves; the increased amplitude corresponds to increased intensity. On the other hand, if two waves combine so that the crests of one coincide with the troughs of the other, the waves are **out of phase**. In this case the waves cancel each other, and the intensity of radiation drops to zero. If the two waves are not exactly out of phase, there is still some interference, resulting in partial cancellation and a decrease in intensity of the radiation. This phenomenon was discussed in Chapter 3 and illustrated in Figure 3.1.

Diffraction patterns are produced whenever light is transmitted through (or reflected by) a structure that consists of a repetitive pattern. The two-slit apparatus described in Chapter 3 is the simplest example of such a structure. A **diffraction grating** is constructed by producing a large number of parallel, closely spaced, transparent lines on an otherwise opaque surface. The grating functions in the same way as the two-slit apparatus, but the lines obtained are much sharper because of multiple reinforcements and interferences. In order for the diffraction pattern to be well-defined, the spaces between lines should be of the same order of magnitude as the wavelength of the radiation used (about 30,000 lines per inch for visible light).

Because crystals are composed of atoms, ions, or molecules arranged in a regular, repeating pattern, and because the distances between these particles are of the same order of magnitude as the wavelengths of x-rays, crystals behave as three-dimensional diffraction gratings for the diffraction of x-rays.

Figure 8.12 shows a schematic representation of an apparatus for x-ray diffraction. The x-rays are collimated into a narrow beam by passage through a hole in a thick lead shield, and the beam is directed onto a crystal of the substance under investigation. As the x-rays penetrate the crystal, they are diffracted through a variety of angles. A photographic film, which becomes exposed whenever x-rays strike it, can be used to detect the diffracted radiation.

The spacings (d) of the planes of the crystal lattice are related to the angle of diffraction (θ) and the wavelength of the x-rays used (λ) by the equation

$$n\lambda = 2d \sin \theta$$

where n is an integer (1, 2, 3, and so on). This equation, named the **Bragg equation** after its discoverer, is useful in analyzing the structure of crystals. Using x-rays of

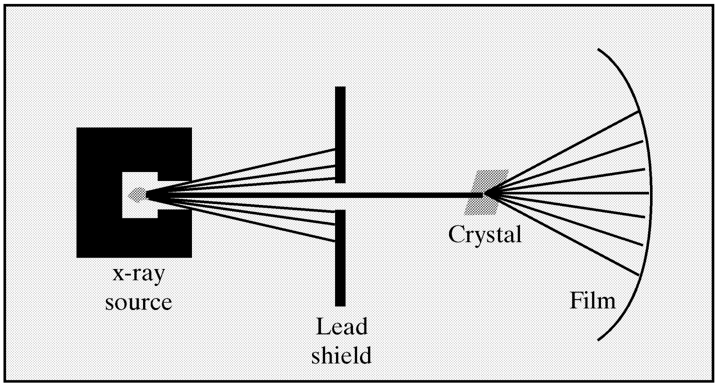


Figure 8.12 An X-ray diffraction apparatus.

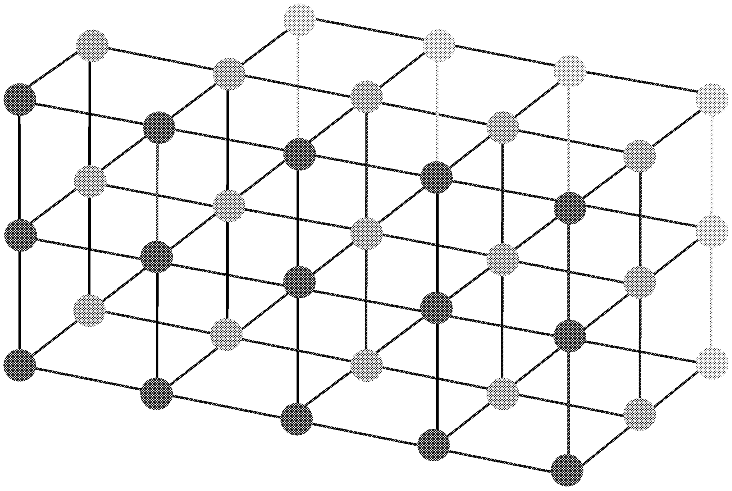


Figure 8.13 A crystal lattice.

known wavelength, the diffraction angles can be measured and the interplanar spacings of the crystal can be computed. In this way, a complete picture of a crystal lattice can be obtained.

A crystal lattice may be pictured as a pattern of points representing the arrangement of the atoms, ions, or molecules that make up the crystal. The points extend in all directions throughout the entire crystal, as illustrated in Figure 8.13.

In describing a crystal lattice, it is often convenient to consider only the smallest section that represents the order of arrangement. If this small section, called the **unit cell**, were moved a distance equal to its own dimensions in various directions, it would generate the entire lattice. Thus, assuming that the lattice points in Figure 8.13 are identical atoms (or ions or molecules), the unit cell of that lattice is represented by the individual cubic structure shown in Figure 8.14. In other words, the crystal consists of repeating unit cells stacked together, and the external symmetry of the crystal as a whole reflects the arrangement within the unit cell.

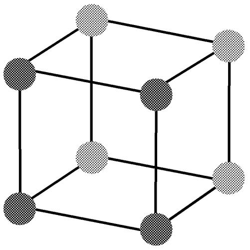


Figure 8.14 A unit cell for the crystal lattice in Figure 9.13.

When one considers the large number of different crystalline substances in existence, it is perhaps surprising that all crystals can be described by only fourteen different space lattices, which can be grouped according to symmetry into only seven different **crystal systems**. The crystal systems may be defined in terms of the relative dimensions of a unit cell along its three axes (a, b, c) and the magnitudes of the angles (α, β, γ) between the sides.

In the foregoing discussion we have visualized lattices as consisting of points connected by imaginary lines, with the points representing centers of atoms, ions, or molecules. But atoms are actually space-filling entities, and some further insight into the internal structure of crystals can be gained by picturing crystals as being composed of spheres packed together.

Close-Packed Structures

In view of the existence of attractive forces holding the particles together in the crystal lattice, it is not surprising that the crystal structures of many substances are those in which the particles are as close together as possible. That is, the most probable structure is the **closest-packed structure**—the one in which the most economical use is made of space.

For a single layer of identical spheres, the symmetrical arrangement shown in Figure 8.15 at first glance appears to make efficient use of space. On further consideration, however, the arrangement in Figure 8.16 clearly leaves less empty space between the spheres. The first arrangement is referred to as **square packing**, whereas the more dense arrangement is referred to as close packing, or **hexagonal packing**. One of the important characteristics of lattice structures is the coordination number, which is defined as the number of equidistant nearest neighbors of the same type. For example, Figure 8.17 shows that

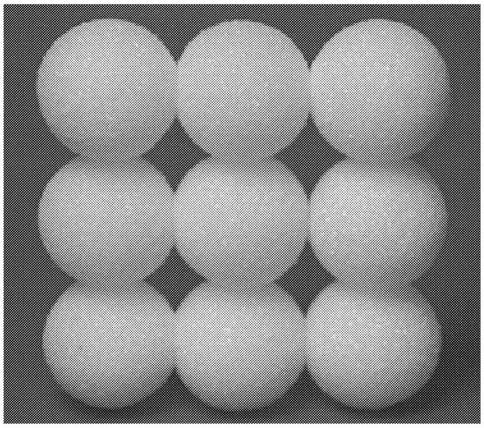


Figure 8.15 Square packing of spheres.

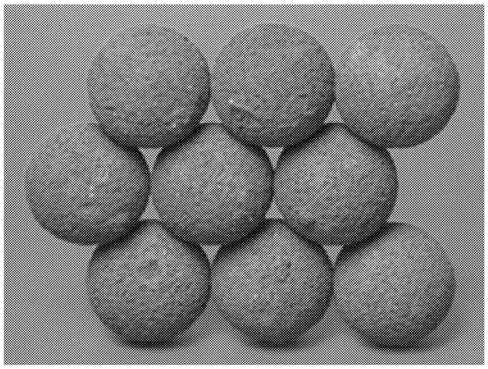


Figure 8.16 Close packing of spheres.

four spheres of the same type (all of the spheres in Figure 8.17 are the same; for example, the same atom or ion) surround the sphere labeled **S**. Thus, the coordination number of any sphere in the square packing structure is four. Similarly, the coordination number in the close packing arrangement is six.

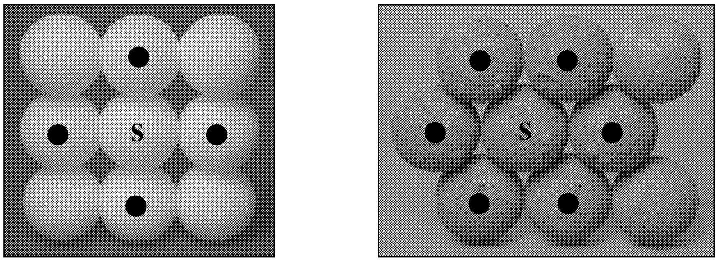


Figure 8.17 The coordination numbers in the square packing and close packing (also called hexagonal packing) structures.

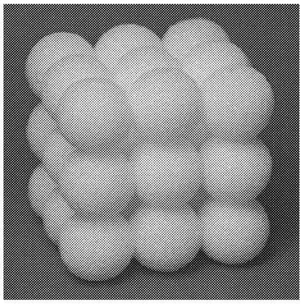


Figure 8.18 Three-dimensional square packing (the simple cubic structure).

When these two one-layer structures are extended to three dimensions, there are four main types of structures. The first is built by placing one square packing layer on top of another, a third on top of those two, and so on. Although this structure, known as the simple cubic structure, does occur in some metals, it is relatively rare, presumably because the atoms can get closer together in other packing schemes. Careful examination of Figure 8.18 will show that the coordination number is six.

A similar scheme that results in more dense packing is derived from the same square packing arrangement. In this case, however, the spheres are separated slightly so that a layer of spheres can be placed in the depressions between the spheres of the first layer. A third layer then goes directly above the spheres of the first layer. This results in the body-centered cubic structure and has a coordination number of eight.

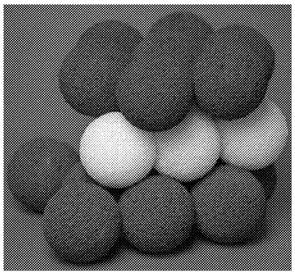


Figure 8.19 Hexagonal close-packing.

The other two structures utilize the close-packing layers. In the first, a second close-packed layer is placed on top of the first in such a way that the spheres of the second layer fit into the depressions of the first layer. A third layer goes directly above the first layer, so that the layers have the sequence ABAB. . . . This sequence is known as hexagonal close packing and has a coordination number of 12* (see Figure 8.19).

In adding a third layer of closest-packed spheres, two different arrangements are possible, and these two arrangements lead to two different overall structures. We can place the third-layer spheres in the depressions directly over the first-layer spheres, resulting in a hexagonal close-packed structure (Figure 8.19). The alternative is to place the third-layer spheres over depressions in the second layer that are over depressions in the first layer. The third layer spheres are therefore not directly over spheres in either of the other

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* If you have trouble seeing the coordination number of 12, try to examine a sphere in the middle layer. This sphere has six nearest neighbors in that layer plus three in the layer above and three in the layer below.

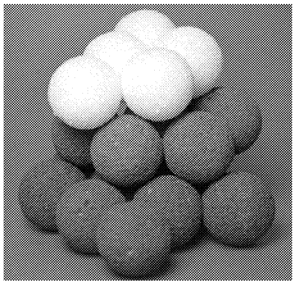


Figure 8.20 The cubic close-packed lattice.

two layers. This gives a continuous sequence of layers ABCABC and results in a cubic close-packed, also called the face-centered cubic, lattice shown in Figure 8.20.

This packing model can be applied to real crystals only if the lattice particles are identical and nearly spherical. Metallic crystals meet both requirements, and indeed, metals provide many examples of hexagonal close-packing (Be, Mg, most of the rare earth metals, and so on) and cubic close-packing (Cu, Ag, Au, Pt, and so on). Molecular crystals that have nearly spherical molecules also display the closest-packed structure; examples include H_2, HCl, H_2S, CH_4, and the inert gases.

The concept of closest-packing can be extended to ionic compounds in which the anion is appreciably larger than the cation. In these cases, the anions are close-packed and the cations fill the holes between them. We can see in Figure 8.21 that two types of holes, or **interstices**, exist between spheres packed in two or more layers. Each of the holes labeled **t** in the figure is surrounded by four nearby spheres, arranged tetrahedrally around the center of the hole. These holes are called **tetrahedral sites**, and although it is not obvious in the illustration, the number of such sites is twice the number of spheres. The holes labeled **o** are surrounded by six nearby spheres and are called **octahedral sites**. The number of octahedral sites is equal to the number of spheres.

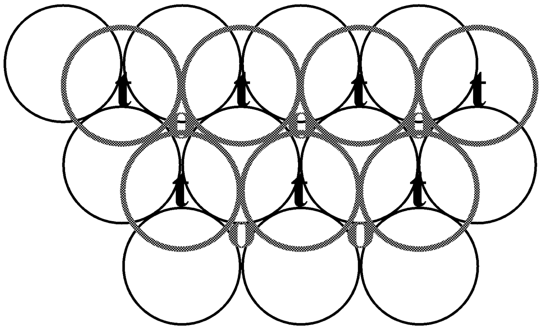


Figure 8.21 The two types of holes between close-packed layers.

Thus, four different basic types of close-packed ionic crystals are possible. The anions can be either hexagonal or cubic close-packed, and for each of these arrangements, the cations can fill either tetrahedral or octahedral sites. Actually, the number of different types is greater than four, because in some ionic compounds only a fraction of the interstices is occupied. In some compounds the cations, rather than the anions, are close-packed and the anions fit in the tetrahedral or octahedral sites. Fluorite (CaF_2) is an example of this scheme. A model showing a cation in an octahedral hole of a hexagonal close-packed structure in shown in Figure 8.22.

Table 8.5 lists some examples of close-packed ionic crystals, arranged according to close-packing of the anions and site occupancy of the cations. It should also be noted that some ionic compounds do not adopt a close-packed arrangement. For example, CsCl utilizes the body-centered cubic structure and the cesium ions have a coordination number of 8.

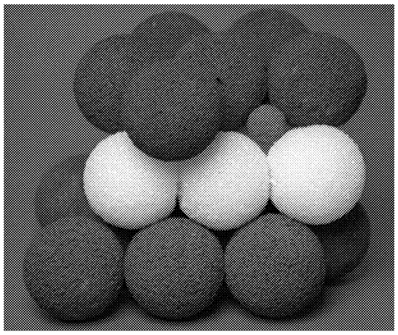


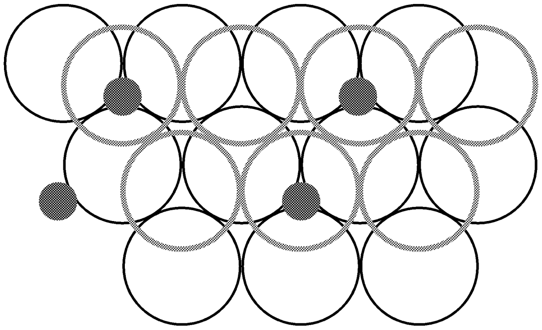
Figure 8.22 A cation in an octahedral hole in a hexagonal close-packed structure.

TABLE 8.5 Examples of Close-Packed Ionic Crystals

CATIONS		ANIONS	
SITES OCCUPIED	FRACTION OF SITES OCCUPIED	CUBIC CLOSE-PACKING	HEXAGONAL CLOSE-PACKING
Tetrahedral	All	Li_2O	(none known)
Tetrahedral	$\frac{1}{2}$	PbO	ZnS (wurtzite)
Tetrahedral	$\frac{1}{3}$	Ga_2S_3	Al_2Se_3
Octahedral	All	NaCl	NiAs
Octahedral	$\frac{1}{2}$	$CdCl_2$	CdI_2
Octahedral	$\frac{1}{3}$	$CrCl_3$	BiI_3

Visualization 8.3

In the following diagram, if the anions have a single negative charge and are close-packed, do the cations have a 1+, 2+, or 4+ charge?



Solution:

Half of the tetrahedral sites are filled (between two layers). Because the number of tetrahedral sites is twice the total number of close-packed spheres, there must be a one-to-one ratio of cation to anion. Hence, if the anions have a 1− charge, the cations must have a 1+ charge in order to preserve electrical neutrality.

Lattice Defects

In our discussion of the structure of crystalline solids, we have assumed them to be perfect crystals, of absolute purity, and with all the structural units (atoms, ions, or molecules) arranged in a precise geometrical pattern. In fact, real crystals, whether found in nature or prepared in the laboratory, contain imperfections, called **lattice defects**.

One of the most common defects in ionic crystals is the dislocation of an ion from its regular lattice site to a position between layers (called an **interstitial position**), as illustrated in Figure 8.23a. Ordinarily it is the cations that are dislocated, since these are usually smaller than the anions.

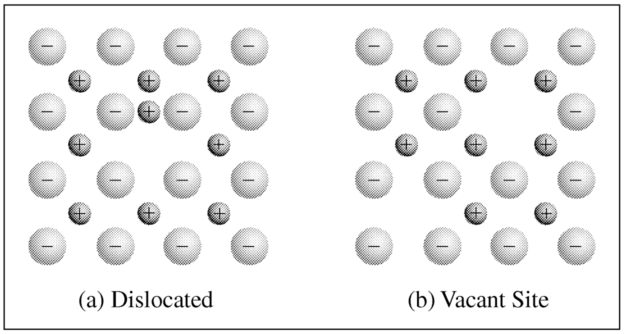


Figure 8.23 Two types of lattice defects in ionic crystals

Another type of ionic crystal defect results from lattice sites being left vacant (Figure 8.23b). The number of vacant cation sites is always equal to the number of vacant anion sites, so that the crystal remains electrically neutral.

Lattice defects may also result from the presence of an impurity in a crystal. If the structural units of the impurity and of the crystal are similar in size, the impurity may occupy some of the lattice positions in the crystal. This type of defect may alter drastically the properties of crystalline materials, even though the impurity amounts to only a few parts per million. For example, extremely pure crystals of iron have a tensile strength nearly 500 times as great as that of ordinary commercial iron.

In some instances, lattice defects lead to highly desirable changes in properties. Perhaps the most important illustration is the production and applications of semiconductors. Silicon and germanium form covalent network crystals of the same lattice structure as diamond. Pure crystals of Si or Ge are nonconductors of electricity because they contain no mobile electrons; all the valence electrons are involved in covalent bonds, as illustrated schematically in Figure 8.24(a). However, if a small amount of arsenic (or phosphorus) is incorporated into the Si (or Ge) crystal, the conductivity of the crystal increases dramatically. This phenomenon can be explained as follows. Arsenic atoms, which have five valence electrons, replace some of the silicon atoms in the crystal lattice. However, only four electrons are required for bonding, so the fifth electron is relatively free and can move through the crystal when an electric field is applied (Figure 8.24b). Because the conductivity in this type of crystal is due to an excess of negative electrons, the crystal is known as an ***n*-type semiconductor**.

The addition of boron as an impurity to Si or Ge also results in increased conductivity. In this case, since boron has only three valence electrons, there is an electron deficiency at the site of each boron atom, producing a positive "hole" (Figure 8.24c). When an electric field is applied to this crystal, an electron from a neighboring atom moves to fill the space, leaving behind another positive "hole," and so on. Because of the positive nature of the defect sites, this type of crystal is referred to as a ***p*-type semiconductor**.

These *n*- and *p*-type semiconductors are used in many important applications. If a wafer of silicon containing arsenic (*n*-type) is placed in contact with a wafer of silicon containing boron (*p*-type), then under the influence of an electric field, electrons flow across the boundary from the electron-rich *n*-type to the electron-deficient *p*-type. Because elec-

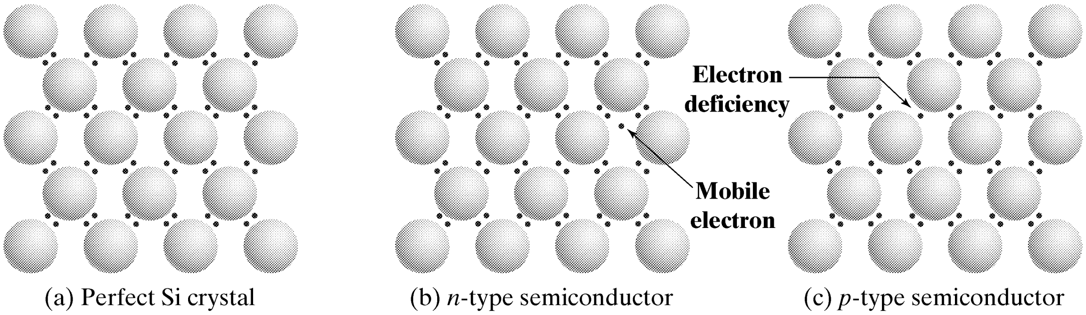


Figure 8.24 Formation of semiconductors from pure silicon.

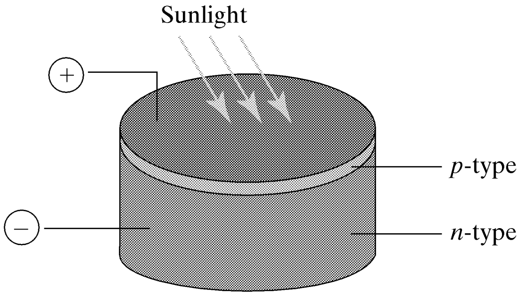


Figure 8.25 Schematic diagram of a solar cell.

trons will flow in only one direction, this device serves as a rectifier; that is, it converts alternating current into direct current. A device consisting of alternating layers of *n*-type and *p*-type semiconductors is called a **transistor**.

The **solar cell**, a device that converts radiant energy into electrical energy, is another example of the application of semiconductors (Figure 8.25). When light strikes a crystal of *n*-type semiconductor, energy is absorbed, causing some of the loosely held electrons to be ejected from the defect sites. These electrons move to the crystal surface, which is covered with a very thin, transparent layer of *p*-type semiconductor. The result is the production of a small voltage. When a large number of such cells are connected, the electrical output can be used to perform useful work (for example, it can be used as a source of power in space vehicles).

THE LIQUID STATE

With few exceptions, substances that exist in the liquid state at ordinary temperatures and pressures are molecular. Ionic, metallic, and covalent bonds are so strong that particles of matter have sufficient kinetic energy to break them only at elevated temperatures. Intermolecular forces, on the other hand, are weak enough to permit many molecular substances to exist as liquids even at very low temperatures.

Our model of the liquid state consists of molecules in motion (and therefore possessing kinetic energy), randomly distributed, and attracted to one another by dipole-dipole attractions and van der Waals forces. Unlike molecules in the solid state, which are held rigidly in a lattice, the molecules of liquids are free to move with respect to one another, within limits determined by the strength of the intermolecular forces. This model enables us to rationalize many of the properties characteristic of the liquid state.

8.5 PROPERTIES OF LIQUIDS

Density

As defined earlier, the density of a substance is the mass of the substance per unit volume. The fact that liquids generally have densities in a range between those of solids and gases means that the average space between molecules in a liquid is greater than in a solid and smaller than in a gas.

For nearly all liquids, an increase in temperature results in a decrease in density. In other words, a liquid expands upon heating; its volume increases and therefore its density decreases. This relationship between temperature and density is easily explained in terms of the kinetic energy of the molecules. As the temperature is raised, the kinetic energy of the molecules is increased. The enhanced vigor of motion decreases the effectiveness of the attractive forces, and the average space between molecules increases.

At a given temperature, the densities of different liquids vary widely, and this variation can be correlated with the relative strengths of the intermolecular forces. The stronger the forces, the more closely the molecules are held together and the higher is the density. This relationship is illustrated in Table 8.6. The two hydrocarbons *n*-pentane and

TABLE 8.6 The Effect of Intermolecular Forces on the Density of Liquids

LIQUID		MOL WT	DENSITY AT 20 °C (g/mL)
n-pentane	(n-C_5H_{12})	72	0.626
n-octane	(n-C_8H_{18})	114	0.703
n-propyl chloride	(n-C_3H_7Cl)	78	0.890

n-octane are nonpolar, so that the only attractive forces involved are van der Waals forces. The hydrocarbon with the higher molecular weight has the stronger van der Waals forces and therefore the higher density. Of the three, the compound with the highest density is *n*-propyl chloride, even though its molecular weight is only slightly higher than that of *n*-pentane. This may be explained by the fact that *n*-propyl chloride is a polar molecule, so there are dipole-dipole attractions in addition to the van der Waals forces.

Methodology 8.1

Which compound in each of the following pairs has the stronger intermolecular forces?

a. acetic acid (CH_3CO_2H) or methyl acetate ($CH_3CO_2CH_3$)
b. methane or SnH_4
c. chlorobenzene (C_6H_5Cl) or methylbenzene ($C_6H_5CH_3$)

How do we approach this problem in general?

We know that there are three types of intermolecular forces—van der Waals, dipole-dipole, and hydrogen-bonding. We also know what factors affect each of these types and that they all depend upon the distances between the molecules. Thus, for each pair of compounds we must look for a difference that would lead to a difference in the intermolecular forces.

What is the difference between acetic acid and methyl acetate?

Acetic acid and methyl acetate differ in two important ways. First, acetic acid has an O-H group (part of the carboxyl group, CO_2H), whereas methyl acetate has a methyl group in place of the hydrogen (CO_2CH_3). This means that acetic acid has hydrogen-bonding but methyl acetate does not. Second, methyl acetate has more electrons than acetic acid and therefore has somewhat stronger van der Waals forces.

Which has the stronger forces—acetic acid or methyl acetate?

Hydrogen-bonding is the strongest of the intermolecular forces and therefore hydrogen-bonding in the acetic acid outweighs the greater van der Waals forces in methyl acetate. Acetic acid has the stronger intermolecular forces.

How do methane and SnH_4 differ?

Both have tetrahedral structures and therefore have no dipole moment. They differ primarily in the number of electrons.

Which compound—methane or SnH_4—has the stronger intermolecular forces?

SnH_4 because of the greater van der Waals forces.

How do chlorobenzene and toluene (methylbenzene) differ?

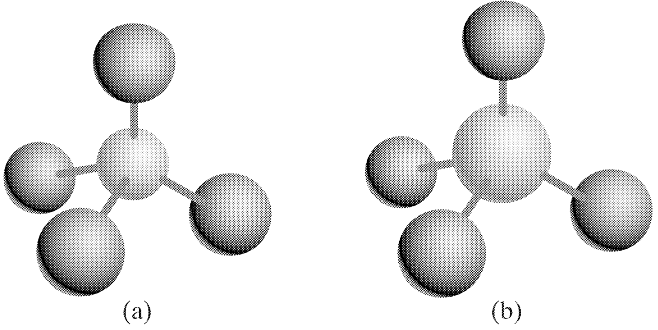
Chlorobenzene has a chlorine atom attached to the benzene ring and therefore has a dipole moment, whereas toluene has a methyl group attached to a benzene ring. The dipole moment of toluene is low because a methyl group has a similar effective electronegativity as the benzene ring.

Which compound—chlorobenzene or toluene—has the stronger intermolecular forces?

Chlorobenzene, because it has a dipole-dipole interaction and also slightly greater van der Waals forces (more electrons).

Visualization 8.4

Which compound has the greater density?



Solution:

Compound (b) has the greater van der Waals forces as a result of the larger central atom (more electrons). Both (a) and (b) are tetrahedral and therefore have no dipole moment. Compound (b) is also heavier (greater molar mass). Density is mass per volume and (b) has the greater mass and the smaller volume (a consequence of its greater van der Waals forces). Thus, (b) has the greater density.

Viscosity

Because the molecules of a liquid are held only loosely, they can move past one another, thus enabling liquids to *flow*. But the tendency to flow, which is expressed in terms of viscosity, differs widely for different liquids. The **viscosity** of a liquid is its resistance to flow; the unit of measurement is the **poise** or, more commonly, the **centipoise** (cp). If we think of a liquid as being stratified in layers, then the force f required to move a layer of the liquid past another layer a distance d centimeters away has been shown to be

$$f = \frac{\eta A v}{d}$$

where A and v are the area and velocity, respectively, of the layer being moved and the symbol η is the **viscosity coefficient**. This coefficient is a measure of the force per unit area required to move a layer of liquid with a velocity of 1 cm/sec past another parallel layer 1 cm away. A poise is that viscosity coefficient requiring a force of one dyne* when A, v, and d are all equal to one in the above equation.

The viscosity of a liquid (that is, its **resistance** to flow) decreases as temperature is increased, an observation that can be readily explained with our liquid model. Increased molecular motion at higher temperature lessens the effectiveness of the intermolecular forces and permits the liquid to flow more easily. Differences in viscosities of different liquids at the same temperature is simply a matter of differences in strengths of intermolecular forces: the stronger the forces, the greater the viscosity. Thus, the high-molecular-weight hydrocarbons contained in motor oil give that liquid a much higher viscosity than gasoline, which contains only hydrocarbons of much lower molecular weight.

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* Remember that a dyne is the unit of force in the gram-centimeter-second system of units. One dyne = 10^{-5} Newton.

Surface Tension

Another property of liquids that is related to intermolecular forces is **surface tension**, which is defined as the force on a liquid surface opposing the expansion of the surface area. Liquids tend to present a minimum surface area, and work is required to expand that surface area. The amount of work necessary is an expression of the surface tension of the liquid. This property is reflected in the observation that a free-falling drop of liquid takes on a spherical shape, since a sphere has the least surface area of any geometrical shape for a given volume.

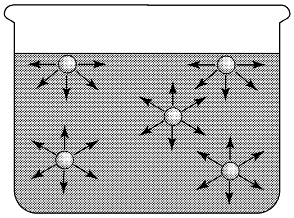


Figure 8.26 Forces on molecules at the surface of a liquid.

As illustrated in Figure 8.26, the molecules in the body of a liquid are subjected to intermolecular forces from all directions, with the result that the *net* force being exerted on any molecule is zero. Molecules on the surface of the liquid, on the other hand, are subjected to forces only from the sides and below, which results in a net force attracting the surface molecules toward the interior of the liquid. This accounts for the tendency of the surface area to be minimized, and thus accounts for the surface tension.

As one would expect, surface tension decreases with increasing temperature. For different liquids at the same temperature, surface tension increases with increasing strength of intermolecular forces.

The surface tension of liquids accounts for the familiar phenomenon of **capillarity**, the rise or fall of liquids in a capillary tube. When one end of an open tube of very small diameter is placed in a liquid, the liquid either rises or falls in the tube. Those liquids that rise do so because their molecules have stronger attraction for the walls of the capillary tube than they do for each other. This type of liquid produces a concave surface and is said to "wet" the surface of the tube. Liquids whose molecules have greater attraction for each other than for the walls of the capillary tube fall instead of rising and produce a convex surface.

The surface tension of liquids that wet glass can be measured by observing the height of their capillary rise. By wetting the inner wall of the capillary, the concave surface that is produced increases the surface area of the liquid. To decrease its surface area, that liquid must rise in the capillary. As soon as this happens, however, the glass is again wet, and again the liquid draws itself upward. This process does not continue indefinitely, but stops when the weight of the column acting downward becomes equal to the force of the surface tension, acting upward. The greater the surface tension of the liquid, the higher it will rise in the tube.

Vapor Pressure

In our discussion of the solid state, **vapor pressure** was described simply as a measure of the tendency of a solid or liquid to become a gas. Let us now examine this property more closely and develop a more specific definition of it.

Consider an open beaker containing a liquid at room temperature. At any given instant, the individual molecules of the liquid will have a variety of kinetic energies, although the average kinetic energy will be determined by the temperature. If a molecule on the surface has a kinetic energy sufficiently above the average and is moving in the right direction, it may overcome the intermolecular forces and enter the vapor phase above the liquid's surface. (The terms **vapor** and **gas** are often used interchangeably, although vapor is usually reserved for the gaseous form of a substance that exists as a liquid at ordinary room conditions.)

This process, illustrated in Figure 8.27, is called **evaporation**, or **vaporization**. Because the container is open, the vapor molecules mingle with the molecules of the air and become distributed throughout the room. Everyone is familiar with the fact that if a glass of water is left standing, the volume of water will gradually diminish.

Suppose we now take the same liquid in the same container at the same temperature, but this time seal the container so that vapor molecules cannot escape into the room. The vapor molecules are in motion above the liquid, and during this random motion some

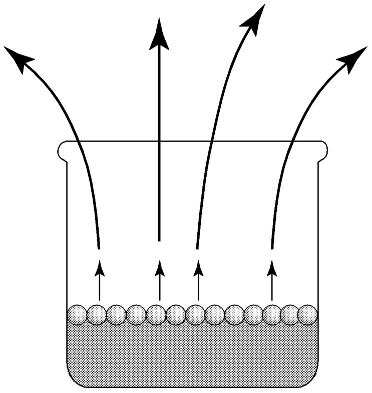


Figure 8.27 Evaporation of molecules from the surface of a liquid.

will certainly collide with the liquid surface. If the vapor molecule's kinetic energy is sufficiently low when one of these collisions occurs, intermolecular forces may take over and the molecule will become part of the liquid again. This process, which is just the opposite of evaporation, is called **condensation**, or **liquefaction** (Figure 8.28). Thus we have two opposing processes occurring:

$$\text{Liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{Vapor}$$

The **rate** of evaporation of a liquid depends upon several factors:

1. The nature of the liquid. Even if all conditions are the same, different liquids will not evaporate at the same rate. This is due to the differences in the strengths of the intermolecular forces, which in turn depend on the molecular weight, structure, and degree of polarity of the molecules.
2. Temperature. For any given liquid, the rate of evaporation increases with temperature. Since the kinetic energy of the molecules increases with temperature, the intermolecular forces will be broken more readily at higher temperatures and the rate of evaporation will therefore increase.
3. Surface area. Since evaporation is a surface phenomenon, enlarging the surface area increases the rate of evaporation. If equal volumes of water are placed in a large, shallow pan and in a tall, narrow cylinder at the same temperature, the water in the pan will evaporate faster than the water in the cylinder.

It follows, then, that for any liquid substance maintained at the same temperature in the same container, the rate of evaporation is constant.

The rate of condensation, on the other hand, depends not only on these three factors, but also on the number of vapor molecules in the phase above the liquid. The greater the number of vapor molecules, the more collisions that will occur with the liquid surface, and therefore the higher the rate of condensation.

Thus, one of these two opposing processes—evaporation—occurs at a constant rate while the other (condensation) begins at zero rate and gradually increases its rate as more and more molecules enter the vapor phase. Eventually, the rates of the two processes

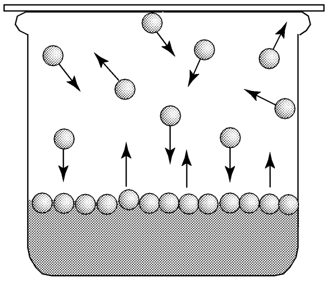


Figure 8.28 The equilibrium between liquid and vapor.

must become equal; molecules will be leaving the vapor phase just as fast as they are entering it. When this point is reached, both rates will continue to be equal and there will be no net change in the quantity of substance in either the liquid or the vapor phase. This situation—two opposing processes occurring at equal rates—is called **dynamic equilibrium**. It must be emphasized that we have not said that evaporation occurs up to a certain point and then stops. On the contrary, although it may *appear* that evaporation has ceased because there is no net change in the amount of liquid present, the two processes will continue to occur *ad infinitum* as long as the conditions of the system are not changed. The concept of dynamic equilibrium is a very important one, for it is useful in explaining many chemical phenomena.

In the liquid-vapor equilibrium just described, the vapor molecules undergo collisions with the walls of the container as well as with the liquid molecules and other vapor molecules. In other words, the vapor molecules exert a pressure; this is called the vapor pressure. Thus, **vapor pressure** is defined as the pressure exerted by the molecules of a vapor in equilibrium with its liquid.

✓ Check Point 8.1

Ortho-dichlorobenzene has two chlorines attached to adjacent atoms of the benzene ring, while *para*-dichlorobenzene has the chlorines directly across the ring from one another (on the 1,4-carbons). Which liquid has the greater vapor pressure?

Solution:

para-dichlorobenzene

◇ ◇ ◇ ◇ ◇

The vapor pressure of any liquid varies with temperature. Suppose we have a liquid and its vapor in equilibrium at 25 °C and we have measured the vapor pressure. Now let us raise the temperature of the liquid to, say, 50 °C. At the higher temperature, the kinetic energy of the liquid molecules is increased, so that the intermolecular forces are more easily overcome, and the rate of evaporation increases. The rate of condensation also increases as the number of vapor molecules becomes larger. Eventually the two rates will become equal again and equilibrium will be reestablished at the new temperature (50 °C). However, at the higher temperature there are more molecules in the vapor phase than there were at the lower temperature. More vapor molecules means more collisions with the container walls and therefore a higher vapor pressure. Furthermore, at the higher temperature the vapor molecules themselves have greater kinetic energy, so that even if the number of vapor molecules had not increased, a greater force would be exerted on the container walls. Both factors contribute to an increase in vapor pressure with increasing temperature.

Heat of Vaporization

Because it is the molecules with high kinetic energy that escape from the surface of a liquid during evaporation, the average kinetic energy of the remaining molecules is lower. Thus, there is a corresponding decrease in temperature. If the liquid were completely isolated from it surroundings, this decrease in temperature would lower the rate of evaporation until, theoretically, evaporation would cease. Under ordinary circumstances, however, evaporation continues because the liquid takes in heat from its surroundings. This phenomenon is easily experienced if a few drops of some very volatile liquid (one with a high vapor pressure), such as ethyl ether, is placed on the skin. As the liquid evaporates, there is a sensation of cold at that spot. Another common example of this phenomenon is the coldness felt after a swim: The water on the body evaporates, taking heat from the surface of the skin. It follows that evaporation is an endothermic process; that is, energy must be supplied to convert a liquid to a gas. This energy, called the **heat of vaporization**, is usually expressed in terms of kilojoules per mole. Like the heat of fusion for solids, the heat of vaporization is a measure of the energy required to overcome attractive forces. Liquids with strong intermolecular forces have correspondingly high heats of vaporization.

The heat of vaporization of any substance varies with temperature. At higher temperatures, the molecules have greater energy, and therefore less energy is required to cause evaporation. In other words, the heat of vaporization decreases as the temperature increases. For example, at one atmosphere of pressure (760 torr) water has a heat of vaporization of 44.4 kJ/mol at 10 °C and 40.7 kJ/mol at 100 °C.

Boiling Point

While evaporation and boiling are both processes whereby liquids are converted into gases, they differ in several respects. Evaporation is a surface phenomenon, whereas boiling involves the formation of bubbles of vapor within the body of the liquid, which rise to the surface and escape. Furthermore, evaporation occurs spontaneously at any temperature and represents a diffusion of individual molecules into the atmosphere. In boiling, the vapor escapes by pushing back and displacing the gas of the atmosphere above the liquid, and therefore boiling will not occur unless the vapor pressure of the liquid is equal to that of the confining atmosphere. Thus, the **boiling point** is defined as that temperature at which the vapor pressure of the liquid is equal to the pressure of the atmosphere above the liquid.

The boiling point of a liquid is not a constant, then, but varies with the pressure of the surrounding atmosphere. Water boils at a lower temperature on a mountain top than it does at sea level, and it may be made to boil at room temperature if the pressure of the atmosphere above it is reduced sufficiently by means of a vacuum pump. If the pressure of the atmosphere over water were, say, 400 torr, then water would boil at a temperature of 83 °C, because at that temperature the vapor pressure of water is 400 torr. By contrast, the boiling point of water would be about 108 °C if the pressure were 1,000 torr.

In order to be able to make direct comparisons of boiling points of different liquids, it is necessary to establish a standard pressure as a reference point. By universal agreement, this standard pressure is **one atmosphere**, equal to the pressure exerted by a column of mercury 760 mm high (760 mm Hg = 760 torr). The temperature at which a liquid boils when the pressure is one atmosphere is called its **normal boiling point**.

Distillation is a process whereby a liquid is converted into a vapor by boiling and the vapor is then condensed back to a liquid by cooling. This process is useful in purifying liquids and in separating substances of widely different boiling points. The diagram in Figure 9.29 illustrates the equipment used in a simple distillation.

Freezing Point

When heat is gradually removed from a liquid, the temperature of the liquid is lowered and the kinetic energy of its molecules decreases. As molecular motion diminishes, the intermolecular forces become more effective, and at a sufficiently low temperature the intermolecular forces "take over." The molecules are "pulled" into a lattice arrangement and crystallization occurs. The temperature at which this occurs is called the **freezing point**, and is, of course, identical to the melting point. The exact freezing point of a liquid varies somewhat with pressure, although not nearly so much as the boiling point. The **normal freezing point** is defined as the freezing point under a pressure of one atmosphere.

At the freezing point, a liquid and its solid are in equilibrium. Thus, for example, if a mixture of ice and water is held at a temperature of exactly 0 °C and no heat is allowed to enter or leave the system, ice will melt and water will freeze at exactly equal rates, resulting in no net change in the amount of ice or water present. The system is in dynamic equilibrium:

$$\text{Solid} \xrightleftharpoons[\text{freezing}]{\text{melting}} \text{Liquid}$$

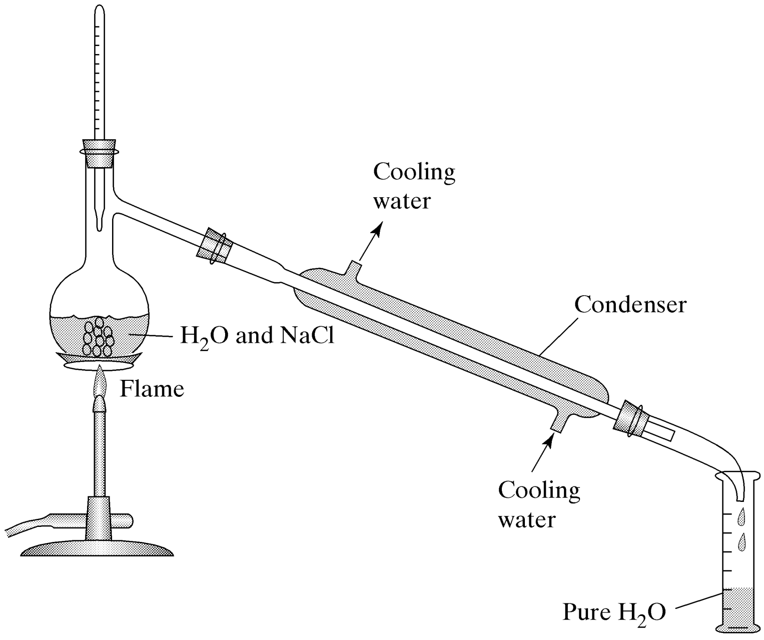


Figure 8.29 **Distillation Apparatus**

During the crystallization (freezing) of a liquid, the temperature remains constant, and heat must be removed from the system in order for crystallization to continue. Thus, crystallization is an exothermic process; that is, energy is given off. The amount of energy given off is called the **heat of crystallization** and is usually expressed in kilojoules per mole. For any given liquid the heat of crystallization is numerically equal (but of opposite sign) to the heat of fusion, discussed earlier in this chapter.

In our discussion of solids, we noted that molecular crystals possess measurable vapor pressures. Molecules on the surface of a crystal may possess sufficient kinetic energy to break away from the lattice and enter the vapor phase. In a closed system, this process of **sublimation** will lead to an equilibrium between solid and vapor. Vapor pressures of solids are defined and measured in the same way as vapor pressures of liquids. The vapor pressure of solids accounts for numerous well-known phenomena. For example, ice will disappear from a sidewalk on a windy day even though the temperature is well below the freezing point. The ice sublimes, and the vapor molecules are carried away by the wind. The fact that some solids have an odor is an indication of their vapor pressure, since in order for us to smell a substance, molecules of that substance must enter the nasal passages.

At the freezing point, the vapor pressure of a solid is equal to the vapor pressure of the liquid. This can be illustrated with the vapor pressure curves for the solid and liquid states of water, shown in Figure 8.30. The temperature at which the curves intersect is the freezing (or melting) point.

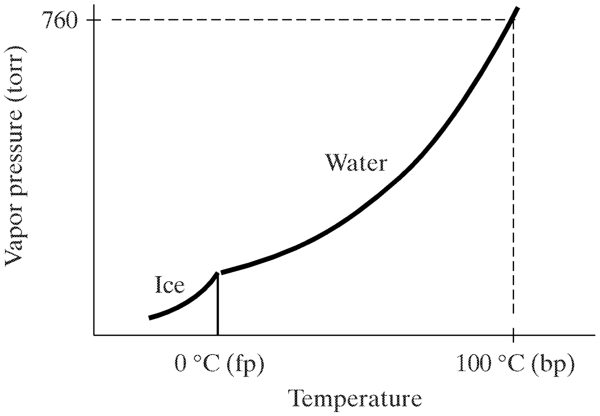


Figure 8.30 The dependence of vapor pressure on temperature.

TABLE 8.7 The Effect of Temperature And Intermolecular Forces On Some Properties of Liquids

PROPERTY	EFFECT OF INCREASING TEMPERATURE	EFFECT OF INCREASED INTERMOLECULAR FORCES
Density	Decreases	Increases
Viscosity	Decreases	Increases
Surface tension	Decreases	Increases
Vapor pressure	Increases	Decreases
Heat of vaporization	Decreases	Increases
Boiling point		Increases
Freezing point		Increases

The effects of temperature and the strength of intermolecular forces on various properties of liquids are summarized in Table 8.7.

8.6 THE HYDROGEN BOND

Certain compounds display properties that suggest the existence of attractive forces far too strong to be explained on the basis of van der Waals forces and dipole-dipole attractions alone. Since the most common compound showing these “strong force” properties is water, let us examine the concept using water as our example. Water has several abnormal properties—abnormal in the sense that they do not follow the trends predicted by consideration of ordinary intermolecular forces. For example, the boiling point and freezing point of water are both abnormally high.

The boiling points of the hydrides of Group IVA elements (Table 8.8) follow the expected trend: They increase with increasing molecular weight. Since these hydrides are nonpolar compounds, the only forces binding their molecules together are van der Waals forces, and the direct relationship to molecular weight (number of electrons) is predictable.

Although the hydrides of Groups VA, VIA, and VIIA show some degree of polarity, this relationship of boiling point to molecular weight seems to prevail within each group, with the important exception of the first member. Ammonia, water, and hydrogen fluoride do not follow the trend, but have boiling points well above the expected values. The same trends and the same exceptions apply also to the melting points of these hydrides. Table 8.9 illustrates these relationships and shows clearly why we may conclude that water, ammonia, and hydrogen fluoride have abnormally high boiling and melting points.

Another abnormal property of water concerns the relationship of density to temperature. For most liquids, as the temperature is lowered, the density increases and continues to increase as the liquid undergoes the transition to the solid state. (In other words, liquids contract on solidification; the solid is more dense than the liquid.) This behavior is easily explained on the basis of van der Waals forces and dipole-dipole attractions. Liquid water shows this same behavior—that is, its density increases as the temperature is lowered—but only down to a temperature of approximately 4 °C. Further cooling of water below this temperature produces a reversal in the trend, and the density *decreases* as the

TABLE 8.8 The Boiling Points Of The Group IVA Hydrides

	CH_4	SiH_4	GeH_4	SnH_4
Molecular weight	16	32	76	123
Boiling point (°C)	−161	−112	−90	−57

TABLE 8.9 The Normal Boiling Points and Melting Points of the Hydrides of Groups V, VI, VIIA‡

COMPOUND	MOL WT	MELTING POINT (° C)	BOILING POINT(° C)
NH_3	17	−77.7	−33.4
PH_3	34	−132.5	−85
AsH_3	78	−113.5	−55
SbH_3	125	−88	−17
H_2O	18	0	100
H_2S	34	−82.9	−59.6
H_2Se	81	−65.7	−41.3
H_2Te	130	−48	−1.8
HF	20	−83	19.4
HCl	36.5	−111	−85
HBr	81	−86	−66.4
HI	128	−50.8	−35.5

‡The tinted blocks highlight exceptions to the trend.

temperature is lowered. Furthermore, when water crystallizes it expands; ice is *less dense* than liquid water. This particular "abnormal" behavior of water is of extreme importance to life as we know it on this planet. If ice were not less dense than liquid water, then ice crystals forming on lakes and rivers in the winter would fall to the bottom; lakes would freeze from the bottom up.

The abnormal properties of water and certain other compounds are explained as follows. Oxygen is a highly electronegative element, with two unshared pairs of electrons. The hydrogen atoms are attached to it by means of highly polar bonds. Each hydrogen atom is extremely small, and because it bears a rather large positive partial charge and has no screening electrons, it is almost like a bare proton. These conditions permit a strong electrical attraction between a hydrogen atom of one water molecule and the lone pair electrons on the oxygen atom of another molecule. This strong attraction is called a **hydrogen bond**. As a result of the hydrogen bond, liquid water consists of aggregates of molecules rather than entirely separate molecules.

Because the hydrogen bond is considerably stronger than ordinary intermolecular forces, more energy is required to separate hydrogen-bonded molecules than would be required to separate the same molecules if they were not hydrogen bonded. In order for ice to melt and in order for liquid water to boil, the water molecules must gain a higher kinetic energy than would be necessary if the hydrogen bond did not exist. Therefore, both the melting point and the boiling point of water are higher than they would be without hydrogen bonding. However, in H_2S, H_2Se, and H_2Te there is no appreciable hydrogen bonding because sulfur, selenium, and tellurium are not sufficiently electronegative. Thus these compounds have melting and boiling points that can be explained by ordinary intermolecular forces alone.

The concept of the hydrogen bond also enables us to account for the unusual density-temperature behavior of water. At elevated temperatures, the relatively high kinetic energy of the molecules keeps them apart, and the amount of hydrogen bonding is small. As the temperature is lowered, the decreased motion of the molecules permits them to approach one another more closely, and hydrogen bond formation occurs to an increasing extent. At 4 °C the average distance between molecules is at a minimum. When the temperature is lowered still further, hydrogen bonding becomes so extensive that the aggregates of molecules begin to assume fixed positions, with each oxygen atom bonded tetrahedrally to four hydrogen atoms (two by covalent bonds, two by hydrogen bonds). This

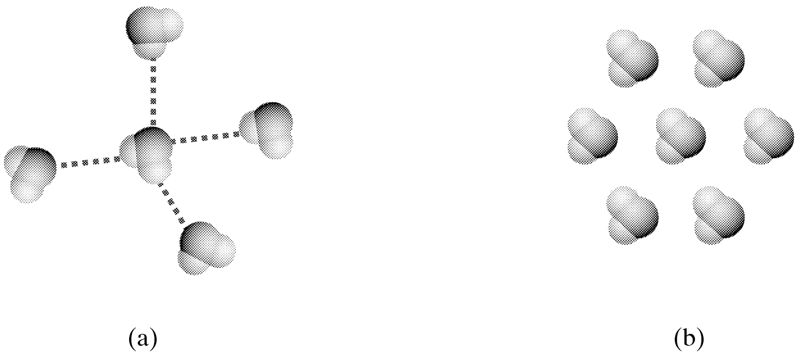


Figure 8.31 The spacing of water molecules (a) with hydrogen bonding and (b) without hydrogen bonding (hypothetical).

results in a molecular orientation in which any given molecule is surrounded by fewer other molecules than would be the case in the absence of hydrogen bonding (Figure 8.31). In other words, the total space between molecules increases because of hydrogen bonding, and the liquid expands rather than contracts.

Finally, at 0 °C, hydrogen bonding is at its maximum, and all of the atoms are involved in this bonding as crystallization occurs. The ice crystal does not consist of separate water molecules attracted to one another by intermolecular forces (as is the case in solid H_2S); instead, it is a network of tetrahedra, with each oxygen atom attached to four hydrogens and each hydrogen atom attached to two oxygens. This arrangement results in hexagonal "open spaces," which accounts for the lower density of ice (Figure 8.32).

The high melting and boiling points of HF and NH_3 can also be explained by the occurrence of hydrogen bonds. Indeed, any molecule in which a hydrogen atom is bonded to a highly electronegative element having at least one pair of unshared electrons is capable of hydrogen bonding. The elements that meet this requirement are fluorine, oxygen, nitrogen, and, to a smaller extent, chlorine. (Although nitrogen and chlorine have the same electronegativity, the chlorine atom is considerably larger, and thus its electron cloud is too diffuse to permit strong hydrogen bonding.) Those compounds that undergo hydrogen bonding include amines (RNH_2), alcohols (ROH), and carboxylic acids (RCOOH).

The strength of the hydrogen bond varies with the particular structure of the molecule. Other things being equal, it depends on the electronegativity of the atom to which

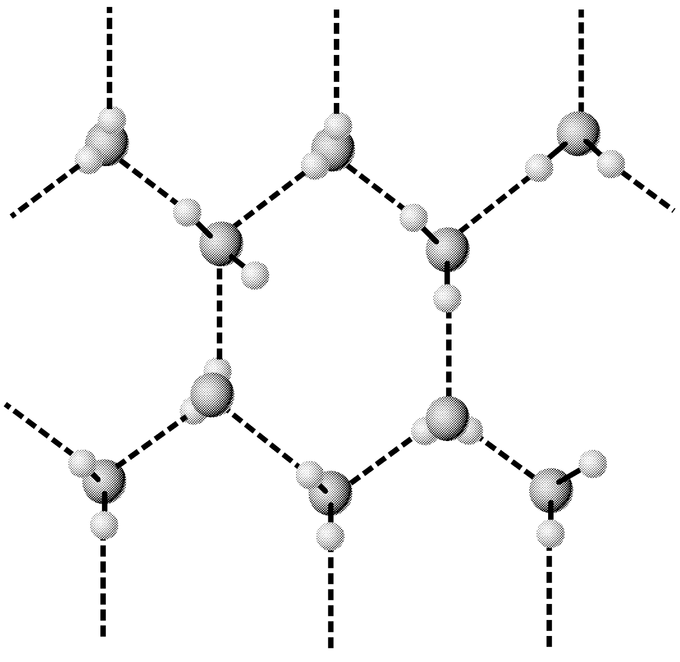


Figure 8.32 Hydrogen-bonding in ice.

TABLE 8.10 The Effect of Hydrogen Bonding on Physical Properties: Water, Methyl Alcohol, and Methyl Ether

	H_2O	CH_3OH	$(CH_3)_2O$
Molecular weight	18	32	46
Dipole moment (D)	1.84	1.68	1.30
Melting point (°C)	0	−97.8	−138.5
Boiling point (°C)	100	64.7	−23.7
Heat of vaporization at bp (kJ/mol)	40.7	35.2	21.5
Viscosity (20 °C; cp)	1.005	0.597	(gas)
Density (20 °C; g/mL)	0.998	0.792	(gas)

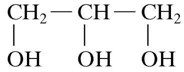
the hydrogen is covalently bonded, and therefore the strength usually decreases in the order F > O > N. The bond energies of hydrogen bonds—the energy necessary to *break* a bond, which is therefore a measure of bond strength—range from about 12 to 42 kJ/mol. This is a relatively strong bond compared with intermolecular forces, but is only about one-tenth the strength of covalent bonds. For example, in liquid water the bond energy for the hydrogen bonds is about 29 kJ/mol, whereas the bond energy for the covalent O—H bonds is 456 kJ/mol.

The effect of hydrogen bonding on the properties of liquids is convincingly demonstrated in Table 8.10 and Table 8.11, where the properties compared are ones whose magnitudes increase as the attractions between molecules become stronger. Table 8.10 compares water (which has two hydrogen atoms available for hydrogen bonding) with methyl alcohol (only one hydrogen available for hydrogen bonding) and methyl ether (no hydrogen bonding). The dipole moments suggest that the strongest forces occur in water and the weakest in methyl ether. However, the differences in dipole moments are not great and would not be expected to lead to large differences in properties. Furthermore, the trend in molecular weights might be expected to counteract the effect of polarity. The striking differences in properties can be accounted for only by hydrogen bonding.

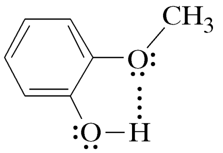
In Table 8.11, three liquids of nearly the same molecular weight are compared: *n*-hexane, a nonpolar molecule in which the only attractions are van der Waals forces; 1-pentanol, a polar compound capable of dipole-dipole attractions and some hydrogen bonding; and glycerol, a trihydric alcohol capable of undergoing very extensive hydrogen bonding.

Hydrogen bonding may also occur between unlike molecules. For example, ketones, which are incapable of hydrogen bonding themselves, will form hydrogen bonds with alcohols, and water molecules will hydrogen bond to alcohol molecules. Furthermore, *intramolecular* hydrogen bonding (hydrogen bonding *within* a mole-

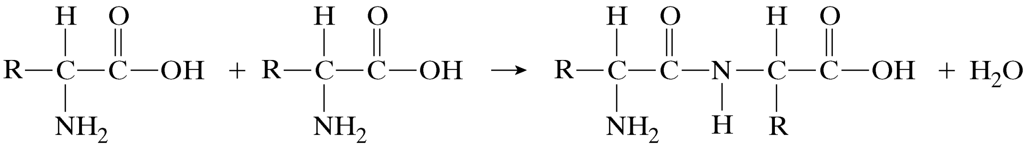
TABLE 8.11 Some Physical Properties of *n*-Hexane, 1-Pentanol, and Glycerol

PROPERTY	$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_3CH_2OH$	 $\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$
Molecular weight	86	88	92
Density (20 °C; g/mL)	0.659	0.810	1.261
Melting point (°C)	−95.3	−78.9	18.2
Boiling point (°C)	68.7	138.1	290
Viscosity (20 °C; cp)	0.33	4.0	1069.0
Surface tension (20 °C; dynes/cm)	18.4	23.8	63

cule) can take place where the structure will permit it, as in *o*-methoxyphenol (below).

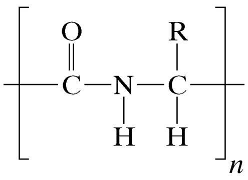


Intramolecular hydrogen bonding is an important structural determinant in certain **polypeptides**. These compounds, which include proteins, are made up of **amino acid units** and can be prepared by the condensation of amino acids. For example, a dipeptide (a peptide containing two amino acid units) would be formed by the reaction



$$R-\overset{\overset{H}{|}}{\underset{\underset{NH_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH + R-\overset{\overset{H}{|}}{\underset{\underset{NH_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH \rightarrow R-\overset{\overset{H}{|}}{\underset{\underset{NH_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH + H_2O$$

Proteins consist of numerous amino acid units and have the general formula



$$\left[-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-\right]_n$$

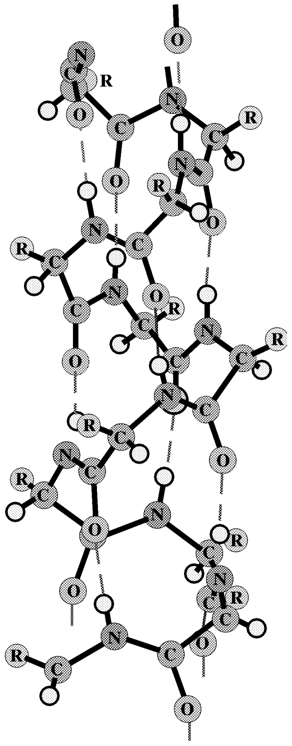


Figure 8.33 The Helical Structure of Certain Proteins. Hydrogen bonds are indicated by the dashed lines.

Proteins of the α-keratin class (found in hair, muscle, and elsewhere) have the helical arrangement shown in Figure 8.33. In this structure the hydrogen atoms attached to the nitrogens are hydrogen-bonded to the oxygens of the carbonyl groups situated above them.

CHAPTER SUMMARY

In your study of this chapter, major emphasis should be placed on the following topics:

1. **The four crystal types: ionic, metallic, molecular, and covalent network.** Learn the differences among these four types of crystals in terms of the particles that compose the lattice and the forces that hold these particles together. You should also know how and why the physical properties of solids differ in these four types of crystals.

   Understanding the differences between the properties of ionic and molecular character and electronegativities, you should now be able to make qualitative predictions about the physical properties of various compounds. For example, in a comparison of LiCl and BCl_3, you can easily determine that LiCl is much more ionic than BCl_3. You can therefore conclude that LiCl has a higher melting point, a higher heat of fusion, a lower vapor pressure, and a greater hardness than BCl_3.
2. **The nature of a crystal lattice.** You should gain an understanding of the use of x-rays in the investigation of lattice structures, of the concept of the unit cell, and of the seven crystal systems and their distinguishing characteristics.
3. **The properties of liquids and how these properties relate to intermolecular forces.**
4. **Intermolecular forces: dipole-dipole attractions, van der Waals forces, and the hydrogen bond.** You should understand the structural factors that determine the strengths of these forces, and be able to predict the kinds of intermolecular forces expected for any given compound. To do this, you will need to apply your

knowledge of electronegativity, bonding, and molecular geometry learned in previous chapters.

TERMS

Some of the important terms introduced in this chapter are as follows:

Crystalline solids Solids in which the structural units (ions, atoms, or molecules) are arranged in a regular, repeating pattern called the lattice.

Amorphous solids or glasses Solids in which the structural units are randomly arranged; these solids have no lattice structure.

Allotropy The existence of two or more different forms of an elementary substance in the same physical state. Diatomic oxygen (O_2) and ozone (O_3) are allotropes of oxygen; diamond and graphite are allotropes of carbon.

Heat of fusion The energy required to convert a solid into a liquid at its melting point.

Dipole-dipole attraction An attractive force between polar molecules in which the positive end of one dipole is attracted to the negative end of another dipole.

van der Waals forces Weak intermolecular attractive forces that are present in all molecular substances.

Unit cell The smallest section of a crystal that represents the order of arrangement. If the unit cell were moved a distance equal to its own dimensions in various directions, it would generate the entire lattice.

Closest packing The arrangement of the structural units of crystals that leads to a minimum of empty space.

Lattice defects Imperfections in a crystal lattice, due to either the dislocation of the structural units or the presence of impurities.

Viscosity A liquid's resistance to flow.

Surface tension The force on a liquid surface that opposes the expansion of the surface area.

Evaporation (vaporization) The transition of a substance from the liquid state to the gaseous state.

Sublimation The transition of a substance from the solid state directly to the gaseous state.

Condensation (liquefaction) The transition of a substance from the gaseous state to the liquid state.

Dynamic equilibrium A situation in which two opposing processes are occurring at the same rate.

Vapor pressure The pressure exerted by the molecules of a vapor (gas) in equilibrium with its liquid.

Heat of vaporization The energy required to convert a liquid into a gas. The heat of vaporization of any substance varies inversely with temperature.

Normal boiling point The temperature at which a liquid boils when the pressure is 1 atm.

Hydrogen bond A special kind of intermolecular force that occurs between a hydrogen atom in one molecule and a highly electronegative atom (F, O, or N) in another molecule. For hydrogen bonding to occur, the hydrogen atom must itself be covalently bonded to a highly electronegative element (F, O, or N). The hydrogen bond is stronger than a dipole-dipole attraction but is much weaker than a covalent bond.

PROBLEMS

1. Distinguish between the terms in each of the following pairs:
   (a) isotope and allotrope
   (b) ionic crystal and molecular crystal
   (c) heat of fusion and heat of crystallization
   (d) polar bond and polar molecule
   (e) vapor pressure and rate of evaporation

2. Make a sketch of a crystalline and an amorphous ionic solid.

3. Would it be conceptually accurate to think of a metal as a semi-amorphous ionic compound?

4. Silicon carbide (SiC) is among the hardest substances known and has a melting point above 2700 °C. Suggest a likely crystal structure for this substance.

5. Predict which of the two compounds $MgCl_2$ and PCl_5 will have
   (a) the higher melting point
   (b) the higher vapor pressure at room temperature
   (c) the higher boiling point
   (d) the greater hardness
   (e) the higher heat of fusion
   (f) the greater electrical conductivity in the liquid state

6. List those properties that distinguish ionic crystals from molecular crystals and explain the differences.

7. If only 25% of the tetrahedral holes in a close-packed structure of anions were filled by cations what would be the formula of the compound?

8. The heat of fusion of silver metal is 11.3 kJ/mol. How much heat energy is absorbed in melting 10.0 g of silver?

9. Gold metal crystallizes in the cubic closest-packed (or face-centered cubic) lattice. The atomic radius of Au is 170 pm. Determine gold's density in units of g/cm^3.

10. Describe the structure of SiO_2 with a suitable drawing and explain why it has a much higher melting point than SiF_4.

11. Which of the following molecular compounds have dipole-dipole attractions? CO_2, PH_3, BCl_3, $SiCl_4$, PCl_5, H_2S

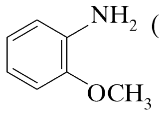
12. In the solid or liquid states where the distance between molecules is small, van der Waals forces are frequently stronger than dipole-dipole attractions, particularly when the number of electrons in the molecule is large and the dipole moment fairly small. Given this observation, which compound would you expect to have the higher boiling point—CH_3F or CH_3I?

13. In most organic molecules the carbon-hydrogen and carbon-carbon bonds do not contribute significantly to the overall dipole moment of the molecule (that is, the bond moments for the C—H and C—C bonds are essentially zero). Which of the following molecules have zero or nearly zero dipole moments?

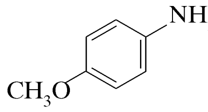
$CH_3CH_2CH_3$, CH_3CH_2Cl, CH_3OCH_3,
C_6H_{12} (cyclohexane), C_6H_6 (benzene)

14. What a difference a row in the Periodic Table can make! H_2O is one of the world's most versatile and useful compounds—a colorless, drinkable liquid; but H_2S is a foul-smelling, pale yellow gas.
   a. Which has the more dipolar bonds?
   b. Which has the larger bond angle?
   c. Which is more covalent?
   d. Which is more acidic?
   e. Why is H_2O a liquid, while H_2S is a gas?

15. For each of the following pairs of compounds, explain the difference in normal boiling points (given in parentheses):
   (a) 1-pentene (30.0 °C) and 1-heptene (93.3 °C)
   (b) silicon tetrachloride (57.6 °C) and phosphorus trichloride (76 °C)
   (c) isopropyl alcohol (82.4 °C) and n-propyl alcohol (97.2 °C)
   (d) acetic acid (118 °C) and sodium acetate (>500 °C)
   (e) methylamine (26.7 °C) and methyl alcohol (64.7 °C)
   (f)

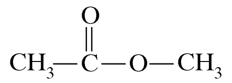


(225 °C)



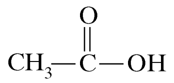
(243 °C)

   (g)



$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}CH_3$$

(57 °C)

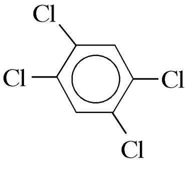


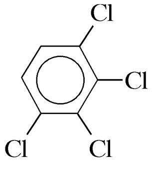
$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH$$

(118 °C)

16. For each of the pairs of compounds in Problem 15, predict which compound has (1) the higher vapor pressure, (2) the greater viscosity, and (3) the greater surface tension, all at 25 °C.

17. For each of the following pairs, predict which has the higher boiling point.
   a. F_2, I_2
   b. NaF, Na_2O
   c. MgF_2, SiF_4
   d. benzoic acid, methanoic acid
   e. NH_3, PH_3
   f. SiO_2, $SiCl_4$
   g. BCl_3, NCl_3
   h. $MgSO_4$, $BaSO_4$
   i. trichloromethane, 2-methylpropane
   j.





   k. K, Ca
   l. 1-pentanol, 2-methyl-2-butanol
   m. methyl ethanoate, propanoic acid
   n. BF_3, BI_3
   o. NH_3, H_2O

18. Which compound in each of the following pairs has the higher vapor pressure?
   a. silicon tetrafluoride, tin tetrafluoride
   b. SiH_4, PH_3
   c. NH_3, PH_3
   d. butanoic acid, 3-hydroxypropanoic acid

e. *para*-dihydroxybenzene, *ortho*-dihydroxybezene
f. benzene, *t*-butylbenzene
g. 1,3,5-tribromobenzene, 1,2,3-tribromobezene

19. A closed vessel is partially filled with a liquid. Why is it that the density of the liquid decreases and the density of the vapor increases with an increase in temperature?

20. Explain the fact that when a liquid is in equilibrium with its solid phase, the vapor pressure of the liquid must equal the vapor pressure of the solid.

21. Rationalize the following experimental observations:
(a) Pressure applied to liquid $TeCl_4$ at a temperature just above its normal freezing point causes the substance to freeze.
(b) Aluminum chloride has a higher vapor pressure than aluminum fluoride.
(c) Methyl ether has a higher vapor pressure than ethyl alcohol at room temperature.

22. Explain the difference between the **meniscus** (the curved upper surface of a column of liquid) in an alcohol thermometer and in a mercury thermometer.

23. A traveler in the deserts of the Middle East, under a temperature of 135 °F, is pleasantly surprised to find that water stored in a porous clay pot is refreshingly cold. Explain.

24. Would it take more or less energy to convert 1 g of water at 90 °C to vapor at 90 °C than to convert 1 g of water at 70 °C to vapor at 70 °C? Explain.

25. Account for the fact that solid H_2S forms a close-packed structure, but solid H_2O does not.

26. The isoelectronic compounds HCN and C_2H_2 have significantly different boiling points. Obtain these boiling points from a reference handbook and account for the difference.

27. Account for the following trends in boiling points:
(a) $HF > HI > HBr > HCl$
(b) $Xe > Kr > Ar > Ne > He$
(c) $SnCl_4 > GeCl_4 > SiCl_4 > CCl_4$
(d) $H_2O > HF > NH_3$
(e) $H_2Se > AsH_3 > GeH_4$
(f) $H_2O > H_2Te > H_2Se > H_2S$

28. Prepare graphs of the data given in Table 8.9.

29. Indicate by checking the appropriate column the kind(s) of intermolecular forces exhibited by each of the following:

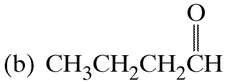
	DIPOLE-DIPOLE	VAN DER WAALS	HYDROGEN BONDING
Isopropyl alcohol			
Ethyl methyl ether			
Ethyl fluoride			
Tin tetrachloride			
Acetic acid			
Hydrogen sulfide			

30. Fill in the blanks

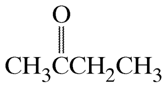
1. Weak attractive forces that exist between all molecules are ____________.
2. The pressure exerted by the molecules of a vapor in equilibrium with its liquid is called the ____________ of the liquid.
3. In ____________ solids, the structural units are randomly scattered.
4. Two or more different forms of the same elementary substance in the same physical state are called ____________.
5. ____________ is the transition of a substance from the solid state directly to the gaseous state.
6. The smallest section of a crystal that represents the lattice of that crystal is called the ____________.
7. The internal structure of a crystal is determined by the diffraction of ____________.
8. The situation in which two opposing processes are occurring at exactly the same rate is described as ____________.
9. The closest packing of identical spheres can result in one of two different arrangements: ____________ and ____________ close-packed structures.
10. In general, the crystal type that exhibits the greatest hardness is ____________.
11. The greater the viscosity of a liquid at a given temperature, the ____________ its intermolecular forces.
12. Water expands when it freezes because of ____________.
13. The type of intermolecular force that is dependent on molecular polarity is called ____________.
14. The boiling point of a liquid is the temperature at which the ____________ of the liquid is equal to the pressure of the surrounding atmosphere.
15. Surface tension ____________ as temperature increases.

31. Multiple-choice questions

1. Which of the following has the highest melting point?
(a) $MgCl_2$ (b) BCl_3
(c) NCl_3 (d) CCl_4
2. Which of the following exhibits the most hydrogen-bonding?
(a) LiH (b) CH_4 (c) NH_3 (d) H_2S
3. Which of the following substances has the greatest electrical conductivity in the solid state?
(a) K (b) KI (c) I_2 (d) IF_3
4. Which of the following has the highest normal boiling point?
(a) CF_4 (b) CCl_4 (c) CBr_4 (d) CI_4
5. Which of the following has the lowest vapor pressure at 25 °C?
(a) $CH_3CH_2{-}O{-}CH_2CH_3$


(b) $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$

(c) $CH_3CH_2CH_2CH_2OH$

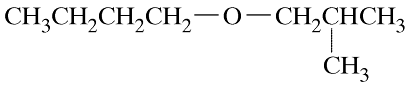
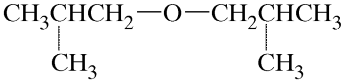
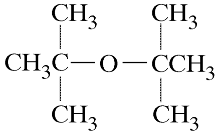
(d) 
$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$

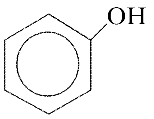
6. Which of the following has the lowest melting point?
   (a) diamond (b) $CaCl_2$ (c) PCl_5 (d) Fe

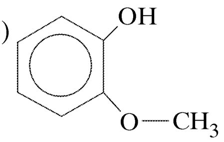
7. The heat of fusion of a typical ionic crystal is
   (a) the same as its lattice energy
   (b) the negative of its heat of crystallization
   (c) higher than the heat of fusion of a typical covalent network crystal
   (d) the heat energy emitted when the crystal melts

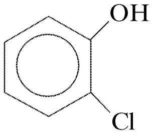
8. The melting points of the alkali metals
   (a) increase with increasing atomic weight
   (b) increase with decreasing atomic weight
   (c) are higher than the melting points of the alkaline earth metals
   (d) none of the above

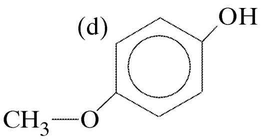
9. Which one of the following substances exhibits no van der Waals forces?
   (a) NH_3 (b) H_2
   (c) Ar (d) none of the above

10. Which ether has the highest boiling point?
    (a) $CH_3CH_2CH_2CH_2\text{—}O\text{—}CH_2CH_2CH_2CH_3$
    (b) 
    $CH_3CH_2CH_2CH_2\text{—}O\text{—}CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$
    (c) 
    $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\text{—}O\text{—}CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$
    (d) 
    $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}O\text{—}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

11. In which of the following is intramolecular hydrogen bonding most likely to occur?
    (a) 

    (b) 

    (c) 

    (d) 

12. Which liquid would you expect to have the highest viscosity at room temperature?
    (a) *n*-octane (b) isooctane
    (c) 2-octanone (d) octanoic acid

13. In which compound are the dipole-dipole attractions weakest?
    (a) HBr (b) H_2Se (c) AsH_3 (d) GeH_4

14. Which of the following is the hardest?
    (a) CaO (b) SiO_2 (c) SO_2 (d) OF_2

15. Freezing is
    (a) an exothermic process
    (b) an endothermic process
    (c) the same as fusion
    (d) the opposite of sublimation

9 Gases and Transitions Between States

The gaseous state of matter may be thought of as a highly diffuse extension of the liquid state. Substances that exist in the gaseous state at normal conditions are composed of molecules (or in the case of the inert gases, of individual atoms) randomly distributed and moving with relatively high velocities. The average distance between gas molecules is much greater than between molecules in the liquid state, and the attractive influence of neighboring molecules is much smaller. Most substances that exist as gases under ordinary conditions (room temperature and atmospheric pressure) have low molecular weights (therefore, high molecular velocities) and weak intermolecular forces.

The large distance between molecules explains the great variation in the density of a gas with changes in pressure and temperature. When the pressure on a confined gas sample is increased, the molecules are simply forced closer together, resulting in increased density. However, when the temperature is raised, the average velocity of the molecules increases. This causes an increase in the intermolecular distances and decreases the density.

At moderately high temperatures (around room temperature and above) and at moderately low pressures (atmospheric and below), the molecules of most gases are so far apart that two approximations may be made concerning them. First, the volume occupied by the molecules themselves is negligible in relation to the total volume of the gas. In other words, the molecules may be thought of simply as points in space. Second, the attractive forces between molecules are negligible. Under conditions of high temperatures and low pressures, many of the properties of gases become a function not of the molecules, but of the space between molecules. Any gas for which these approximations—negligible molecular volume and negligible intermolecular forces—are valid under all conditions is called an **ideal gas**. The behavior of this hypothetical gas can be described by several quantitative statements called the ideal gas laws.

9.1 THE IDEAL GAS LAWS

The volume occupied by any gas sample is determined by three factors: the pressure, the temperature, and the number of molecules in the sample. The **ideal gas laws** are statements of the relationship of volume to each of these factors.

Variation of Volume with Pressure: Boyle's Law

Gases exert pressure on any surface with which they come into contact. This pressure is interpreted as the result of collisions of the moving molecules with the surface. Since the earth's atmosphere is a mixture of gaseous substances, the atmosphere exerts a pressure on all objects on the earth's surface. This **atmospheric pressure** is approximately 1.013×10^5 N/m^2 (14.7 lb/in^2), but varies with elevation and fluctuates even in the same location.

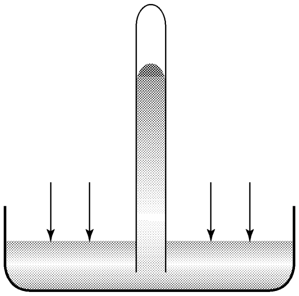


Figure 9.1 Measurement of atmospheric pressure: a barometer.

The pressure exerted by the atmosphere may be demonstrated as follows. We fill a long glass tube with mercury. The mouth of the completely filled tube is covered, and the tube is inverted into a dish of mercury so that the mouth of the tube is beneath the surface of the mercury in the dish (Figure 9.1). When the cover is removed from the mouth of the tube, some of the mercury runs into the dish, but the mercury within the tube maintains a level well above that in the dish (about 76 cm above it). The column of mercury in the tube is being supported by the pressure of the atmosphere on the surface of the mercury in the dish. Any other liquid could be used in this demonstration, but most liquids have a much lower density and thus the column of liquid would be prohibitively high. If water were used, for example, the column would be over 10 m high.

Since the height of the column of mercury is proportional to the pressure supporting it, this affords a convenient way of measuring atmospheric pressure. In chemistry, gas pressures are almost always expressed in millimeters of mercury (mm Hg); one millimeter of mercury is also called a **torr** (after the Italian physicist Evangelista Torricelli). A device used for measuring atmospheric pressure based on the simple apparatus just described is called a **mercurial barometer**. One atmosphere (atm) is defined as 760 torr (760 mm Hg). The SI unit for pressure is the **pascal** (Pa): one pascal is one newton per square meter. One atmosphere is equal to 101,325 Pa.

The principle employed in the mercurial barometer can also be used to measure the pressure of a confined gas sample. Figure 9.2 shows a flask containing a gas. The flask is fitted with a U-tube containing mercury and open to the atmosphere at one end. The gas within the flask is exerting pressure on the mercury in one arm of the U-tube, while the other arm is subjected to atmospheric pressure. If the pressure of the gas sample is exactly equal to that of the atmosphere, the mercury stands at the same height in both arms (Figure 9.2a). Figure 9.2b represents the case where the pressure inside the flask is greater than atmospheric pressure, and in Figure 9.2c atmospheric pressure is greater than the pressure of the gas. By measuring the difference in the heights of the two columns and determining the atmospheric pressure with a barometer, the pressure of the confined gas sample can be determined by simple arithmetic. For example, suppose that the mercury columns are positioned as in Figure 9.2c and that the difference in the heights of the columns is 36 mm. Suppose further that atmospheric pressure has been found to be 742 torr. The pressure of the gas in the flask, then, is 742 − 36 = 706 torr. This U-tube device is called a **manometer**.

The pressure of a gas sample can be related to its volume by **Boyle's Law**, named after the English chemist Robert Boyle, who first described it in 1662:

For any given mass of gas, the volume varies inversely with the pressure, provided the temperature is held constant.

This law is illustrated in Figure 9.3, where a sample of a gas is shown confined in a cylinder with a movable piston. The total pressure required to keep the piston in place is equal to the pressure being exerted on the piston by the gas molecules. When the pressure is *P*,

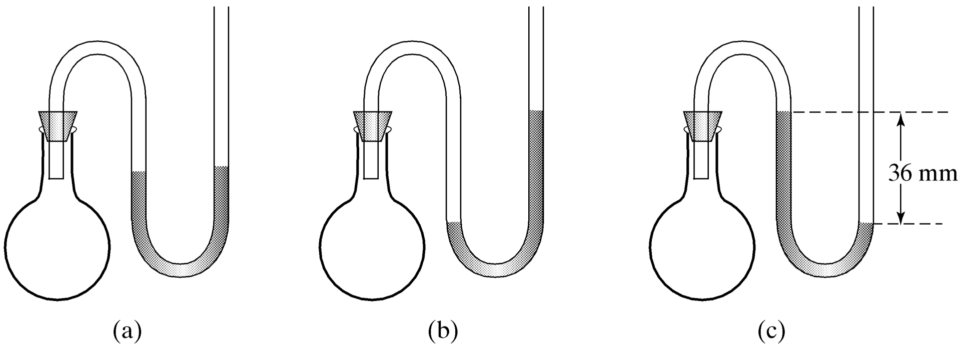


Figure 9.2 A manometer used to measure the pressure of a confined gas.

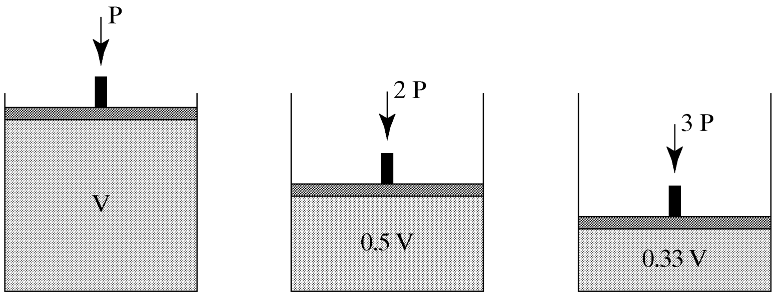


Figure 9.3 An Illustration of the Relationship Between Pressure and Volume: Boyle's Law

the gas in the cylinder has a volume of V. If the pressure is raised to $2P$ and the temperature is held constant, the volume of the gas will be reduced to $\frac{1}{2}V$. Similarly, if the pressure is raised to $3P$, the volume becomes $\frac{1}{3}V$. This relationship may be expressed mathematically as

$$V \propto \frac{1}{P} \quad \text{or} \quad V = \frac{k}{P}$$

where k is a proportionality constant. Therefore, PV = constant, and for any gas sample that goes from a volume of V_1 and a pressure of P_1 to a volume of V_2 and a pressure of P_2 (temperature and number of molecules remaining constant), the following relationship holds:

$$P_1V_1 = P_2V_2$$

Boyle's Law enables us to make quantitative predictions about the effect that a particular pressure change will have on the volume of a gas, and vice versa.

Problem 9.1

If a certain sample of nitrogen has a volume of 250 mL at a pressure of 735 torr, what will the volume of the sample be at a pressure of 1 atm (760 torr)?

Solution:

Using the relationship $P_1V_1 = P_2V_2$, we have $P_1 = 735$ torr, $V_1 = 250$ mL, $P_2 = 760$ torr, and V_2 = unknown. When these values are substituted into the equation, we obtain

$$735 \times 250 = 760 \times V_2$$

Solving for V_2 gives us

$$V_2 = \frac{735 \text{ torr} \times 250 \text{ mL}}{760 \text{ torr}} = 242 \text{ mL}$$

The same results can be obtained by a "reasoning" method as follows. The volume of 250 mL is to be "corrected" for a pressure change; that is, the volume must be multiplied by a ratio of the two pressure values. Since the pressure change is an increase, and since pressure and volume vary inversely, the volume must decrease. Thus, we must multiply the 250 mL by a "correction factor" of less than one, that is, by 735/760.

$$250 \text{ mL} = \frac{735}{760} = 242 \text{ mL}$$

Problem 9.2

If a sample of oxygen has a volume of 800 mL at a pressure of 740 torr and a temperature of 30 °C, what pressure will be required to compress the oxygen sample to 500 mL, keeping the temperature constant?

Solution:

$P_1 = 740$ torr, $V_1 = 800$ mL, $P_2 =$ unknown, $V_2 = 500$ mL. Therefore:

$$P_2 = \frac{P_1V_1}{V_2} = \frac{740 \text{ torr} \times 800 \text{ mL}}{500 \text{ mL}} = 1184 \text{ torr}$$

The same result is obtained by reasoning that the "new" pressure is simply the "old" pressure multiplied by the ratio of the two volumes. Since volume and pressure vary inversely, and the volume in this example is decreasing, the pressure must increase. Therefore, the ratio of the volumes must be a factor that is greater than one, namely, 800/500.

$$P_2 = 740 \text{ torr} \times \frac{800}{500} = 1184 \text{ torr}$$

Variation of Volume with Temperature: Charles' Law

Experiments by the French scientist Jacques Charles around 1787 resulted in a statement of the relationship between gas volume and temperature. Confirmation and elaboration of these results was published by another Frenchman, Joseph Gay-Lussac, in 1802. This relationship resulted from the observation that different gases expand by the same fractional amount for the same rise in temperature if the pressure is held constant. It was found that the volume of a gas increases by 1/273 of its volume at 0 °C for each degree Celsius that the temperature is raised. If, for example, we had 273 mL of a gas at 0 °C and at some pressure *P*, then raising the temperature to 1 °C (keeping the pressure constant) would increase the volume of the gas by a factor of 1/273, or 1 mL. The volume at 1 °C would therefore be 274 mL. Raising the temperature to 2 °C would expand the volume to 275 mL; at 10 °C the volume would be 283 mL, and so on. Naturally, if the temperature of the same gas sample were lowered to −1 °C, its volume would contract to 272 mL, and at −10 °C the volume would be 263 mL.

This relationship implies that if the temperature were lowered far enough, to −273 °C, the volume of a gas would become zero. Of course, any real gas would liquefy before this low temperature was reached, but a hypothetical, nonliquefiable gas would "disappear" at −273 °C, suggesting that this temperature represents a degree of coldness beyond which it is impossible to go. This temperature, or more precisely, −273.15 °C, is known as **absolute zero** and represents the zero point on the **absolute temperature scale**, also called the **Kelvin scale**. The units of this scale, called Kelvins (K), can be converted from Celsius degrees by the relationship K = °C + 273.

The temperature of a sample of gas can be related to its volume by a formal statement known as **Charles' Law**:

For any given mass of gas, the volume varies directly with the absolute temperature, provided the pressure remains constant.

Expressed mathematically, this becomes

$$V \propto T \quad \text{or} \quad V = kT$$

Therefore

$$\frac{V}{T} = \text{constant}$$

and

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles' Law has the same usefulness in predicting volume-temperature relationships as Boyle's Law has for volume-pressure relationships.

Problem 9.3

A sample of methane gas has a volume of 1.50 L at 25 °C and 1 atm pressure. What volume will it occupy at 50 °C and 1 atm pressure?

Solution:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 1.50\ \text{L}$

$T_1 = 25\ °\text{C} + 273 = 298\ \text{K}$

$T_2 = 50\ °\text{C} + 273 = 323\ \text{K}$

$V_2 = \text{unknown}$

Solving for V_2 and substituting the appropriate values into the equation gives

$$V_2 = \frac{V_1}{T_1} \times T_2 = \frac{1.50\ \text{L}}{298\ \text{K}} \times 323\ \text{K} = 1.63\ \text{L}$$

We can also reason that since volume and temperature vary directly, the increase in temperature from 25 °C to 50 °C must result in an increase in volume. Therefore, the initial volume of 1.50 L must be multiplied by the ratio of the two temperatures, and this ratio must be a factor that is greater than one, namely, 323/298.

$$1.50\ \text{L} \times \frac{323}{298} = 1.63\ \text{L}$$

✓ Check Point 9.1

A gas occupies a volume of 2.0 L at 0.0 °C. If the pressure is maintained at a constant value, but the temperature is increased to 136.0 °C, what will the volume (in L) of the gas be?

Solution:

3.0 L

◇ ◇ ◇ ◇ ◇

Consideration of the effects described by Boyle's Law and Charles' Law leads to a simple relationship between pressure and temperature. Increasing the temperature tends to expand the volume (Charles' Law); if this expansion of volume is to be prevented, it can only be done by increasing the pressure (Boyle's Law). Thus, according to a statement sometimes referred to as **Gay-Lussac's Law**:

At constant volume, the pressure and absolute temperature of a gas vary directly.

Problem 9.4

The gas in a steel bomb exerts a pressure of 1.00 atm at 33 °C. What will the pressure be if the temperature is raised to 100 °C? (Note that the volume cannot change, unless, of course, the bomb bursts.)

Solution:

The temperature increase from 33 °C (306 K) to 100 °C (373 K) will cause the pressure to be raised by a factor of 373/306.

$$1.00\text{ atm} \times \frac{373}{306} = 1.22\text{ atm}$$

Let us consider now how the volume of a gas is affected by changes in both temperature and pressure. Suppose, for example, we have 100 mL of a gas at 35 °C and 740 torr. What will be the volume of the gas sample at **standard temperature and pressure**? (Standard temperature and pressure, abbreviated STP, is defined as a temperature of 0 °C and a pressure of 1 atm.)

In this case it might appear that the gas laws are not applicable in predicting the new volume, since Boyle's Law assumes constant temperature and Charles' Law assumes constant pressure. However, the same final volume is reached if the changes are brought about in two steps. First, let us hold the temperature constant and change the pressure. Second, holding the *new* pressure constant, let us change the temperature. In the two-step process, the first step is a simple Boyle's Law correction of the initial volume, and the second step is a Charles' Law correction of the intermediate volume. The problem is therefore solved as follows:

1. Holding T constant, we change P from 740 torr to 760 torr. Since increasing the pressure decreases the volume, the correction factor is less than one.

$$100\text{ mL} \times \frac{740\text{ torr}}{760\text{ torr}} = \text{intermediate volume (mL)}$$

2. Holding P constant, we change T from 308 K to 273 K and calculate the effect on the intermediate volume. Since decreasing the temperature causes a decrease in volume, the temperature correction factor, like the pressure correction factor, is less than one.

$$100\text{ mL} \times \frac{740\text{ torr}}{760\text{ torr}} \times \frac{273\text{ torr}}{308\text{ torr}} = 86.3\text{ mL}$$

Variation of Volume with Number of Molecules: Avogadro's Law

In 1811, the Italian scientist Amedeo Avogadro summarized the relationship between the volume of a gas and the number of molecules present. This relationship, sometimes called Avogadro's Law, may be stated as follows: Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules. For example, one liter of chlorine contains the same number of molecules as one liter of methane or one liter of nitrogen or one liter of any gas, provided the temperature and pressure are the same in all cases. Furthermore, two liters of chlorine contain twice as many molecules as one liter, if again the temperature and pressure are the same. In other words, according to Avogadro's Law, the volume of a gas is directly proportional to the number of molecules of that gas at constant temperature and pressure. This relationship may be stated mathematically as

$$V \propto N \quad \text{or} \quad V = kn$$

where n represents the number of molecules.

Visualization 9.1

Which of the following diagrams illustrates Avogadro's Law (temperature is constant)?

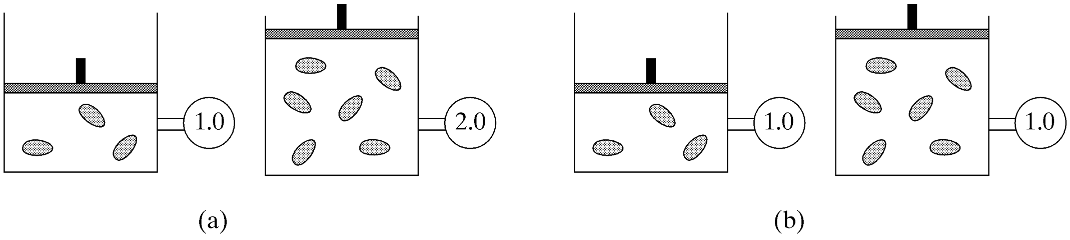


Diagram (b) illustrates Avogadro's Law because it indicates that twice as many molecules will double the volume if the pressure remains constant.

Because we usually deal with very large numbers of molecules, it is often more convenient to express the quantity of gas in terms of the number of moles rather than the number of molecules. Keeping in mind that a mole of any substance contains the same number of molecules as a mole of any other substance, **Avogadro's Law** may be restated:

The volume of a gas is directly proportional to the number of moles of the gas if the temperature and pressure are constant.

Therefore:

$$V \propto n \quad \text{or} \quad V = kn$$

where n equals the number of moles.

It follows from this relationship that one mole of any gas occupies the same volume as one mole of any other gas at the same temperature and pressure. At standard conditions (0 °C and 760 torr), one mole of any gas occupies 22.414 L. This volume, which for most purposes can be rounded off to 22.4 L, is called the **molar gas volume at standard temperature and pressure**.

Avogadro's Law and the establishment of the molar gas volume enable us to relate the weight of a gas sample to its volume in a number of useful ways. We can calculate the volume occupied by a given weight of a particular gas at STP or—by applying Charles' and Boyle's Laws—at any other temperature and pressure.

Problem 9.5

What is the volume of 10.0 g of CO_2 at STP?

Solution:

One mole of CO_2 weighs 44.0 g. Therefore:

$$10.0 \text{ g of } CO_2 = \frac{10.0}{44.0} \text{ mol of } CO_2$$

Since one mole occupies 22.4 L at STP, we obtain

$$\frac{10.0 \text{ g}}{44.0 \text{ g/mol}} \times \frac{22.4 \text{ L}}{1 \text{ mol}} = 5.09 \text{ L at STP}$$

Problem 9.6

What is the volume of 5.0 g of CH_4 at 30 °C and 735 torr?

Solution:

The volume of 5.0 g of CH_4 at STP, following the procedure in Problem 9.5, is

$$\frac{5.0\ \text{g}}{16.0\ \text{g/mol}} \times \frac{22.4\ \text{L}}{1\ \text{mol}}$$

Correcting this volume for a temperature increase (0 °C to 30 °C) and a pressure decrease (760 torr to 735 torr), we have

$$\frac{5.0\ \text{g}}{16.0\ \text{g/mol}} \times \frac{22.4\ \text{L}}{1\ \text{mol}} \times \frac{303\ \text{K}}{273\ \text{K}} \times \frac{760\ \text{torr}}{735\ \text{torr}} = 8.0\ \text{L}$$

The density of any gas can also be readily calculated. Since the weight of a mole and the volume of a mole at STP are known, the density of a gas at STP (in grams per liter) is simply its molecular weight divided by 22.4. The density at any other conditions of temperature and pressure can be found by applying Boyle's and Charles' correction factors to the density at STP.

Problem 9.7

What is the density of acetylene (C_2H_2) at 100 °C and 800 torr?

Solution:

The molecular weight of C_2H_2 is 26.0; that is, one mole weighs 26.0 g. The density of C_2H_2 at STP, then, is

$$\frac{26.0\ \text{g/mol}}{22.4\ \text{L/mol}}$$

Increasing the temperature from 0 °C to 100 °C will decrease the density by a factor of 273/373. Increasing the pressure from 760 torr to 800 torr will increase the density by a factor of 800/760. Therefore, the density of acetylene at 100 °C and 800 torr is

$$\frac{26.0\ \text{g/mol}}{22.4\ \text{L/mol}} \times \frac{273}{373} \times \frac{800}{760} = 0.894\ \text{g/L}$$

Since one mole of any gas occupies the same volume as one mole of any other gas, the densities of various gases (at any stated temperature and pressure) are in the same ratio to one another as the ratios of their molecular weights. Thus, the density of O_2 (molecular weight = 32) is 16 times the density of H_2 (molecular weight = 2) at the same temperature and pressure; CH_4 (molecular weight = 16) has a density one-half that of O_2; and so on.

Avogadro's Law also leads us to certain conclusions regarding the volumes of gaseous substances consumed and produced in chemical reactions. A chemical equation tells us nothing about the relative volumes of substances involved in chemical reactions if those substances are in the solid or liquid states; calculations of reacting volumes would require that the densities of the substances be known. However, for gases this is not the case. Because equal volumes of gases contain equal numbers of molecules (at the same temperature and pressure), and because the coefficients in a balanced equation represent ratios of numbers of molecules, we may state the following relationship, discovered by Gay-Lussac in 1808 and called the **Law of Combining Volumes**:

The coefficients in a balanced chemical equation represent the ratios of volumes of gaseous substances involved in a chemical reaction, assuming the volumes are measured at the same temperature and pressure.

By way of illustration, consider the reaction whereby ammonia is produced by direct combination of nitrogen and hydrogen. The balanced equation for this reaction is

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

This equation indicates that one volume of N_2 will combine with three volumes of H_2 to yield two volumes of NH_3, all volumes being measured at the same temperature and pressure. In other words, 100 L of N_2 will yield 200 L of NH_3, or 10 cu ft of N_2 will react with 30 cu ft of H_2, and so on.

Furthermore, because of our knowledge of the molar gas volume at STP, it is possible to relate the volume of a gaseous reactant or product to the weights of the other substances taking part in the reaction.

Problem 9.8

When solid potassium chlorate is heated, it decomposes to give oxygen, as follows:

$$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$$

What volume of oxygen (measured at STP) will be produced from the decomposition of 10.0 g of $KClO_3$?

Solution:

Since the formula weight of $KClO_3$ is 122.6, we have

$$10.0 \text{ of } KClO_3 = \frac{10.0}{122.6} \text{ mol of } KClO_3$$

The equation tells us that 2 mol of $KClO_3$ yield 3 mol of O_2. Therefore, the number of moles of O_2 produced is

$$\left(\frac{10.0}{122.6} \times \frac{3}{2}\right) \text{mol}$$

At STP, each mole of O_2 occupies a volume of 22.4 L, and therefore the volume of oxygen produced is

$$\frac{10.0 \text{ g } KClO_3}{122.6 \text{ g/mol } KClO_3} \times \frac{3 \text{ mol } O_2}{2 \text{ mol } KClO_3} \times \frac{22.4 \text{ L}}{1 \text{ mol } O_2} = 2.74 \text{ L } O_2$$

The volume of oxygen can be calculated for any other temperature and pressure by application of Boyle's and Charles' correction factors.

9.2 THE IDEAL GAS EQUATION

Boyle's Law ($V \propto 1/P$), Charles' Law ($V \propto T$) and Avogadro's Law ($V \propto n$) can be combined into one mathematical statement:

$$V \propto \frac{nT}{P}$$

This statement can be written as a mathematical equation by use of a proportionality constant, which we will designate as R,

$$V = \frac{RnT}{P}$$

or, more commonly,

$$PV = nRT$$

This equation, called the **ideal gas equation**, describes the relationship between pressure, volume, number of moles, and absolute temperature for an ideal gas. Thus, if the value of the **ideal gas constant**, R, is known, then the value of any one of the four variables—P, V, n, T—can be determined if the values of the other three variables are known.

The ideal gas constant, R, can be evaluated rather simply from our knowledge of the molar gas volume at STP; that is, from our knowledge that one mole of gas occupies 22.4 L at STP. In other words, when $n = 1$ mol, $P = 1$ atm, and $T = 273$ K, then $V = 22.4$ L. Solving the ideal gas equation for R and substituting these values into it gives

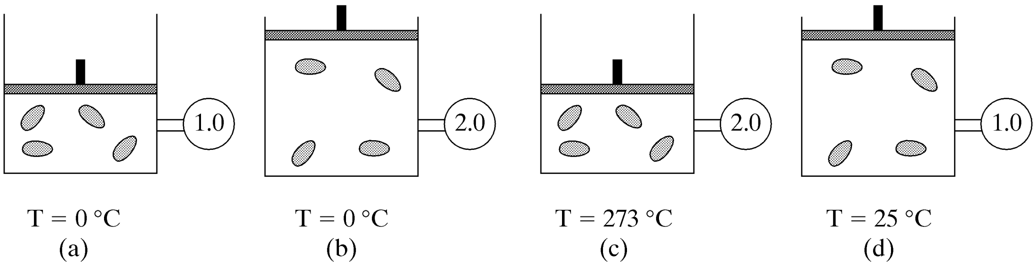
$$R = \frac{PV}{nT} = \frac{1\text{ atm} \times 22.4\text{ L}}{1\text{ mol} \times 273\text{ K}} = 0.0821\,\frac{\text{L-atm}}{\text{mol-K}}$$

The magnitude and units of R depend on the units in which the variables are expressed. If, for example, we had used 760 torr for P, then the value of R would be 62.4 L-torr/mol-K. The value of 0.0821 L-atm/mol-K is the value most commonly used for R.

Now, with R evaluated, the ideal gas equation can be employed to solve a variety of problems by direct substitution of the proper values. It should be noted, however, that the ideal gas equation does not enable us to solve any "new" kinds of problems. It is simply an alternative route to the solution of problems that can be solved by the application of the individual gas laws using the methods illustrated in earlier examples. Problems 9.9–9.12 illustrate the solution of a number of problems using the ideal gas equation, including several that were solved earlier.

Visualization 9.2

Assume that diagram (a) represents the starting point and that the other diagrams represent changes to (a). Which of these changes is consistent with the ideal gas law?



Solution:

(c)

Problem 9.9

A certain gas sample has a volume of 100 mL at 35 °C and 740 torr. What will be the volume of the sample at STP?

Solution:

Using the expression $PV = nRT$, all quantities are known about the original gas except n, the number of moles.

$$P = 740 \text{ torr} = \frac{740}{760} \text{ atm}$$

$$V = 100 \text{ mL} = 0.100 \text{ L}$$

$$T = 35\ °\text{C} = 308 \text{ K}$$

$$R = 0.082l \text{ L-atm/mol-K}$$

Substituting these quantities into the equation and solving for n, we have

$$n = \frac{PV}{RT} = \frac{740 \text{ torr}}{760 \text{ torr}} \times \frac{0.100}{0.0821 \times 308} = 0.00385 \text{ mol}$$

Now, changing P and T will change V, but will have no effect on n. Therefore, under the final conditions,

$$P = 1 \text{ atm}$$

$$n = 0.00385 \text{ mol}$$

$$T = 0\ °\text{C} = 273 \text{ K}$$

$$R = 0.0821$$

Solving the ideal gas equation for V and substituting these values give

$$V = \frac{nRT}{P} = \frac{0.00385 \times 0.0821 \times 273}{1} = 0.0863 \text{ L} = 86.3 \text{ mL}$$

Problem 9.10

What is the volume of 5.0 g of CH_4 at 30°C and 735 torr?

Solution:

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$n = \frac{5.0 \text{ g}}{\text{mol wt CH}_4} = \frac{5.0 \text{ g}}{16 \text{ g/mol}} = \frac{5.0}{16} \text{ mol}$$

$$R = 0.0821 \text{ L-atm/mol-K}$$

$$T = 30°\text{C} = 303 \text{ K}$$

$$P = 735 \text{ torr} = \frac{735}{760} \text{ atm}$$

Therefore:

$$V = \frac{5.0}{16} \times 0.0821 \times 303 \times \frac{760}{735} = 8.0 \text{ L}$$

Problem 9.11

What is the density of acetylene (C_2H_2) at 100 °C and 800 torr?

Solution:

Densities of gases are usually expressed in terms of grams per liter. Therefore, what we are seeking in this problem is the weight (in grams) of one liter of the gas, which can be expressed as g/V. The relationship between the weight (in grams) of any substance and the number of moles of that substance is

$$n = \frac{\text{grams}}{\text{grams/mol}} = \frac{g}{M}$$

where M is the molecular weight of the substance. Hence, the ideal gas equation may be expressed in the form

$$PV = \frac{g}{M} RT$$

The problem, then, is to find the value of g/V when

$$P = 800 \text{ torr} = \frac{800}{760} \text{ atm}$$

$$R = 0.0821 \text{ L-atm/mol-K}$$

$$T = 100 \text{ °C} = 373 \text{ K}$$

$$M = 26.0 \text{ g/mol (the molecular weight of } C_2H_2\text{)}$$

Solving for g/V and substituting the appropriate values gives

$$\frac{g}{V} = \frac{PM}{RT} = \frac{800}{760} \times \frac{26.0}{0.0821 \times 373} = 0.894 \text{ g/L}$$

✓ Check Point 9.2

What weight of N_2 will occupy a volume of 2.5 L at a pressure of 1.0 atm and a temperature of 200 °C?

Solution:

1.8 g

◇ ◇ ◇ ◇ ◇

One of the major practical applications of the ideal gas law is in the experimental determination of molecular weights of gases or very volatile liquids. Although a number of different techniques can be used, they all involve the measurement of gas density; that is, the accurate measurement of the weight and the volume of a gas sample and observation of the temperature and pressure at the time of measurement. The general procedure may be illustrated as follows: A glass bulb, of accurately known volume and fitted with a stopcock, is evacuated and weighed. The bulb is then filled with the gas under investigation, the temperature is noted, and the pressure of the gas in the bulb is measured. Finally, the filled bulb is weighed in order to determine the weight of the gas sample. The molecular weight of the gas can be determined by applying the ideal gas equation to the measured data, as in Problem 9.12.

Problem 9.12

A glass bulb is filled with an unknown gas at 25 °C and 742 torr. The bulb has a volume of 203 mL. Use the following data to determine the molecular weight of the gas:

Weight of bulb + sample	20.3951 g
Weight of evacuated bulb	19.8765 g
Weight of gas sample	0.5186 g

Solution:

$$T = 25.0\ ^\circ\text{C} = 298\ \text{K}$$

$$P = 742\ \text{torr} = \frac{742}{760}\ \text{atm}$$

$$V = 203\ \text{mL} = 0.203\ \text{L}$$

$$PV = \frac{g}{M}\,RT$$

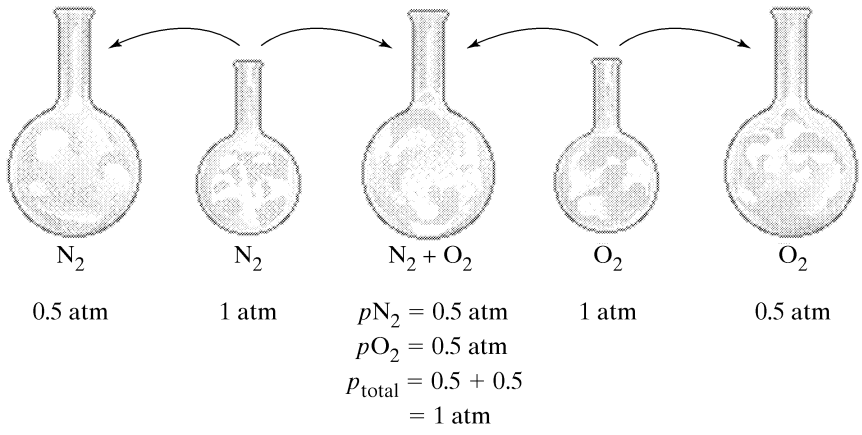
$$M = \frac{gRT}{PV} = \frac{0.5186 \times 0.0821 \times 298}{(742/760) \times 0.203} = 64.0\ \text{g/mol}$$

9.3 DALTON'S LAW OF PARTIAL PRESSURES

In 1803, the English chemist John Dalton published a statement concerning the pressures exerted by a mixture of gases. This statement, referred to as **Dalton's Law of Partial Pressures**, may be summarized as follows:

> **In a mixture of gases, each gas exerts the same pressure as it would if it were in the container alone. The sum of these individual pressures, called the partial pressures, is the total pressure of the mixture.**

As an illustration of this law, consider two 1-L containers, one filled with N_2 and the other with O_2, both at 1 atm pressure (see below). Suppose further that we have a completely empty 2-L flask. Now, if the 1 L of N_2 is in some way transferred into the empty 2-L flask, we will then have 2 L of N_2 at a pressure of 0.5 atm. (The number of molecules has remained constant, but the volume of the N_2 has doubled, and therefore the pressure is halved.) In the same way, if we were to transfer the O_2 to the empty 2-L flask, we would have 2 L of O_2 at 0.5 atm. Now suppose that we transfer the contents of *both* 1-L flasks into the empty 2-L flask. We will then have 2 L of a mixture of N_2 and O_2. The N_2 in the mixture is exerting the same pressure that it would if it were in the flask alone—0.5 atm. Therefore, the **partial pressure** of N_2 (symbolized p_{N_2}) is 0.5 atm. The O_2 in the mixture also has a **partial pressure** (p_{O_2}) of 0.5 atm. The total pressure, then, is 0.5 atm + 0.5 atm = 1 atm.



One very useful application of Dalton's Law is in calculations involving gases collected over water or other liquids. A convenient method of collecting gases produced by chemical reactions is by displacement of water. A delivery tube carries the gas to the collection vessel, which is filled with water and inverted in a beaker of water. The gas, being much less dense than water, bubbles to the top of the vessel, pushing water out of the vessel into the pan. (Naturally, if the gas in question undergoes a chemical reaction with water, or is very soluble in water, then some other liquid must be used.)

A gas collected over water in this manner is not pure; it is saturated with water vapor. The pressure of the collected sample is not the pressure exerted by the gas itself, but the sum of the partial pressures of the gas and of the water vapor ($p_{\text{total}} = p_{\text{gas}} + p_{H_2O}$). The partial pressure of the water vapor is dependent on the temperature; in fact, it is the **vapor pressure** of water at that particular temperature.

Problem 9.13

If 275 mL of oxygen is collected over water at a temperature of 23 °C and a pressure of 700 torr, what weight of O_2 has been collected? The vapor pressure of pure water is 21 torr at 23 °C.

Solution:

Because the problem requires us to solve for the weight of oxygen, it is convenient to express $PV = nRT$ as

$$PV = \frac{g}{M}RT$$

We then use the values

$$V = 0.275\ \text{L}$$

$$M = 32\ \text{g/mol}$$

$$T = 296\ \text{K}$$

However, P in the expression refers to the pressure of oxygen, which in this case is the partial pressure of oxygen, p_{O_2}. The value 700 torr is the combined pressure of oxygen and water vapor, or

$$p_{O_2} + p_{H_2O} = 700\ \text{torr}$$

The vapor pressure of water at 23 °C is 21 torr. Therefore:

$$p_{O_2} + 700 - 21 = 679\ \text{torr} = \frac{679}{760}\ \text{atm}$$

Solving for g and substituting, we have

$$g = \frac{PVM}{RT} = \frac{679}{760} \times \frac{0.275 \times 32}{0.0821 \times 296} = 0.324\ \text{g}$$

9.4 DIFFUSION OF GASES

Diffusion is the ability of a gas to spread out spontaneously and to move through another gas until it completely fills the container. For example, suppose a container of a particularly odorous gas, say hydrogen sulfide, were opened in the front of a crowded lecture hall. Those people in the front row would soon detect it, and gradually the odor would become noticeable to people sitting farther and farther back, until eventually the gas could be smelled in every spot in the room. The H_2S molecules would spontaneously make their way throughout the entire room, moving between and intermingling with the molecules of the air.

A process closely related to diffusion is that of **effusion**, which involves the passage of a gas under pressure through a small orifice into a vacuum. The rate of effusion of a gas is easier to measure than the rate of diffusion, and since both rates are functions of molecular velocity, they are proportional to each other.

In 1833 the Scottish chemist Thomas Graham conducted a series of experiments on the rates of effusion of gases. As a result of his investigations, he formulated the following law, known as **Graham's Law of Effusion (Diffusion)**:

At constant conditions of temperature and pressure, the rate of effusion of a gas is inversely proportional to the square root of its density.

That is,

$$\text{rate of effusion} \propto \sqrt{\frac{1}{d}}$$

Thus the rates of effusion of two different gases under identical conditions are related by the expression

$$\frac{\text{rate of gas 1}}{\text{rate of gas 2}} = \sqrt{\frac{\text{density of gas 2}}{\text{density of gas 1}}}$$

At the time of Graham's work, molecular weights were not very well understood. However, as described earlier in this chapter, the densities of two gases (at the same temperature and pressure) are in the same ratio as the ratio of their molecular weights. This knowledge permits us to express Graham's Law in the more useful form

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where r_1 and r_2 are the rates of diffusion of gas 1 and gas 2, respectively, and M_1 and M_2 are their molecular weights.

Graham's Law provides another method for experimentally determining the molecular weight of a gas. If we measure the rates of diffusion of the gas under investigation and some known gas at constant temperature and pressure, we can then insert these rates and the molecular weight of the known gas into Graham's equation and solve for the molecular weight of the unknown gas.

Problem 9.14

In an effusion apparatus, pure N_2 effused at the rate of 0.311 mol/min, and an unknown gas (at the same temperature and pressure) effused at the rate of 0.133 mol/min. What is the molecular weight of the unknown gas?

Solution:

To solve for molecular weight, we express Graham's Law as

$$\frac{\text{rate }(\mathrm{N_2})}{\text{rate}(x)} = \sqrt{\frac{\mathrm{M}(x)}{\mathrm{M}(\mathrm{N_2})}}$$

and substitute the appropriate values.

$$\frac{0.311}{0.133} = \sqrt{\frac{\mathrm{M}(x)}{28.0}}$$

Squaring both sides of the equation gives

$$\frac{0.0967}{0.0177} = \frac{\mathrm{M}(x)}{28.0}$$

and solving for M(x)

$$\mathrm{M}(x) = \frac{0.0967}{0.0177} \times 28.0 = 153 \text{ g/mol}$$

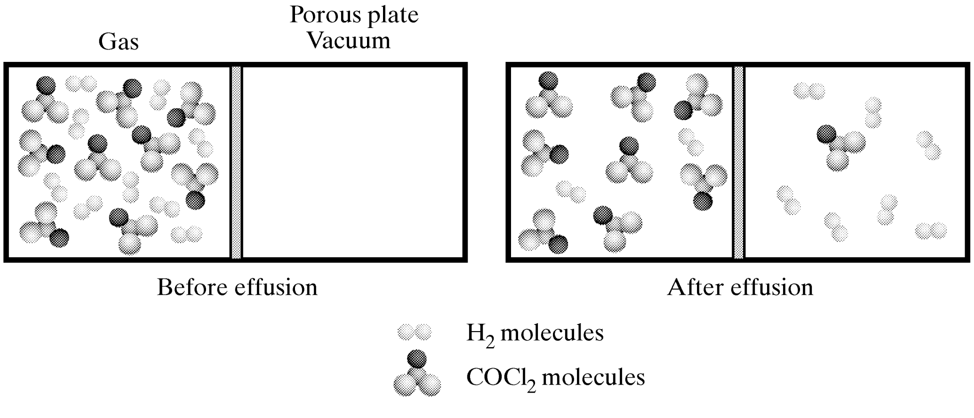


Figure 9.4 The dependence of rate of diffusion on molecular weight.

Mixtures of gases can sometimes be separated into their constituents by taking advantage of their differing rates of diffusion. The greater the difference in the molecular weights of two gases, the more easily they can be separated. Consider, for example, a mixture of hydrogen and phosgene ($COCl_2$), which have molecular weights of 2 and 99, respectively. According to Graham's Law, H_2 effuses approximately seven times as rapidly as $COCl_2$:

$$\frac{\text{rate } H_2}{\text{rate } COCl_2} = \sqrt{\frac{99}{2}} = \sqrt{49.5} \cong 7$$

If a mixture containing equal numbers of molecules of these two gases is allowed to effuse through a porous plate into a vacuum, seven H_2 molecules will pass through for each $COCl_2$ molecule that passes through (as shown in Figure 9.4).

An example of an important application of this principle is the separation of the two principal isotopes of uranium, $^{235}_{92}U$ and $^{238}_{92}U$. Since ^{235}U undergoes nuclear fission, it was important to the development of nuclear energy to obtain this isotope in relatively pure form. However, ^{235}U accounts for only about 0.7% of the uranium atoms in nature, almost all the rest being ^{238}U, and the isolation of ^{235}U is extremely difficult. It has been accomplished, however, by converting uranium to uranium hexafluoride (UF_6), which is a gas above 56 °C, and permitting the gas to effuse through a porous plate. Since the molecules containing ^{235}U atoms are of lower mass, they effuse somewhat faster than the molecules containing ^{238}U atoms, so that after a time the gas mixture that has effused through the plate contains a greater proportion of ^{235}U than that which has not effused. By repeating this procedure with the ^{235}U-enriched mixture, the proportion of ^{235}U is increased still further. After numerous repetitions of this process, a separation is achieved.

9.5 THE KINETIC MOLECULAR THEORY

We must emphasize here that all of the laws of gas behavior discussed in the preceding pages were the products of experimentation. They represent statements of fact based on observations of the behavior of matter in bulk. Some of the gas laws were firmly entrenched many years before Dalton's atomic theory, and their authors knew nothing of molecules. All of these laws predated the concept of intermolecular forces. (In fact, it was the failure of gases to obey the ideal gas law at high pressures and low temperatures that led van der Waals in the 1870s to suggest the existence of intermolecular forces.) Furthermore, these early workers did not possess the means of achieving either very high pressures or very low temperatures, and the term "ideal" gas could not possibly have occurred to them. They were simply describing the behavior of gases as they knew them.

As more was learned about the **particulate** nature of matter, attempts were begun to explain the macroscopic properties of gases in terms of the particles of which matter is composed. Around the middle of the nineteenth century, there emerged a series of postulates aimed at explaining the behavior of gases as described by the gas laws. Taken together, these postulates are known as the **kinetic molecular theory**. The major points of this theory are as follows:

1. Gases are composed of molecules, which are in rapid, random, straight-line motion (translational motion). Because molecules have mass and motion, they possess kinetic energy $\left(\mathrm{KE} = \frac{1}{2}mv^2\right)$.
2. Molecules undergo collisions with the walls of the container and with one another. These collisions are perfectly **elastic**; that is, there is no net loss of kinetic energy during the collision. Although there may be a transfer of kinetic energy between two colliding molecules, their *average* kinetic energy remains the same.
3. The molecules are separated by average distances much larger than the molecules themselves. Thus the space occupied by the molecules is negligible compared with the volume of the container.
4. The molecules exert no attractive or repulsive forces on one another.
5. At any given instant, the molecules do not all have the same kinetic energy, but the *average* kinetic energy of the molecules is directly proportional to the absolute temperature. It follows that at any given temperature, the average kinetic energy of the molecules is the same for all gases. Since $\mathrm{KE} = \frac{1}{2}mv^2$, the velocity of a gas decreases as the molecular weight increases.

The kinetic molecular theory provides an interpretation of gas pressure on a molecular level. The constant, rapid motion of the molecules results in countless collisions with the walls of the container during each tiny fraction of a second. Because molecules have mass, these collisions are constantly exerting a force on the container's walls, and pressure is simply the force per unit of surface area. The pressure exerted by a gas, then, depends on the number of molecules colliding with the container walls per unit of time and on the kinetic energy of the molecules making those collisions (which, in turn, depends on the temperature).

With this interpretation of pressure and the postulates stated above, the behavior of an ideal gas can be easily rationalized. First, to explain Boyle's Law, consider a gas confined in a container that permits variable volume, such as a cylinder fitted with a piston. In the container there is some definite volume of gas, V_1, which consists of N_1 molecules at pressure P_1 and temperature T_1. Now suppose we wish to increase the pressure of the gas to P_2. There are several ways this might be accomplished. We could add more molecules, thus increasing the number of collisions per unit of time, or we could raise the temperature, which would raise the average kinetic energy of the molecules, causing more frequent and more forceful collisions. Although either of these changes would raise the pressure, the conditions of Boyle's Law require that both the temperature and the number of molecules remain constant. The only other way that the pressure can increase—that is, that the force exerted by the molecules per unit of area can increase—is for the volume of the gas to decrease to V_2. There will then be more molecules per unit of volume, although the total number of molecules has remained constant. Thus, we have accounted for Boyle's Law, because the temperature and number of molecules are held constant, and the pressure and volume vary inversely.

The explanation of Charles' Law follows a similar line of reasoning. Assume that the same volume of gas, V_1, is in the same cylinder under the same conditions, P_1, T_1, N_1. Now, without changing the number of molecules, we increase the temperature of the gas to T_2. This causes an increase in the kinetic energy of the molecules so that their collisions become more frequent and more forceful. If the number of molecules cannot change, the pressure will necessarily increase. But Charles' Law deals with a constant pressure. Thus, in order to hold the pressure constant, we must increase the surface area over which the collisions occur; that is, we must increase the volume of the container.

Avogadro's Law states that volume and the number of molecules are directly proportional at constant pressure and temperature. Starting with N_1 molecules of gas in volume V_1, suppose we increase the number of molecules to N_2. If N_2 molecules now occupy volume V_1, there will be more collisions (increased pressure) unless the temperature is lowered. The only way the number of molecules can be increased without an increase in pressure or a decrease in temperature (or both) is for the volume to increase, so that the number of molecules per unit volume remains as it was at the start.

Dalton's Law of Partial Pressures also can be explained with the kinetic molecular theory. If there are no attractive forces between molecules, then each molecule strikes the container walls with the same frequency and force as it would if no other molecules were present. Thus the pressure exerted by a gas in a mixture is the same as if no other gas were present.

Finally, the relationship described in Graham's Law of Effusion is predictable from the kinetic molecular theory. Consider two different gases at the same temperature. The average kinetic energy of the molecules of gas 1 is given by the expression

$$\mathrm{KE}_1 = \frac{1}{2} m_1 v_1^2$$

Similarly, the average kinetic energy of the molecules of gas 2 is

$$\mathrm{KE}_2 = \frac{1}{2} m_2 v_2^2$$

Now, according to the kinetic molecular theory, the average kinetic energy of the molecules is the same for all gases at the same temperature. Therefore:

$$\mathrm{KE}_1 = \mathrm{KE}_2$$

and

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

Rearranging this expression gives

$$\frac{v_1^2}{v_2^2} = \frac{m_2}{m_1}$$

or

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

Since the rate of diffusion of a gas is proportional to the average molecular velocity, the ratio of the molecular velocities of the two gases is directly proportional to the ratio of their rates of diffusion (r_1 and r_2). Therefore:

$$\frac{v_1}{v_2} = \frac{r_1}{r_2}$$

Furthermore, since the molecular weight of a substance is directly proportional to the mass of a single molecule of that substance, we have

$$\frac{m_2}{m_1} = \frac{M_2}{M_1}$$

Thus we have derived Graham's Law from theoretical considerations:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

9.6 REAL GASES: DEVIATION FROM IDEALITY

The kinetic molecular theory adequately explains the behavior of gases as described by the gas laws discussed in this chapter. As mentioned earlier, a gas that would adhere to these laws under any conditions, no matter how extreme, is called an **ideal gas**. An ideal gas is purely hypothetical; no such gas really exists. Many real gases do obey the gas laws quite closely when the temperature is relatively high and the pressure relatively low, but at low temperatures and high pressures, all gases deviate from ideal behavior.

Suppose, for example, we pose the question: What volume will 0.50 mol of a gas occupy at a pressure of 740 torr and a temperature of 50 °C? The ideal gas equation will permit us to calculate an answer to our question. Now, suppose we go into the laboratory and subject 0.50 mol of a gas to a temperature of 50 °C and a pressure of 740 torr, and actually measure its volume as accurately as we can. We will find that the measured volume and the calculated volume agree very closely. The gas behaves just as the ideal gas laws predict it will behave; it is behaving ideally. Suppose, then, we pose another question about the same gas: What volume will 0.50 mol occupy at a pressure of 100 atm and a temperature of −100 °C? Again, we can calculate the answer using the ideal gas equation. However, if we actually measure the volume of 0.50 mol of our gas at 100 atm and −100 °C, the measured volume and the calculated volume will differ. The actual volume may be less or greater than that predicted by the ideal gas equation, depending on the specific gas used in the experiment. At these conditions of high pressure and low temperature, the gas is not adhering to the gas laws—it is deviating from ideality.

The deviation of gases from ideality with increasing pressure may be shown graphically by plotting the product of the pressure and volume (*PV*) against pressure (*P*). Assume we have taken 1 mole of gas at 0 °C, measured its volume at a given pressure, and multiplied these together to get *PV*. We then increase the pressure to some new value, measure the volume at that pressure, determine *PV* again, and so on. We can plot *PV* as a function of *P*, as in Figure 9.5.

Since the temperature and number of moles of gas are held constant throughout these measurements, for an ideal gas, $PV = nRT$ = constant = 22.4 L-atm. The plot for an ideal gas is shown as a straight line in the diagram below. We can now compare the behavior of several other gases, N_2 and CO_2, in addition to H_2. Whereas the curves for the three gases show ideal behavior at very low pressures, they deviate drastically as the pressure is increased. Note that hydrogen deviates steadily in the positive direction—the real volume is *larger* than that predicted by the ideal gas laws—but that both nitrogen and carbon dioxide deviate first in a negative direction and then, at higher pressures, in a positive direction.

The effect of temperature on deviation from ideality is illustrated in Figure 9.6, where plots of *PV* versus *P* at three different temperatures are given for methane. These are compared with the plots for an ideal gas at each temperature (broken lines). Note that as the temperature becomes lower, the extent of deviation increases.

One of these assumptions of the kinetic molecular theory is that the volumes of the molecules themselves is negligible. At conditions of high temperature and low pressure, this is a reasonable assumption to make, for under these conditions the average space between molecules is so great that only a tiny fraction of the total volume of a gas sample is occupied by the molecules themselves (Figure 9.7a). However, at high pressure and/or

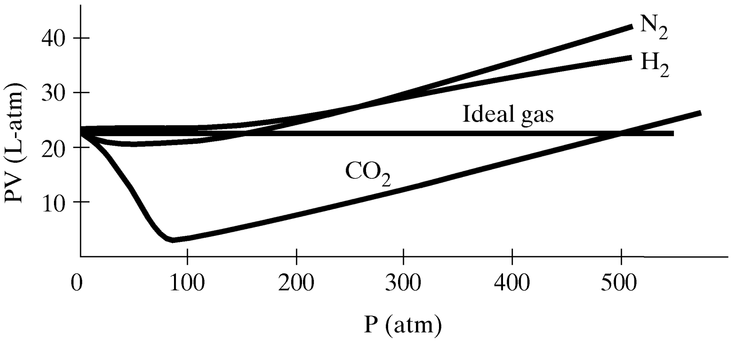


Figure 9.5 A plot of *PV* versus *P* for H_2, N_2, and CO_2 (T = 0 °C, n = 1 mol).

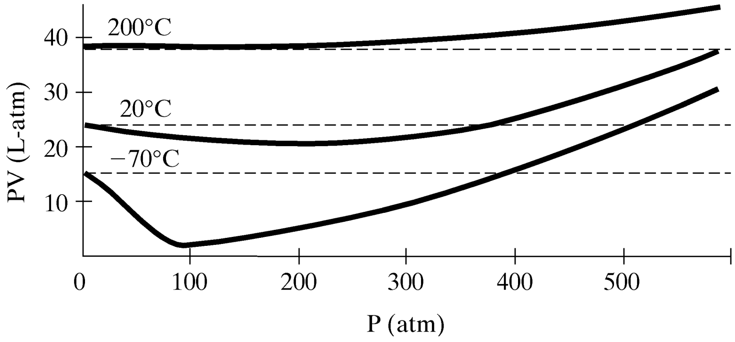


Figure 9.6 A Plot of *PV* versus *P* for CH_4 at three different temperatures.

low temperature, the molecules are much closer together and their volumes cannot be neglected (Figure 9.7b). The gas laws' predictions concerning the volume of a gas are really predictions concerning the volume of the space *between* the molecules. When conditions are such that the volumes of the molecules themselves are not negligible, the volume of a real gas is larger than is predicted for an ideal gas, and this results in a positive deviation from ideality in a *PV* plot.

A second assumption of the kinetic molecular theory is that there are no attractive forces between molecules. This is, of course, incorrect. As we have seen in the preceding chapter, intermolecular forces—however weak they may be—exist between all molecules. It is reasonable to assume that these forces may be ignored when the temperature is relatively high and the pressure low. Under these conditions the molecules are moving so rapidly and the average distance between them is so large that the effect of intermolecular forces may indeed be negligible. However, high pressure and low temperature bring the molecules closer together and reduce their velocity, so that intermolecular attractions may no longer be discounted. These attractive forces pull the molecules even closer together, reducing the intermolecular spaces to a greater extent than is predicted by the ideal gas laws and giving the real gas a smaller volume than an ideal gas would have. This effect appears as a negative deviation on a plot of *PV* versus *P*.

Thus, two factors are responsible for the deviation of real gases from ideal behavior. And these two factors are in competition, in the sense that they tend to cause deviations in opposite directions. The actual deviation shown by a specific gas is the result of a combination of these factors, and depends on the size of the molecules and the strength of the intermolecular forces.

The relationship among deviation, molecular volume, and intermolecular forces can be illustrated by a consideration of the three gases shown previously in Figure 9.5. The hydrogen molecule, possessing only two electrons, has extremely weak van der Waals forces. (Recall that the strength of van der Waals forces increases as the number of electrons in the molecule increases.) As a result, their effect is not observed at 0 °C, and the only deviation shown must be ascribed to the volumes of the molecules. But the hydrogen molecule is also very small, and thus we would not expect the effect of volume to be very great. This accounts for the fact that of the three gases being compared, hydrogen shows the least deviation. The nitrogen molecule has both a larger volume and stronger van der Waals forces than hydrogen. At pressure up to approximately 100 atm, the forces are more important than the volume, and we see a negative deviation. At still higher pressures, however, the molecules are so close together that the effect of their volumes coun-

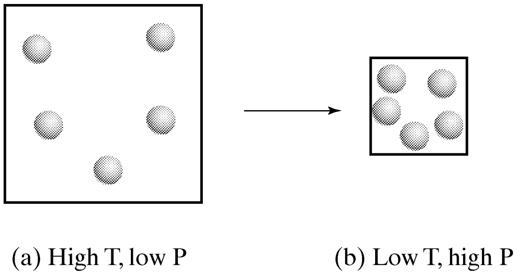

(a) High T, low P (b) Low T, high P

Figure 9.7 An illustration of deviation from ideality due to the volume of the molecules.

TABLE 9.1 Some Critical Temperatures and Pressures

GAS	CRITICAL TEMPERATURE (K)	CRITICAL PRESSURE (atm)
H_2O	647	217.7
NH_3	406	111.5
HCl	324	81.6
O_2	153	49.7
N_2	126	33.5
H_2	33	12.8
He	5	2.3

teracts the effect of van der Waals forces and the direction of deviation is reversed. Thus the greater deviation of N_2 compared with H_2 at very high pressures can be accounted for by the nitrogen molecule's greater size. Carbon dioxide has much stronger intermolecular forces than either of the other two gases and therefore shows the greatest negative deviation, but even this gas shows the effect of molecular volume at sufficiently high pressures.

Figure 9.7 illustrates well the effect of temperature on the importance of van der Waals forces. As the temperature is lowered, the velocity of the molecules decreases. This, in turn, permits an increase in the effectiveness of the intermolecular attractions and causes a greater decrease in the volume.

An ideal gas could not be liquefied because it would have no intermolecular forces. Any real gas, however, will liquefy if subjected to sufficiently high pressure and sufficiently low temperature. In order for a gas to become a liquid, the kinetic energy of the molecules must be reduced to the point at which the intermolecular forces can "take over." Therefore, for each gas there is a temperature above which it will not liquefy no matter how high a pressure is applied. This temperature is called the **critical temperature**. At temperatures below the critical temperature, a gas can be liquefied by application of sufficient pressure, and as the temperature decreases, less pressure is required. The pressure necessary to liquefy a gas at its critical temperature is called its **critical pressure**. The critical temperature of a gas is related to the strength of its intermolecular forces. The stronger these forces, the more easily the gas can be liquefied and therefore the higher is its critical temperature. In general, polar substances can be expected to have higher critical temperatures than nonpolar ones, and among nonpolar substances—where only van der Waals forces exist—higher molecular weights can be expected to correspond to higher critical temperatures. This relationship is illustrated in Table 9.1.

Transitions Between States

Throughout our discussion of matter in bulk, we have referred to the processes that occur when a substance changes from one physical state into another. These transitions between states are summarized in Figure 9.8. Transitions that occur in the direction from

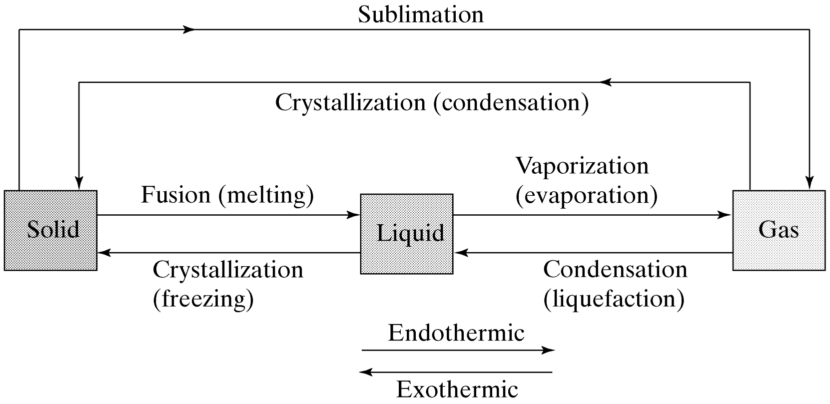


Figure 9.8 Transitions between states.

left to right in the diagram are endothermic (energy is absorbed), while those that occur from right to left are exothermic (energy is released).

9.7 ENTHALPY

The absorption or evolution of energy accompanying any chemical or physical change may be conveniently described in terms of the thermal energy of the system. Every substance under any given set of conditions possesses a certain amount of energy called its **heat content**, or **enthalpy**, represented by the symbol H. Heat lost or gained during a chemical or physical change represents a *change* in enthalpy of the system. Notice that heat content (enthalply) is not the same as heat. If heat is absorbed, then the system at its *final* state (after the change) must have a higher enthalpy than it did in its *initial* state (before the change). Conversely, evolution of heat during a change means the enthalpy of the final state is lower than that of the initial state. Thus the change in enthalpy (ΔH) is defined as the sum of the enthalpies of all the substances in the final state minus the sum of the enthalpies of the substances in the initial state. For example, in a hypothetical process in which substances A and B undergo some sort of change resulting in C and D (represented as $A + B \rightarrow C + D$), the enthalpy change for that process is

$$\Delta H = (H_C + H_D) - (H_A + H_B)$$

Note that higher enthalpy in the final state results in ΔH being positive, while a lower enthalpy in the final state means that ΔH is negative. In other words, a positive ΔH represents an endothermic change, and a negative ΔH represents an exothermic change The magnitude of ΔH depends not only on the particular substances involved in the change, but also on the quantities of these substances. Generally, ΔH is expressed in terms of kilojoules or kilocalories per mole.

This concept is applicable to all the kinds of changes that matter undergoes, including transitions between states. The enthalpy changes accompanying the various transitions are assigned names that identify the particular transition. Thus the quantity of energy per mole involved in the melting of a solid is called the heat of fusion (ΔH_{fus}), and the enthalpy changes of other transitions of state are the heat of sublimation (ΔH_{sub}), heat of vaporization (ΔH_{vap}), heat of crystallization (ΔH_{cryst}), and so forth. The enthalpy change for the transition from one physical state to another is numerically equal (but of opposite sign) to the enthalpy change for the reverse transition. Thus, for example, for the melting of ice at 0 °C and 1 atm, $\Delta H = +6.02$ kJ/mol; for the freezing of water under the same conditions, $\Delta H = -6.02$ kJ/mol.

There is often a temptation to assume that exothermic processes occur spontaneously, while endothermic ones do not. This assumption is based on our everyday experiences, which suggest that any system should tend to go in the direction of lowest energy (water runs downhill, clock springs wind down, hot water cools to the surrounding temperature). However, the assumption is incorrect. Although many exothermic changes are spontaneous, so are many endothermic ones. A piece of ice melts spontaneously at room temperature—an endothermic change. Solid carbon dioxide (dry ice) sublimes spontaneously—another endothermic process (Figure 9.9). In fact, if spontaneity were determined by enthalpy change alone, all substances would tend toward the solid state, for that is the state with lowest enthalpy.

9.8 ENTROPY

Another factor that determines the spontaneity of a process is the property of matter called **entropy** (S), which is a measure of the degree of randomness, or disorder, in a system. It is a kind of probability factor, because there are many more ways of producing disordered arrangements than there are of producing ordered ones. For example, suppose you throw a handful of pennies into the air, and they are allowed to fall back onto a table. The probability that the pennies will fall into some neat arrangement of columns and rows, or into a single vertical pile, or into any other orderly arrangement, is extremely

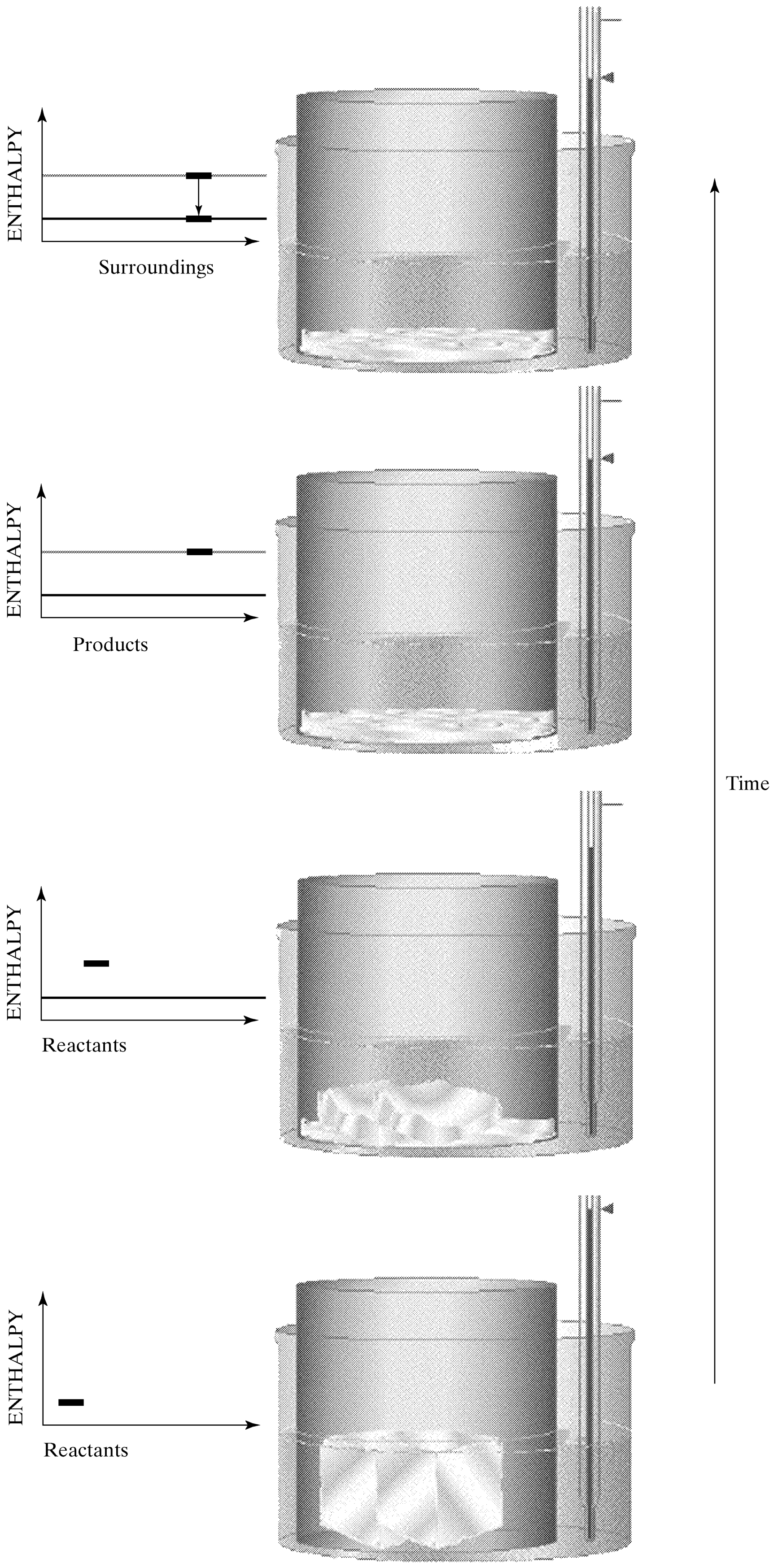


Figure 9.9 Change in enthalpy during the melting of ice.

slight. Time after time they will fall in some random, disordered way. Similarly, what is the probability that all the seedlings produced from a maple tree in the forest will be growing in straight, evenly spaced rows? What is the probability that each of four hands of cards, dealt from a shuffled deck, will contain all the cards of a single suit? In short, disorder is far more probable than order, and so disorder is favored in nature.

Every substance under a given set of conditions possesses a certain entropy, and when a substance undergoes a physical or chemical change, there is a change in entropy. This change in entropy is denoted by ΔS and is expressed in terms of joules per mole per Kelvin unit. It is defined in a way similar to that for enthalpy change; the entropy change is equal to the sum of the entropies of all the substances in the final state minus the sum of the entropies of the substances in the initial state.

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

$$\Delta S = (S_{\mathrm{C}} + S_{\mathrm{D}}) - (S_{\mathrm{A}} + S_{\mathrm{B}})$$

Note that when the entropy of the final state is greater than the entropy of the initial state, ΔS is positive; when the reverse is true (when entropy has decreased), ΔS is negative. Since disorder is favored over order, and since ΔS is a measure of the increase in disorder, changes that have a positive ΔS are favored changes, and those that have a negative ΔS are not.

The application of the concept of entropy to transitions between states is readily apparent. A crystalline solid is more ordered than either a liquid or a gas, and the gaseous state is the most disordered of the three. Thus the changes represented by fusion, vaporization, and sublimation have positive entropy changes, while those of crystallization and condensation have negative entropy changes (Figure 9.10).

Referring to the scheme in Figure 9.8, note that each transition occurring from left to right is favored by the entropy change but not favored by the enthalpy change, while transitions from right to left in the figure are favored by the enthalpy change but not favored by the entropy change.

9.9 FREE ENERGY

It is the combination of enthalpy and entropy, along with temperature, that determines whether or not a given change will occur spontaneously. The property that represents this combination is called the **free energy**, represented by G. Every substance at a specific set of conditions has a free energy, which is defined as

$$G = H - TS$$

where H and S are the enthalpy and entropy, respectively, and T is the absolute temperature. The free energy, G, may be thought of as the freely *available* energy, and the product of temperature and entropy, TS, may be considered the *unavailable* energy. Thus, the above relationship states that the available energy is less than the enthalpy by the amount TS.

The change in free energy (ΔG) that accompanies a physical or chemical change is defined in the same way that ΔH and ΔS are defined. For the process

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

the change in free energy is

$$\Delta G = (G_{\mathrm{C}} + G_{\mathrm{D}}) - (G_{\mathrm{A}} + G_{\mathrm{B}})$$

It follows that for a change occurring at constant temperature, the free-energy change may be defined as

$$\Delta G = \Delta H - T\Delta S$$

This is a very significant equation, for it permits us to predict whether or not a process is spontaneous. **A change can occur spontaneously only if there is a decrease in free energy,**

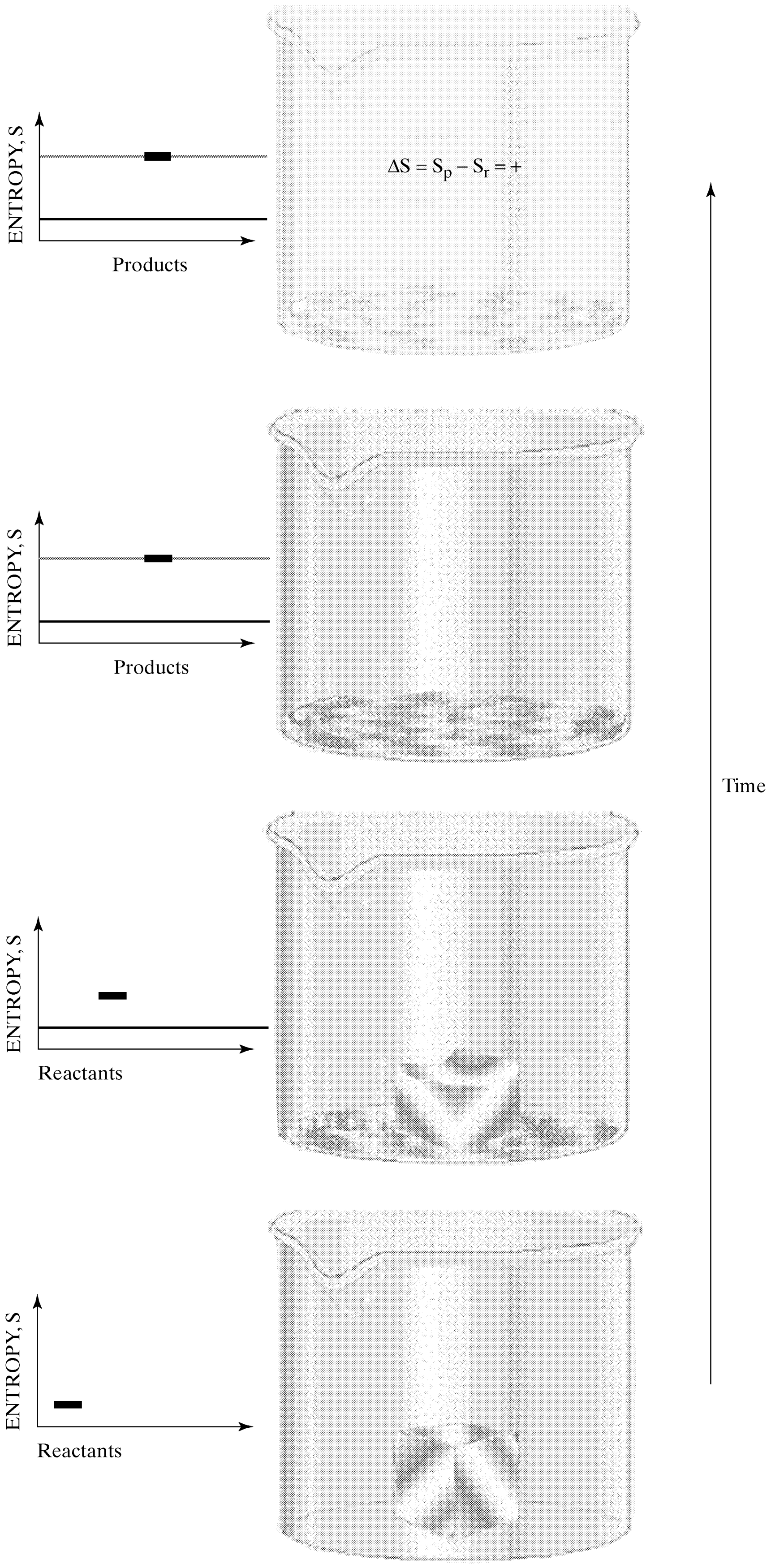


Figure 9.10 The entropy change during the melting of ice.

that is, only if ΔG is negative. If ΔG for a process is positive, then the reverse of that process is spontaneous. When a system is in equilibrium (in other words, when a change has the same tendency to occur in both directions), ΔG is equal to zero.

If a process is favored by both the enthalpy change and the entropy change (ΔH is negative and ΔS is positive), then according to our equation, ΔG must be negative, indicating a spontaneous change:

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = (-) - (+) = -$$

Similarly, if a process is not favored by either the enthalpy change or the entropy change (ΔH is positive and ΔS is negative), then ΔG must be positive:

$$\Delta G = (+) - (-) = +$$

Thus the change in question will not occur spontaneously, but its reverse will.

In those cases where a process is favored either by enthalpy or by entropy but not by both, spontaneity is determined by the factor that has the greater effect. For example, where a positive ΔS is sufficiently large, it may outweigh a positive ΔH and lead to a spontaneous process. This explains why some endothermic processes are spontaneous (such as the melting of ice at room temperature).

To illustrate the application of the free energy change, let us determine whether benzoic acid is a solid or a liquid at 150 °C, given that the heat of fusion (ΔH_{fus}) for benzoic acid is 17.3 kJ/mol and its entropy of fusion (ΔS_{fus}) is 43.9 J/mol-K.

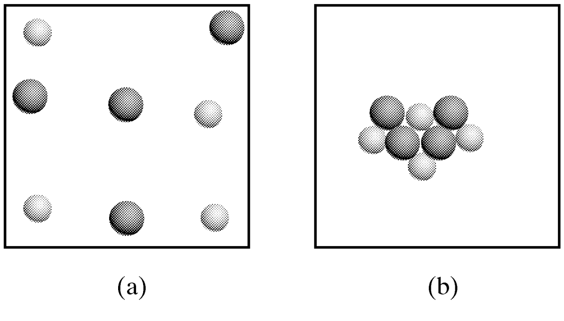
$$\text{Benzoic acid (solid)} \longrightarrow \text{Benzoic acid (liquid)}$$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 17{,}300\ \text{J/mol} - (423\ \text{K})(43.9\ \text{J/mol-K}) \\ &= 17{,}300\ \text{J/mol} - 18{,}570\ \text{J/mol} = -1270\ \text{J/mol}\end{aligned}$$

Therefore, the process is spontaneous, and benzoic acid exists as a liquid at 150 °C.

Visualization 9.3

The two diagrams below represent (a) ions in the gas phase and (b) the same ions in the solid state. (The condensation of ions from the gas phase to the solid phase is the lattice energy discussed in Chapter 5.)



For the process (a) → (b),

1. Is ΔH negative or positive?
2. Is ΔS negative or positive?
3. Is ΔG negative or positive?

Continued on next page

Visualization 9.3 *Continued*

Solution:

1. The energy of the ions in the solid state is lower and therefore ΔH is negative (heat is given off).
2. The ions are more ordered in the solid state (the entropy is less) and therefore ΔS is negative.
3. The change in free energy is given by $\Delta H - T\Delta S$. In this case, ΔH is negative and will contribute to a negative free-energy change, but ΔS is also negative and will contribute to making ΔG more positive. Because the lattice energy is always a large number, it is safe to assume that ΔH will outweigh ΔS and that ΔG will be negative. Thus, the process (a) → (b) is a favorable, spontaneous process.

Enthalpy, entropy, and free energy are often called thermodynamic properties, and their relationships are embodied in the Laws of Thermodynamics. These will be discussed in connection with chemical reactions in Chapter 14.

Problem 9.15

Is benzoic acid a solid or a liquid at 100 °C?

Solution:

This problem is similar to that presented in the text. hence, we use those values of ΔH_{fus} and ΔS_{fus},

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S\\ &= 17{,}300\ \text{J/mol} - (373\ \text{K})(43.9\ \text{J/mol-K})\\ &= 17{,}300\ \text{J/mol} - 16{,}370\ \text{J/mol} = 930\ \text{J/mol}\end{aligned}$$

The positive ΔG indicates that benzoic acid exists as a solid at 100 °C. Liquid benzoic acid will spontaneously solidify at that temperature.

Problem 9.16

What is the melting point of benzoic acid?

Solution:

At the melting point, the solid and liquid states are in equilibrium and $\Delta G = 0$. The question is, then, at what temperature is ΔG for the fusion process equal to zero?

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T\Delta S = \Delta H$$

$$T = \frac{\Delta H}{\Delta S} = \frac{17300\ \text{J/mol}}{43.9\ \text{J/mol-K}} = 394\ \text{K}$$

The melting point of benzoic acid is 394 K, or 394 − 273 = 121 °C.

CHAPTER SUMMARY

The observed behavior of gases under normal conditions is summarized by a number of laws. Boyle's Law, Charles' Law, and Avogadro's Law relate the volume of a gas sample to pressure, temperature, and number of molecules, respectively. Taken together, these laws are known as the **ideal gas laws** and can be combined into a mathematical statement called the **ideal gas equation**. Two additional laws describing the behavior of gases are Dalton's Law of Partial Pressures and Graham's Law of Effusion. You should become familiar with all of these laws and should understand their mathematical implications.

It will be necessary for you to master a large variety of calculations based on the individual gas laws and on various combinations of these laws. In performing these calculations, two constants are so frequently used that you should commit them to memory: (1) the molar gas volume at STP = 22.4 L/mol, and (2) the ideal gas constant (R) = 0.0821 L-atm/mol-K. One type of calculation resulting from Avogadro's Law involves computing the volume of a gas that takes part in a chemical reaction.

The **kinetic molecular theory** explains ideal gas behavior. You should become familiar with the postulates of this theory and be able to use them to rationalize gas behavior.

The ideal gas laws have limitations, and real gases deviate widely from ideal behavior at high pressures and/or low temperatures. Deviations from the ideal gas laws can be accounted for by the volumes of the molecules themselves and by the attractive forces between these molecules—both of which become increasingly important as gas volume decreases. Review the factors that determine the strength of intermolecular forces (Chapter 9) until you can use these factors to make qualitative predictions about the extent to which various gaseous compounds deviate from ideality. These factors will also enable you to predict the relative magnitude of the **critical temperature** and the **critical pressure** of a compound.

You also will need to have an understanding of transitions between states of matter. The thermodynamic properties of **enthalpy**, **entropy**, and **free energy** and the relationships that exist between these properties are introduced here. These are very important concepts that can generally be applied to all kinds of changes in matter, both chemical and physical. They will be discussed in much greater detail in Chapter 14, but mastering them now in connection with the relatively simple processes of the transitions between states of matter will enable you to better apply them as advanced concepts later.

TERMS

The new terms in this chapter are as follows:

Boyle's Law For any given mass of gas, the volume varies inversely with the pressure, provided the temperature is held constant. Stated mathematically, PV = constant (when n and T are constant).

Charles' Law For any given mass of gas, the volume varies directly with the absolute temperature, provided the pressure remains constant. Stated mathematically, V/T = constant (when n and P are constant).

Avogadro's Law Equal volumes of all gases, at the same pressure and temperature, contain the same number of molecules. Stated another way, the volume of a gas sample varies directly with the number of moles, provided the temperature and pressure are held constant; that is, V/n = constant (when P and T are constant).

Ideal gas laws Boyle's Law, Charles' Law, and Avogadro's Law taken together. A statement of the relationship of gas volume to the temperature, pressure, and number of moles of gas. The mathematical statement, called the **ideal gas equation**, is $PV = nRT$.

Ideal gas constant The constant R in the ideal gas equation. The value of this constant is 0.0821 L-atm/mol-K, or 62.4 L-torr/mol-K.

Atmospheric pressure The pressure exerted by the earth's atmosphere on the earth's surface. Atmospheric pressure varies from place to place and from time to time, but it is approximately equal to 760 torr.

Dalton's Law of Partial Pressures In a mixture of gases, each gas exerts the same pressure as it would if it were in the container alone. The pressure exerted by each gas in the mixture is the **partial pressure** of that gas, and the total pressure of the mixture is the sum of the partial pressures.

Graham's Law of Effusion At the same temperature and pressure, the rates of effusion of gases are inversely proportional to the square roots of their molecular weights.

Ideal gas A hypothetical gas whose behavior would adhere to the ideal gas laws under all conditions.

Enthalpy At any given set of conditions, each substance possesses a certain amount of energy called its enthalpy, or **heat content**, symbolized by H. Heat lost or gained during any process represents an **enthalpy change**, designated ΔH. In an endothermic process, ΔH is positive; in an exothermic process, ΔH is negative.

Entropy A property of matter that represents the degree of randomness, or disorder, in the system, denoted by S. A change in entropy accompanying any process is designated ΔS.

Free energy At any given set of conditions, each substance possesses a free energy G that is a function of the enthalpy and the entropy of the substance and the absolute temperature, or $G = H - TS$. The change in free energy that accompanies any process at constant temperature is therefore $\Delta G = \Delta H - T\Delta S$. Any given chemical or physical change can occur spontaneously only if it is accompanied by a decrease in free energy (that is, if ΔG is negative). A process for which ΔG is positive does not occur spontaneously. When a system is in equilibrium, $\Delta G = 0$.

PROBLEMS

1. A sample of carbon dioxide has a volume of 450 mL at 0 °C and a pressure of 800 torr. What volume will the sample have at STP?
2. If the gas sample in the preceding problem is to be compressed into a volume of 100 mL (keeping the temperature constant), what pressure will be required?
3. One liter of oxygen at STP is heated to 250 °C while the pressure is held constant. What will the new volume be?
4. What is the volume of 1.00 mol of N_2 at 75 °C and 850 torr?
5. What pressure is required to compress 10 L of O_2 at STP to 3.5 L at 50 °C?
6. A tank of nitrogen contains 1.5 lbs of N_2 at a temperature of 50 °C and 100 atm pressure. What is the volume of the cylinder?
7. If the gas in the tank in question 6 is allowed to expand into a room that measures $10' \times 10' \times 10'$, what will the pressure in the room be at 50 °C?
8. A steel bomb having a volume of 500 cm^3 is filled with air at 28 °C and 742 torr. If the bomb is heated to 100 °C, what pressure will be exerted by the confined gas?
9. What is the density of phosgene gas ($COCl_2$) at STP?
10. What volume is occupied by 50.0 g of H_2 at a temperature of 25 °C and a pressure of 740 torr?
11. What is the density of F_2 at 32 °C and 1.00 atm?
12. If 10.0 g of methane is confined in a rigid container having a volume of 250 cm^3 at a temperature of 50 °C, what is the pressure exerted by the gas?
13. A sample of carbonoxysulfide gas (COS) occupies a volume of 200 mL at 27 °C and a pressure of 750 torr. How many moles of gas are in the sample? What weight of COS is in the sample?
14. What is the temperature required for 25 g of nitrous oxide (N_2O) to occupy a volume of 1.0 L at a pressure of 2.0 atm?
15. A so-called vacuum tube is sealed off at a pressure of 1.0×10^{-5} torr and 100 °C. Calculate the number of remaining molecules of gas per milliliter.
16. Calculate the density of NH_3 gas at 30 °C and 742 torr.
17. A sample of natural gas is 87% methane, CH_4, and 13% ethane, C_2H_6, by mass. What is the density of natural gas at 12°C and 755 torr in g/L?
18. A sample of a gaseous compound weighing 1.075 g occupies a volume of 275 mL at 29 °C and 744 torr. Calculate the molecular weight of the compound.
19. Calculate the molecular weight of a gas that has a density of 3.00 g/L at 100 °C and 100 torr.
20. Calculate the molecular weight of a gas that has a density of 1.0 g/L at 273 K and 380 mm Hg.

21. Determine the molecular formula of a gas which contains only C, F, and Cl given the information below:

density of the gas:	4.98×10^{-3} g/mL
temperature:	50 °C
pressure:	368 torr
percent C by mass:	8.78%
percent F by mass:	13.90%

22. A sample of a gaseous compound weighing 0.110 g was found to occupy a volume of 51.0 mL when measured at 28 °C and 744 torr. Calculate the molecular weight of the compound.

23. If 1.50 g of a certain gas collected over water at 30 °C has a volume of 350 mL at a pressure of 740 torr, what is the molecular weight of the gas?

24. A certain gas has a density of 2.37 g/L at 25 °C and 735 torr. What is the molecular weight of the gas?

25. Calculate the molecular weight of a gas that weighs 0.20 g and occupies a volume of 1.0 L at 500 mm Hg and 25 °C.

26. A gas sample weighing 0.523 g has a volume of 456 mL when measured over water at 30 °C and a pressure of 752 torr. What is the molecular weight of the gas?

27. A gaseous compound has a percentage composition of 88.8% C and 11.2% H and has a density of 2.12 g/L at 31 °C and 742 torr. Calculate (a) the empirical formula, (b) the molecular weight, and (c) the molecular formula of the compound.

28. Passing carbon monoxide gas over powdered nickel metal at 40 °C gives a volatile compound of the following composition: 34.30% Ni, 28.10% C, and 37.60% O. The density of the gaseous product at this temperature and 750 torr is 6.57 g/L. Calculate (a) the empirical formula and (b) the molecular formula.

29. A compound contains 9.22% B and 91.78% Cl.
(a) How many atoms of boron are there in 10 grams of the compound?
(b) Calculate the empirical formula of the compound.
(c) The compound has a density of 10.4 g/L at STP. Calculate the molecular weight.
(d) What is the molecular formula of the compound?
(e) The compound does not have a B—B bond. Write a structural formula for the compound

30. A 150-mL flask was evacuated and into it was forced 50.0 mL of H_2 under a pressure of 750 torr, 75.0 mL of Ar under a pressure of 450 torr, and 100 mL of O_2 under a pressure of 350 torr. (The temperature was held constant.) Determine the partial pressure of each of the gases in the 150-mL flask and the total pressure of the gas mixture.

31. The composition of air, expressed as a percentage by volume, is 20.95% oxygen, 78.09% nitrogen, and 0.93% argon. The remaining 0.03% may be considered as CO_2.
(a) Calculate the apparent molecular weight of air.
(b) How many moles of argon are present per mole of air?
(c) Calculate the partial pressure of the CO_2 if the total pressure is 1 atm.

32. A sample of oxygen collected over water at 30 °C and 750 torr has a volume of 222 mL. What volume will the sample occupy *dry* and at STP?

33. If 5.00 g of methane is collected by bubbling it through water at 25 °C and 758 torr, what is the volume collected?

34. Dry air was bubbled through water at 25 °C and 1.00 atm pressure so that it became saturated with water vapor. Ten liters of the "wet" air at 25 °C and 1.00 atm were then passed through a calcium chloride tube (a water-absorbing tube), which increased in weight by 0.2304 g.
(a) What is the vapor pressure of water at 25 °C?
(b) What is the volume of the dry air (at 25 °C and 1 atm pressure) after removal of the water vapor?

35. When air is saturated with benzene vapor at 20 °C, 5.0 L of the air contain 1.5912 g of C_6H_6. What is the vapor pressure of benzene at 20 °C?

36. A research laboratory is 13 m long, 5.5 m wide, and 3.5 m high. The temperature is 299 K and the relative humidity is a comfortable 40%. (Relative humidity is defined as the ratio of the partial pressure of the water vapor in the air to the vapor pressure of pure water.) Calculate the grams of water in the air of the laboratory.

37. List the following gases in order of increasing rate of diffusion at STP: H_2S, CH_4, Cl_2, CO_2, N_2, SO_2.

38. The rate of effusion of a certain gas was measured in a laboratory apparatus and found to be 10.0 mL/s. Pure oxygen in the same apparatus at the same temperature and pressure effused at a rate of 14.1 mL/s. Calculate the molecular weight of the gas.

39. Uranium-235 is separated from uranium-238 through the gaseous diffusion of the hexafluorides. Calculate the relative rates of diffusion.

40. Explain the following observed facts on the molecular level:
(a) A sealed glass bottle breaks when heated in an oven.
(b) When a real gas is allowed to escape through the valve of a compressed gas tank, the gas cools.
(c) Gases deviate from ideal behavior at high pressures.
(d) The critical temperature of ammonia is much higher than that of nitrogen.
(e) The critical temperature of argon is −122 °C, while that of helium is much lower (−268 °C).
(f) The critical temperature of dimethyl ether is 126.9 °C, while that of ethyl alcohol is much higher (243 °C).

41. Explain why it is that at room temperature hydrogen gas cannot be converted to a liquid no matter how high the applied pressure.

42. The heat of fusion of aluminum is 10.9 kJ/mol. Calculate the entropy of fusion (ΔS_{fus}) for aluminum at its melting point (660 °C).

43. The heat of fusion of ordinary water is 6.02 kJ/mol, while the heat of fusion of heavy water (D_2O) is 6.49 kJ/mol. Assuming the entropy of fusion is the same for D_2O as for H_2O, predict the freezing point of heavy water. (The symbol D is commonly used to designate deuterium.)

44. The assumption made in the preceding problem is apparently not valid, for the actual freezing point of D_2O is 3.8 °C. Calculate the entropy of fusion of H_2O and of D_2O at their freezing points.

45. The heat of fusion of CCl_4 is 650 cal/mol and the entropy of fusion is 2.6 cal/deg-mol. Calculate the melting point of CCl_4.

46. Cesium metal has a heat of fusion of 2.09 kJ/mol and an entropy of fusion of 6.95 J/mol-K. Is cesium a solid or a liquid at body temperature (98.6 °F)?

47. The normal boiling point of methyl alcohol is 64.7 °C, and the heat of vaporization at that temperature is 35.2 kJ/mol. Calculate the entropy of vaporization of methyl alcohol at its boiling point.

48. Two allotropes of sulfur are monoclinic and rhombic. Converting rhombic to monoclinic at room temperature produces an enthalpy change of 71 cal/mol and an entropy change of 0.16 cal/mol-K. Which allotrope is stable at room temperature (assume 25 °C)?

49. Multiple-choice questions:

1. Which of the following gases deviates most from ideal behavior?
   (a) nitrogen (b) oxygen
   (c) methane (d) hydrogen chloride

2. Which process is exothermic?
   (a) $H_2(l) \rightarrow H_2(g)$ (b) $O_2(s) \rightarrow O_2(g)$
   (c) $H_2O(g) \rightarrow H_2O(l)$ (d) $Na(g) \rightarrow Na(g)^+ + e^-$

3. Which of the following gases has the greatest density at a temperature of 30 °C and a pressure of 750 torr?
   (a) methane (b) ammonia
   (c) carbon dioxide (d) sulfur dioxide

4. Which of the following gases diffuses most rapidly at STP?
   (a) N_2 (b) NO (c) N_2O (d) NO_2

5. Which of the following occupies the greatest volume at 25 °C and 700 torr?
   (a) 100 g of CO_2 (b) 100 g of C_2H_4
   (c) 100 g of Cl_2 (d) 100 g of NO_2

6. Which of the following has the greatest entropy per mole?
   (a) ice
   (b) water
   (c) steam
   (d) all have the same entropy, because all three are H_2O

7. The molecules of which of the following gases have the highest average velocity at STP?
   (a) C_2H_2 (b) CO_2 (c) NO_2 (d) N_2O

8. Suppose that 50 mL of gas are confined in a cylinder at a pressure of 1 atm and a temperature of 23 °C. By moving a piston, the volume of the gas is changed to 35 mL without a change in temperature. The pressure of the gas increases because
   (a) the gas molecules strike the cylinder walls harder
   (b) more molecules strike each square centimeter of the cylinder walls per second
   (c) the average distance between the gas molecules increases
   (d) the gas obeys Charles' Law

9. A certain gas sample has a volume of 1 L. If both the absolute temperature and the pressure are tripled, the volume of this gas sample will be
   (a) $\frac{1}{3}$ L (b) 1 L (c) 3 L (d) 9 L

10. If gas X has a molecular weight four times that of gas Y, gas X's rate of diffusion will be
    (a) one-fourth that of gas Y
    (b) one-half that of gas Y
    (c) twice that of gas Y
    (d) four times that of gas Y

11. A gas cools when it expands rapidly from a small to a large volume because
    (a) Charles' Law predicts this effect
    (b) the pressure decreases
    (c) the average kinetic energy of all gas molecules is the same
    (d) attractive forces between molecules must be overcome

12. Which of the following inert gases has the highest critical temperature?
    (a) He (b) Ne (c) Ar (d) Kr

13. Increasing the pressure of a gas while holding its temperature constant causes an increase in the gas's
    (a) volume (b) critical temperature
    (c) density (d) entropy

145. When any system becomes more orderly, its
    (a) enthalpy increases (b) free energy increases
    (c) entropy increases (d) none of the above

15. Which of the following substances has the highest critical temperature?
    (a) methane (b) methanol
    (c) propane (d) propanol

16. One mole of N_2 at 100 atm and 273 K has a volume of 205 mL. This illustrates
    (a) that N_2 is an ideal gas
    (b) that N_2 molecules have a measurable size
    (c) the effect of van der Waals forces
    (d) that N_2 cannot be liquefied

17. In which of the following processes is there an increase in both enthalpy and entropy of the system?
    (a) freezing of water
    (b) evaporation of water
    (c) condensation of steam
    (d) none of the above

18. For the process $C_6H_6(l) \rightarrow C_6H_6(s)$ at a temperature above the freezing point,
    (a) ΔS is positive (b) ΔH is positive
    (c) ΔG is positive (d) $\Delta G = 0$

19. What is the density of carbon dioxide at STP?
    (a) 1.96 kg/L (b) 1.96 g/mL
    (c) 1.96 mg/L (d) 1.96 mg/mL

20. What volume will be occupied by 43.4 g of xenon at STP?
    (a) 8.08 L (b) 972 L (c) 1060 L (d) 7.40 L

21. What is the volume of a bubble of air when it breaks the surface of the ocean if the bubble had a volume of 2.0 mL at a depth of 300 feet? The ocean surface temperature was 52 °F and the ocean water temperature at 300 feet was 43 °F. Assume that the pressure at a depth of 300 feet is about 10 atmospheres.
(a) 2.0 mL (b) 0.20 mL
(c) 20 mL (d) 37 mL

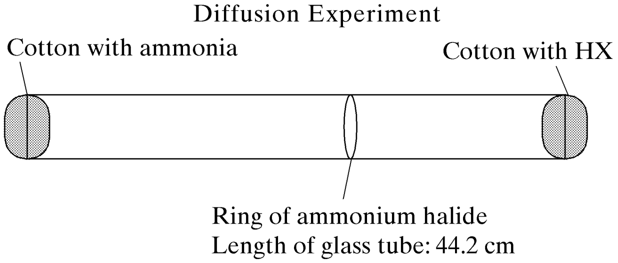
22. A sample of nitrogen gas that was collected over water at 25 °C and at a pressure of 720 torr fills a volume of 750 mL. What is the pressure of nitrogen in the sample?
(a) 720 torr (b) 696 torr
(c) 744 torr (d) Cannot be determined.

23. At 950 °C and 2.34 torr, the density of a given element is 6.15 mg/L. The element is:
(a) xenon (b) lead
(c) mercury (d) sodium

24. An unidentified alcohol exerted a pressure of 733 torr at 89 °C in a 1.00-L flask. When the alcohol was condensed, it had a mass of 1.95 g. The alcohol is:
(a) methanol (b) ethanol
(c) propanol (d) butanol

25. Uranium isotopes may be separated by effusion of uranium hexafluoride. If total separation of ^{235}U and ^{238}U can only be achieved when the distances traveled by $^{235}UF_6$ and $^{238}UF_6$ differ by 120 cm, then what length of tubing is required for this separation?
(a) 280 mm (b) 280 cm
(c) 280 m (d) 280 km

26. A diffusion experiment was performed with ammonia and an unidentified hydrogen halide, HX. The white ring of NH_4X formed 30.31 cm from the source of the ammonia. A diagram of the experiment is given below. What was the identity of HX?
(a) HF (b) HCl (c) HBr (d) HI



50. Multiple choice questions:

1. A 3.45-L sample of xenon at a pressure of 755 torr is compressed until the pressure is 1125 torr. What is the new volume of the xenon sample?
(a) 2.32 L (b) 2.32 mL
(c) 5.14 L (d) Cannot be determined.

2. An ideal gas at 298 K fills a volume of 45.0 L at 745 torr. What pressure must be applied to the gas to reduce its volume by 20%?
(a) 149 torr (b) 931 torr
(c) 3725 torr (d) 596 torr

3. A sample of helium at 100 K occupies a volume of 23.2 L. What volume will this sample occupy at 335 K?
(a) 6.93 L (b) 77.7 L
(c) 23.2 L (d) Cannot be determined.

4. A 44.9-g sample of neon occupies a volume of 20.5 L at a given temperature and pressure. What volume will be occupied by 23.9 mol of neon at the same temperature and pressure?
(a) 23.9 L (b) 10.9 L (c) 220 L (d) 20.5 L

For questions 5–7: Consider two flasks, A and B, which are connected to each other by a gas-tight valve. Initially, flask A contained 434 torr of helium and flask B held a vacuum. When the valve was opened the pressure in flask A decreased to 107 torr.

5. What was the pressure in flask B after the valve was opened?
(a) 327 torr (b) 434 torr
(c) 217 torr (d) 107 torr

6. If the volume of flask A was 1.25 L, then what was the volume of flask B in this experiment?
(a) 5.07 L (b) 0.31 L (c) 3.82 L (d) 1.25 L

7. In a second experiment, 434 torr of helium were placed in flask B and flask A was evacuated. What was the new pressure of helium in the flasks when the valve between the flasks was opened?
(a) 107 torr (b) 217 torr
(c) 327 torr (d) 1326 torr

8. A pressure of 152 torr is equivalent to:
(a) 152 mm Hg
(b) 20.3 kPa
(c) 0.200 atm
(d) 2.94 psi
(e) All of the above
(f) Two of the above

9. 150.0 L of neon at 29.92 in of Hg can be changed to 45.0 L at constant temperature by changing the pressure to:
(a) 29.92 torr (b) 2530 torr
(c) 338 Pa (d) 99.7 atm

10. A 25-L glass vessel, which can withstand internal pressures up to 15.0 atm before it shatters, contains 89.9 g of argon at 25.0 °C at a pressure of 223.1 kPa. At what temperature will the glass vessel shatter?
(a) 1757 °C (b) 170 °C
(c) 2030 °C (d) 170 K
(e) None of the above.

For questions 11–13: A 2.50-L flask was filled with 1.00 g of xenon at 27 °C.

11. What is the gas pressure in the flask?
(a) 9.85 atm (b) 5.13 torr
(c) 57.0 torr (d) 673 torr

12. What will be the new pressure in the flask if an additional 2.55 g of xenon are added to the flask and the temperature is decreased to −43 °C?
(a) 0.204 torr (b) 155 torr
(c) 0.147 atm (d) 26.8 torr

13. A small amount of helium (400.0 mg) was added to the flask in Question 12. What was the resulting pressure in the flask?
    (a) 0.958 torr (b) 0.754 atm
    (c) 573 torr (d) 728 torr

14. What mass of nitrogen must be placed in a 35.9-L storage tank at room temperature (25 °C) if the pressure in the tank is required to be 574 kPa?
    (a) 117 g (b) 233 g (c) 23.6 kg (d) 2.78 kg

15. How many atoms are present in 1.25 L of CO_2 at 17 °C and 1.270 kPa?
    (a) 1.19×10^{21} (b) 3.97×10^{20}
    (c) 2.03×10^{22} (d) 6.77×10^{21}

16. What mass of helium must be placed in a 25-mL flask at 27 °C in order to obtain an internal pressure of 25 MPa?
    (a) 10.0 g (b) 1.0 g (c) 10 mg
    (d) 0.25 g (e) 11 g

For questions 17 & 18: A diatomic gas has a density of 2.824 g/L at 25 °C and 98.66 kPa.

17. What is the molecular weight of the gas?
    (a) 38.00 (b) 8.89 (c) 5.95 (d) 70.91

18. What is the probable identity of this gas?
    (a) fluorine (b) Be (c) He-H
    (d) bromine (e) chlorine

19. If 4.75 g of $KClO_3$ decomposed to potassium chloride and oxygen, what volume would the oxygen fill at 30 °C and 754 torr?
    (a) 0.971 L (b) 144 mL (c) 1.46 L

20. What is the lifting capacity of a ballon which has been filled with 435 kg of helium at 23 °C on a day when the barometric pressure is 29.50 in. of mercury? The mass of the empty balloon is 11.2 kg. The density of air under these conditions is 1.177 g/L.
    (a) 11.2 kg (b) 3.15×10^6 g (c) 2.71×10^6 g

10 Solutions

Thus far in our discussion of matter in bulk, we have dealt almost exclusively with pure substances. But **mixtures** of substances are also important forms of matter. Indeed, most matter as it occurs in nature is in the form of mixtures; the atmosphere, the oceans, the contents of every living cell are all mixtures. Every chemical reaction carried out in the laboratory requires the chemist to deal with a mixture. Of particular interest are those mixtures that consist of a single phase: **homogeneous mixtures**, commonly called **solutions**. (Review the classification of matter in Chapter 2.)

Although in everyday usage the term "solution" brings to mind a solid dissolved in a liquid, solutions can exist in any of the three physical states: gas, liquid, or solid. Air is an example of a gaseous solution, as is moist oxygen or a mixture of iodine vapor and nitrogen. Some **alloys** (mixtures of metals) are solid solutions. For example, brass is a solution of zinc in copper. An amalgam of copper and mercury (the term **amalgam** means any alloy containing mercury) is a solid solution formed from a solid and a liquid. Liquid solutions may be obtained by mixing a liquid with a gas, a solid, or another liquid.

In describing solutions, it is customary to refer to the component that retains its original physical state as the **solvent**. The other components of the solution are called **solutes**. Thus, in moist oxygen, the solvent is oxygen and the solute is water, because the solution is a gas. In the liquid solution formed from salt and water, the solvent is water and the solute is salt. And in a copper-mercury alloy, copper is the solvent, because the solution is in the solid state. In solutions in which all components have the same physical state, the one present in the greatest amount is called the solvent and the other components are called solutes. Thus, in a solution formed from 20 mL of ethyl alcohol and 500 mL of water, water is the solvent and ethyl alcohol is the solute. Liquid solutions are by far the most common, and we shall deal primarily with these in the discussions that follow.

10.1 THE SOLUTION PROCESS

The difference between solutions and heterogeneous mixtures lies in the size of the dispersed particles. In a solution these particles are individual molecules or ions, whereas in a heterogeneous mixture they are larger aggregates. In order to gain some understanding of how this molecular dispersion comes about, we must examine the solution process on the molecular level.

As an illustration, let us consider the dissolution of a crystalline molecular solid (for example, sugar) in a molecular liquid (say, water). Three kinds of intermolecular forces must be considered in this system. First, there are the intermolecular forces between solute molecules—the forces holding the molecules together in the crystal lattice. Second, there are attractive forces between the molecules of the liquid solvent. Both these types of forces tend to prevent the formation of a solution. The forces within the crystal must be overcome if solute molecules are to leave the crystal and intermingle with the solvent molecules, and the forces between solvent molecules must be overcome if solute molecules are to disperse among the solvent molecules. The third type of force at work in the system is the intermolecular attraction that exists between solute and solvent molecules. This third force tends to counteract the other two and bring about dissolution. Therefore, the stronger the attractions between solute and solvent molecules, the more likely the solute-solute and solvent-solvent forces can be overcome. It is the overall balance of these three types of forces that determines how readily the solute will dissolve in a particular solvent. If conditions are favorable for dissolution, the surface molecules leave the crystal, enter the liquid phase, and by diffusion become dispersed among the solvent molecules. The next layer of solute molecules becomes the surface layer, and these in turn enter the liquid phase, and so on, as the crystal dissolves.

The **rate** at which this dissolution occurs (the number of solute molecules entering the liquid phase per unit of time) depends on the nature of the solute and the solvent, since the strengths of the various intermolecular forces are determined by the particular structure and composition of the substances involved. For a given solute-solvent system, the rate of solution varies with temperature and with the surface area of the solute.

An increase in temperature has several effects on the system, all of which combine to increase the rate of solution. Higher temperatures increase the kinetic energy of the solute molecules, thus lessening the effectiveness of the lattice forces. The kinetic energy of the solvent molecules is also increased at higher temperatures, so that solvent-solvent attractions are more easily overcome. Finally, higher temperatures increase the rate with which solute molecules diffuse through the solvent.

Because dissolution of a solid solute is a surface phenomenon, the greater the surface area of the solid, the higher will be its rate of solution. Thus a pulverized solid will dissolve *faster* than the same substance in one large lump, because pulverization increases the surface area. Stirring or agitation of the mixture will also increase the rate of solution, because this action increases the amount of surface in contact with the liquid. Stirring also aids in diffusion of the dissolved molecules.

As the solution process continues, more and more solute molecules enter the liquid phase. These "dissolved" molecules are in random motion along with the solvent molecules. As a result of this motion, solute molecules in the liquid phase undergo collisions with the surface of the crystal. If a collision occurs when a "dissolved" molecule has a sufficiently low kinetic energy, it may be "captured" by the lattice forces at the surface of the crystal and become part of the crystal again. This process, which is the reverse of dissolution, is called crystallization. Thus, two opposing processes operate in the system, which can be represented by the expression

$$\text{Undissolved solute} \rightleftharpoons \text{Dissolved solute}$$

The rate of crystallization is determined by the same factors that determine the rate of solution—the nature of the solute and solvent, the temperature, and the surface area of the solute—and by one additional factor, the number of solute molecules in the liquid phase.

As was indicated above, for a given solute and solvent at a given temperature and with a given surface area, the rate of solution is essentially constant with time. The rate of crystallization, however, begins at zero and gradually increases as the number of dissolved solute molecules increases. Eventually, the rates of the two opposing processes must become equal, and a state of dynamic equilibrium is reached. (Note the similarity to the evaporation of a liquid in a closed system, discussed in Chapter 9.) In this state, if the temperature is held constant, solute will continue to dissolve and to crystallize at the same rate, and there will be no net change in the amount of solute dissolved. A solution in which this situation exists—that is, one in which the dissolved solute is in equilibrium with the undissolved solute—is called a **saturated** solution. When a solution contains *less* dissolved solute than the equilibrium amount, it is said to be **unsaturated**; if it contains *more* than the equilibrium amount, it is referred to as **supersaturated**.

Let us now consider the dissolution of an ionic solid in a liquid, such as sodium chloride in water. In general, our discussion of the dissolution of a molecular solid applies also

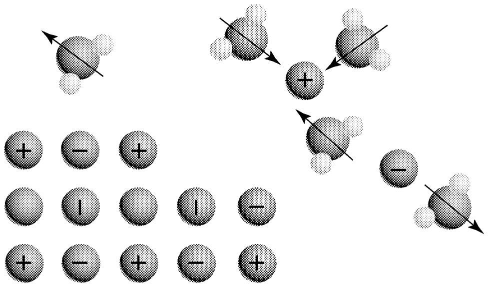


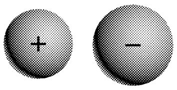
Figure 10.1 The ion-dipole interaction.

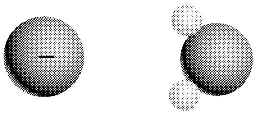
to an ionic solid, with some modifications necessary because of the difference in the nature of the attractive forces.

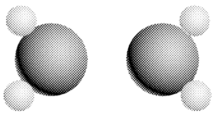
Recall that an ionic solid consists of positive and negative ions arranged alternately in the crystal lattice and held together by rather strong electrostatic attractions. Since ions in the body of the crystal are surrounded by some number of ions of opposite charge, they are subjected to attractions in all directions. But the electrostatic attractions on the surface ions, which are the ions that come into contact with the solvent molecules, are unbalanced. Because water molecules are dipoles, they are attracted to these surface ions, and they align their positive ends to the anions and their negative ends to the cations. This attractive force between an ion and a polar molecule, called an **ion-dipole attraction**, permits the ions to leave the surface of the lattice and become part of the liquid phase (see Figure 10.1). The dissolved ions diffuse through the solution surrounded by their attached water molecules. In this condition, the ions are said to be **hydrated**, and the process of their formation is called **hydration**. (These terms are used when the solvent is water. The more general terms *solvated* and *solvation* are used to indicate the attachment of molecules of any solvent.) As in the case of molecular solutes, if sufficient ionic solute is present, an equilibrium will be established between the dissolved and undissolved ionic substance, giving a saturated solution.

Visualization 10.1

Determine whether each of the following electrostatic interactions leads to higher or lower potential energy.







Solution:

(a) lowers the potential energy because of the attraction of the oppositely charged ions. (b) represents the interaction of an anion with a water molecule. The dipole of the water molecule has its negative end at the oxygen and the positive end closer to the negative ion. Therefore the dipole is attracted to the anion and the potential energy is lowered. In (c) two water molecules have the negative end of their dipoles pointing toward one another. There is a repulsion of the dipoles and the potential energy increases.

10.2 SOLUBILITY

The amount of a solute present in the dissolved state in a saturated solution is called the **solubility** of the solute. Solubility is a measure of the *extent* to which one substance will dissolve in another and should not be confused with the *rate* of solution. It may be expressed

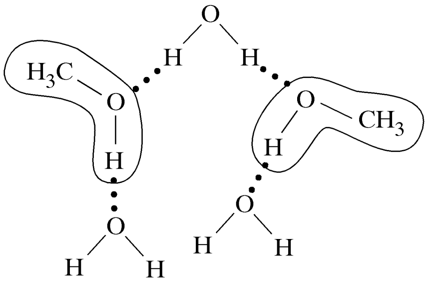


Figure 10.2 Hydrogen-bonding between solvent (water) and solute (methyl alcohol).

either as the amount of solute in a given amount of solvent (for example, grams of sugar per 100 grams of water) or as the amount of solute in a given amount of solution (for example, grams of sugar per liter of solution). The solubility of a substance is dependent on a number of factors, which we shall treat in turn.

Nature of the Solute and Solvent

The solubility of one substance in another varies widely with the structural and compositional nature of the two substances and is related to the three kinds of attractive forces discussed earlier. In order for solution to occur, solvent-solute attractions must overcome solute-solute and solvent-solvent attractions, and so it is the balance among these forces that determines the solubility of a given solute in a particular solvent.

In general, solutes tend to be more soluble in solvents to which they are structurally and electrically similar. This is the often-quoted rule of "like dissolves like." More specifically, solubility is likely to be greater if both solute and solvent are polar, or if both are nonpolar, than if one is polar and the other nonpolar. If both solute and solvent are polar (or if hydrogen bonding is possible between them), then the solute-solvent attractions are strong, and solubility is enhanced. Thus, substances such as sugar, methyl alcohol, and glycerol have high solubilities in water and other polar solvents (see Figure 10.2). On the other hand, sugar is almost completely **insoluble** in such nonpolar liquids as benzene or gasoline (a mixture of hydrocarbons). In these cases, the very weak solute-solvent attractions are not strong enough to overcome the strong solute-solute attractions. Similarly, ionic compounds dissolve only in polar solvents, where ion-dipole attractions can occur; their solubility in nonpolar liquids is generally negligible.

A nonpolar substance such as carbon tetrachloride has only a very slight solubility in water. The strong attractive forces between water molecules (solvent-solvent attractions) are much stronger than the solvent-solute attractions (Figure 10.3). On the other hand, carbon tetrachloride shows a high solubility in ethyl ether (a less polar molecule than water and one in which hydrogen bonding does not occur), because the solvent-solvent forces are weak enough to allow carbon tetrachloride molecules to enter between ether molecules.

Covalent network crystals, such as diamond or quartz, are not soluble in any liquid. No solute-solvent forces are strong enough to break down the network of covalent bonds.

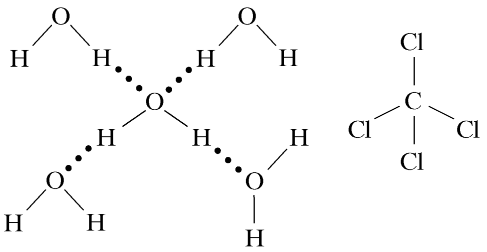
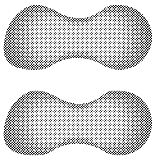
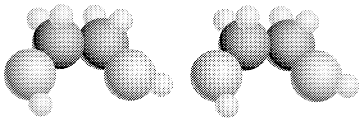


Figure 10.3 Hydrogen-bonding only between solvent molecules.

Visualization 10.2

Which of the following represent reasonably strong interactions in a mixture of ethyleneglycol ($HOCH_2CH_2OH$) and I_2?


(a)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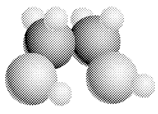
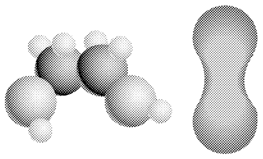

(c)


(d)

Solution:

In (a) there are only van der Waals forces (which are fairly strong because of the large number of electrons in I_2). In (b) one ethyleneglycol molecule is hydrogen-bonding to a neighboring molecule. This is a strong interaction. In (c) there is intramolecular hydrogen-bonding within one ethyleneglycol molecule. This is a strong interaction, but it does not affect intermolecular forces. In (d) there is only very weak hydrogen-bonding and van der Waals forces.

Temperature

The solubility of gases in water (and in most other liquids) usually decreases with increasing temperature. An open bottle of carbonated drink goes “flat” more quickly when it is warm than it does if it is kept cold; at higher temperatures the dissolved carbon dioxide escapes more rapidly because its solubility is lower. Everyone has observed the formation of small bubbles when water is heated; these are bubbles of air released from the solution as the solubility decreases with increasing temperature.

There is no general rule regarding the effect of temperature on the solubility of liquid or solid solutes in liquid solvents. While it is true that most solids show an increase in solubility with increasing temperature, this trend is certainly not observed for all solids; many have decreasing solubilities with increasing temperatures. Furthermore, the extent to which a given temperature change will change the solubility varies greatly among substances. There is no simple equation that expresses solubility-temperature relationships. These relationships must be determined experimentally and are usually presented as solubility curves in which solubility is plotted against temperature. The solubility curves for a substance whose solubility increases with increasing temperature (KCl), a substance whose solubility decreases with increasing temperature (Li_2CO_3), and one whose solubility is hardly affected by temperature change (NaCl) are shown in Figure 10.4.

The effect of temperature change on solubility is related to the energetics of the solution process. The dissolution of a solute in a solvent is accompanied by a change in enthalpy; that is, heat is either absorbed or evolved. This change in enthalpy is the net result of the energy required to break the solute-solute and solvent-solvent attractions and the energy released in the formation of solute-solvent attractions. The quantity of energy involved in the change, called the **heat of solution** (ΔH_{soln}), is a function not only of the amount of solute but also of the amount of solvent in which it is dissolved. Thus, heats of solution are usually expressed in terms of kilojoules per mole of solute dissolved in a specified number of moles of solvent. We can determine experimentally whether a solution process is endothermic ($\Delta H_{\text{soln}} = +$) or exothermic ($\Delta H_{\text{soln}} = -$) by dissolving some of the solute in a solution that is already nearly saturated, thereby eliminating any significant change in concentration. If the solution increases in temperature, the process is exothermic, and if it decreases in temperature, the process is endothermic.

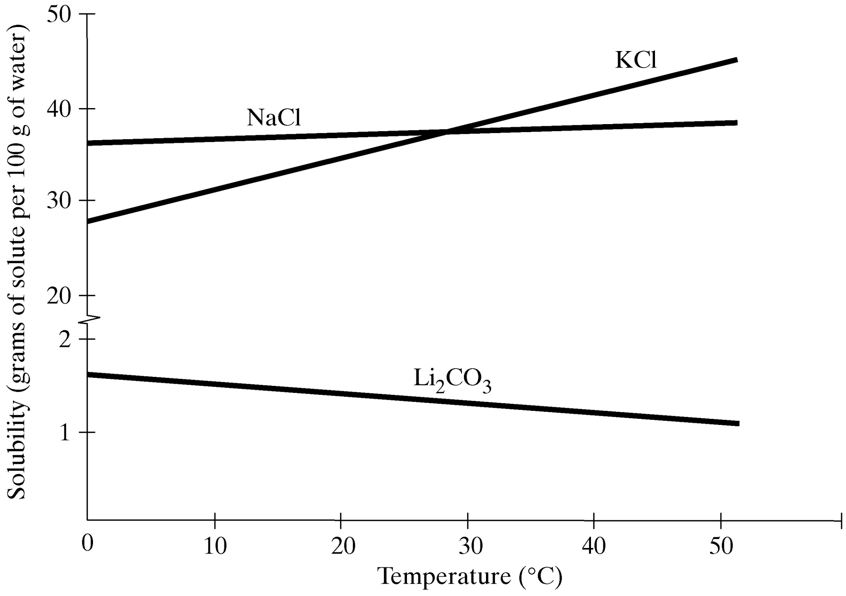


Figure 10.4 Dependence of solubility on temperature.

From a knowledge of whether a given solution process is endothermic or exothermic, we may predict how the solubility will change with temperature by applying a useful concept known as **Le Châtelier's Principle**. This principle, proposed by Henri Le Châtelier in the 1880s, may be stated as follows:

If a stress is applied to a system in equilibrium, the system will readjust in such a way as to relieve the stress and establish a new equilibrium state.

Since a state of equilibrium exists when two opposing processes are occurring at the same rate, Le Châtelier's Principle may be restated in the following way: If **the conditions of a system in equilibrium are altered, that process which tends to restore the original conditions will be favored**.

Since the solubility of a substance is a measure of the amount of that substance present in a saturated solution (that is, the equilibrium amount), it may be described as the amount of dissolved solute in an equilibrium that can be represented by one of the following expressions:

$$\text{(1)} \quad \text{Undissolved solute} \longrightarrow \text{Dissolved solute} + \text{Heat } (\Delta H = -)$$

$$\text{(2)} \quad \text{Undissolved solute} + \text{Heat} \longrightarrow \text{Dissolved solute } (\Delta H = +)$$

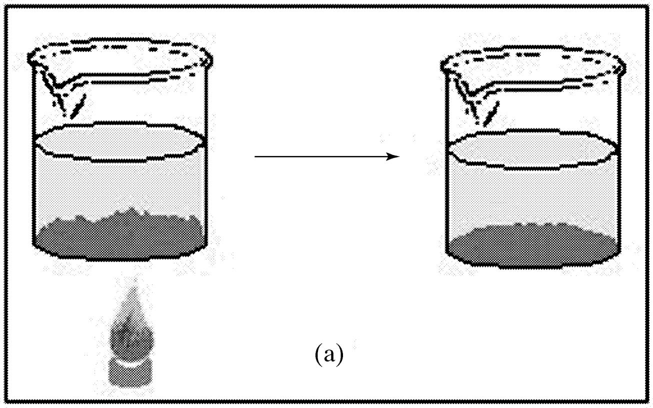
Equation (1) represents an exothermic solution process (heat is given off when the solute dissolves) and equation (2) is an endothermic process (heat is absorbed when the solute dissolves).

Heat is one of the forms of "stress" referred to in Le Châtelier's Principle. Therefore, in raising the temperature of a solution by the addition of heat, the equilibrium is disturbed. According to Le Châtelier's Principle, the process that consumes the added heat will be favored until the equilibrium is restored. In the exothermic solution process, represented by equation (1), the process going to the *left* will be favored (that is, more undissolved solute will be formed). Thus, when equilibrium is reestablished at the new, higher temperature, there will be less dissolved solute than there was at equilibrium at the lower temperature. In other words, the solubility will have *decreased.* In the situation represented by equation (2), raising the temperature will favor the process to the *right* (the process that consumes heat), causing an increase in the amount of dissolved solute. In this case, then, the solubility will have *increased.* To summarize, we may say that solutes with exothermic heats of solution (the enthalpy change is negative) show *decreasing* solubility with increasing temperature, while solutes with endothermic heats of solution (the enthalpy change is positive) show *increasing* solubility with increasing temperature.

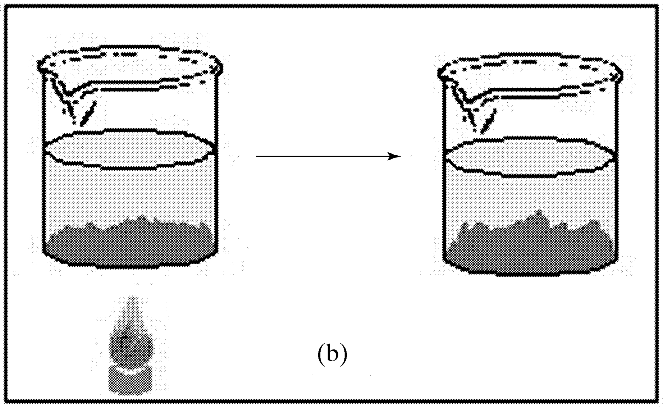
The change in the solubility of a substance with a change in temperature may result in a supersaturated solution. For example, suppose we prepare a saturated solution of KCl in water at 50 °C (the solubility at this temperature is 42.6 g of KCl per 100 g of water). Now we very carefully filter the solution at 50 ° to remove any undissolved KCl as well as any particles of dust or other foreign matter. The solution is then allowed to cool, without any disturbance, to room temperature, say 25 °C. If we have been very careful in our operations, the solution may cool to 25 ° without any solute crystallizing out. If so, we have a solution containing 42.6 g of KCl per 100 g of water, even though the solubility of KCl at 25 °C is only 35.5 g per 100 g of water. Our solution contains more than the equilibrium amount of solute and is therefore supersaturated. Such solutions are not stable; if they are agitated or if a crystal of the solute is introduced, crystallization of solute from the solution will quickly occur and equilibrium will be established.

Visualization 10.3

Describe ΔH for each of the following processes:



(a)



(b)

Solution:

In (a) the mixture is heated and some of the solid disappears (dissolves). The dissolution process is therefore endothermic (heat is required). In (b) more of the solid comes out of solution when the mixture is heated and therefore the dissolution process is exothermic. Thus, in (b) we could represent the solution process as

$$\text{solute} + \text{solvent} \longrightarrow \text{solution} + \text{heat}$$

When heat is added this stress is relieved by having the process go to the left, where more solute is produced.

Pressure

For solutions of solids or liquids, in liquid solvents, the effect of pressure on solubility is negligible. However, this is not the case for solutions of gases in liquid solvents. The relationship between solubility and pressure for a gas in a liquid is given by **Henry's Law**, named after the English chemist William Henry, who devised it in 1803:

For solutions of gases in liquids, the solubility of a gas is directly proportional to the partial pressure of the gas above the solution.

This relationship is illustrated in Figure 10.5.

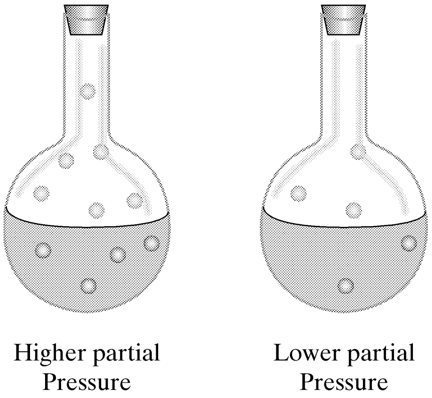


Figure 10.5 Illustration of Henry's Law.

Problem 10.1

The solubility of hydrogen in water at a temperature of 25 °C and a hydrogen pressure of 1 atm is 1.54 mg per liter of water. What is the solubility of H_2 in H_2O at a hydrogen pressure of 700 torr if the temperature is held constant?

Solution:

The solubility of the hydrogen is proportional to the pressure above the solution. Therefore,

$$\frac{700\text{ torr}}{760\text{ torr}} = \frac{1.54\text{ mg }H_2}{1\text{ L }H_2O} = 1.42\text{ mg }H_2/\text{L }H_2O$$

One of the most common applications of this pressure-solubility relationship is in the preparation of soda water. Carbon dioxide is dissolved in water, bottled, and tightly sealed, all under high pressure. When the bottle cap is removed at ordinary atmospheric pressure, the decreased solubility of the carbon dioxide causes it to escape from the solution, imparting the "fizz" to the liquid.

Another illustration of this phenomenon can be seen in caisson disease, commonly called "the bends." This ailment is sometimes contracted by divers and others who work under high pressures when they experience a decrease in pressure too quickly. Inhalation of air at the high pressure necessary for deep sea diving results in the solution of a large amount of nitrogen in the blood and body tissues—a much larger amount than could dissolve at atmospheric pressure. When the diver returns to the surface, the decrease in pressure causes a lower solubility of nitrogen, which leaves the blood in the form of bubbles. If the decompression takes place slowly enough, the bubbles can escape from the body with no ill effects. But if the pressure decrease occurs too suddenly, the rapid formation of nitrogen bubbles within the body can cause intense pain and even death.

10.3 THE ENERGETICS OF SOLUTION

The solubility of a given solute in a particular solvent—that is, the extent to which the solution process occurs—is a function of the free energy change (ΔG) that accompanies the process. Thus, since ΔG is a function of the enthalpy change and the entropy change, both these thermodynamic properties play a role in solubility.

$$\Delta G = \Delta H - T\Delta S$$

As we discussed earlier, the enthalpy change (heat of solution) may be either positive or negative, and it represents the net result of the energy required to overcome the solute-solute and solvent-solvent attractions and the energy given off in the formation of solute-solvent attractions. We may therefore consider the process of solution formation as the sum of several steps involving these various forces. The nature of the forces depends on the nature and physical state of the solute and solvent. In our discussion, we will consider the following types of solutions: (1) an ionic solid dissolved in water; (2) a molecular solid dissolved in a liquid; (3) a liquid dissolved in a liquid; and (4) a gas dissolved in a liquid.

An Ionic Solid in Water

The dissolution of an ionic solid in water may be thought of as occurring in two imaginary steps. First, the crystal lattice breaks down to form isolated ions in the gaseous state. Using NaCl as an illustration, this step may be represented as

(1) $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ (ΔH is positive; unfavorable)

Note that this is the reverse of the equation used previously to define lattice energy (Chapter 5). Since energy is required, the enthalpy change is positive, and the process is not favored.

The second step involves the hydration of the gaseous ions, which may be represented by the equation

(2) $Na^+(g) + Cl^-(g) \longrightarrow Na^+(aq) + Cl^-(aq)$ (ΔH is negative; favorable)

The enthalpy change for this process—called the **hydration energy**—is negative and therefore favors the process. (The hydration energy is actually the net of the energy released in the formation of solute-solvent attractions and that absorbed in overcoming solvent-solvent attractions. Because these two energy changes are extremely difficult to determine separately, they are lumped together as hydration energy.)

The addition of these two equations results in an expression that represents the process of the dissolution of solid sodium chloride in water. Therefore, the heat of solution (ΔH_{soln}) is the sum of the enthalpy changes of the two imaginary processes.

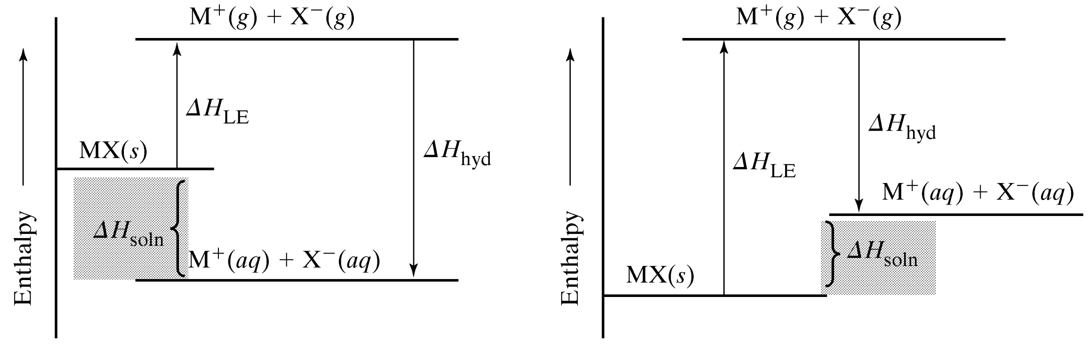
(1) $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ ΔH = lattice heat

(2) $\underline{Na^+(g)Cl^-(g) \longrightarrow Na^+(aq) + Cl^-(aq)}$ $\underline{\Delta H \text{ = heat of hydration}}$

(3) $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$ ΔH = heat of solution

Since ΔH of step 1 is always positive and ΔH of step 2 is always negative, the sign of the heat of solution depends on which of them is greater. If the heat of hydration is larger than the lattice energy, the solution process will be exothermic and therefore favored (Figure 10.6a). On the other hand, if the lattice energy is larger than the heat of hydration, the solution process will be endothermic and not favored (Figure 10.6b).

The direction of the **entropy** change when a solid is dissolved in a liquid is easily predicted. Certainly, the random dispersion of solute and solvent particles in a solution represents greater disorder (and therefore higher entropy) than either a crystal lattice or



(a) Exothermic solution process (ΔH_{soln} is negative)

(b) Exothermic solution process (ΔH_{soln} is positive)

Figure 10.6 The effects of the lattice energy (ΔH_{LE}) and heat of hydration (ΔH_{hyd}) on the heat of solution (ΔHs_{oln}) when an

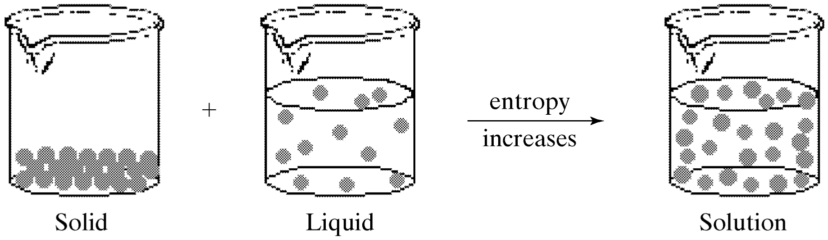


Figure 10.7 The increase in entropy during the solution process.

an unmixed liquid (see Figure 10.7). Dissolution of a solid in a liquid, then, usually results in an increase in entropy (ΔS is positive), and this *favors* the process.

Let us apply these considerations to the free energy change ($\Delta G = \Delta H - T\Delta S$). Since ΔS is generally positive when a solid dissolves in a liquid, ΔG will be negative (that is, dissolution will occur) only if ΔH is negative or if its magnitude is less than the product $T\Delta S$. But if ΔH is a very large positive number (if the solution process is highly endothermic), dissolution will not take place or will occur only to a very limited extent.

A Molecular Solid in a Liquid

Similar considerations can be applied to the solution of molecular solids in liquids. The energy required to break up the lattice of molecular crystals is not as great as in the case of ionic crystals, but the solvation energy is also lower for molecular substances. Again, it is convenient to imagine the dissolution of the solute as occurring in two steps. First the solid melts, and then the molecules of the two liquids mix to form a solution, as illustrated in the following expressions:

$$\begin{array}{rl}
\text{solute(s)} \longrightarrow \text{solute (l)} & \Delta H_{\text{fus}} = \text{positive, unfavorable} \\
 & \Delta S_{\text{fus}} = \text{positive, favorable} \\
\text{solute}(l) + \text{solvent}(l) \longrightarrow \text{solution}(l) & \Delta H_{\text{mix}} = \text{positive, unfavorable} \\
 & \qquad\quad \text{or negative, favorable} \\
 & \Delta S_{\text{mix}} = \text{positive, favorable} \\
\hline
\text{solute}(s) + \text{solvent}(l) \longrightarrow \text{solution}(l) & \Delta H_{\text{soln}} = \text{positive, unfavorable} \\
 & \qquad\quad \text{or negative, favorable} \\
 & \Delta H_{\text{soln}} = \text{positive, favorable}
\end{array}$$

The melting process is endothermic, and therefore the heat of fusion is positive and *unfavorable* to the solution process. The enthalpy of mixing may be favorable or unfavorable, depending on the relative strengths of the various intermolecular forces involved. On the other hand, both processes lead to greater disorder, and so the entropy change is *favorable* to dissolution. Thus, solubility in this case is determined primarily by the magnitude of the heat of mixing (ΔH_{mix}), which in turn is determined by the nature of the solvent, particularly the strength of solvent-solvent attractive forces.

This relationship is illustrated by the relative solubility of a simple, nonpolar molecular solid such as iodine (I_2) in water and in a less polar solvent such as chloroform ($CHCl_3$). The solution process is the same in the two cases, but the solubility of I_2 is much lower in water (only 0.03 g per 100 g of water at 25 °C) than in $CHCl_3$ (3.1 g per 100 g of $CHCl_3$ at 25 °C). Clearly, the enthalpy change is more unfavorable when water is the solvent, even though the heat of fusion of iodine is identical in both cases. The difference lies in the heats of mixing. Water, with its hydrogen bonding, possesses strong solvent-solvent attractive forces. In order for mixing to occur, these attractions must be “broken” to allow homogeneous dispersion of the I_2 molecules, and a large input of energy is required. Thus, the mixing process is highly endothermic and ΔH_{mix} is very unfavorable. The intermolecular forces between $CHCl_3$ molecules, however, are much weaker than those between water molecules, so less energy is required to “make room for” the I_2 molecules. Hence, when I_2 dissolves in $CHCl_3$, the mixing process is much less endothermic and ΔH_{mix} is not nearly so unfavorable as when water is the solvent. The net result is a more favorable free-energy change (and therefore greater solubility) in the I_2-$CHCl_3$ system.

A Liquid in a Liquid

The reasoning employed in analyzing the energetics of solution of a molecular solid in a liquid can be applied also to the solution of a liquid in a liquid. Since both solute and solvent are liquids, no lattice need be broken and no imaginary change of state need be considered. The solution process is simply one of mixing. The heat of solution is the heat of mixing, and the entropy of solution is just the entropy of mixing. Thus, whether the factor favoring solution, $T\Delta S$, will outweigh an unfavorable heat of mixing depends only on how endothermic the mixing process is.

A Gas in a Liquid

Finally, let us consider briefly the energetics of solution of a gas in a liquid. The two imaginary steps in this case are:

1. Condensation of the gas to a liquid. This is an exothermic process, so it is *favored* by the enthalpy change. But since it represents a decrease in disorder, the entropy factor is *unfavorable.*
2. Mixing of the molecules of the two liquids. The entropy change here is *favorable.* However, the enthalpy change may be either favorable or unfavorable, depending on whether the forces of attraction are stronger or weaker in the solution than they are in the two unmixed liquids.

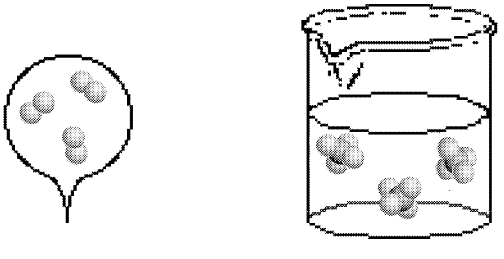
$$\begin{array}{rll}
\text{Solute}(g) \longrightarrow \text{Solute}(l) & \Delta H_{\text{cond}} & = \text{negative, favorable} \\
 & \Delta S_{\text{cond}} & = \text{negative, unfavorable} \\
\text{Solute}(l) + \text{Solvent}(l) \longrightarrow \text{Solution} & \Delta H_{\text{mix}} & = \text{negative, favorable} \\
 & & \quad \text{or positive, unfavorable} \\
 & \Delta S_{\text{mix}} & = \text{positive, favorable}
\end{array}$$

The entropy change in the liquefaction step is greater than the entropy change of mixing, so that the overall entropy effect in the solution of a gas in a liquid is *unfavorable* to the process. (Recall that for solid and liquid solutes the entropy in all steps is favorable to dissolution.)

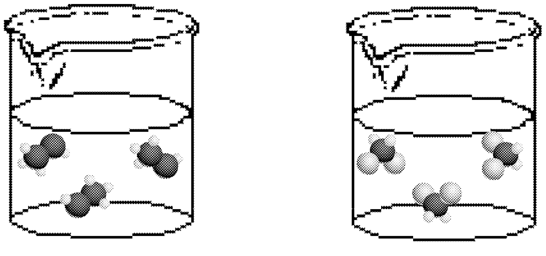
If the liquid solvent has strong intermolecular forces (as in water), the mixing process is highly endothermic (ΔH_{mix} is unfavorable). This, together with the unfavorable entropy factor, accounts for the observation that most gases (except those that undergo chemical reaction with water) have very low solubilities in water.

Visualization 10.4

The following diagrams represent solutes and solvents. For each set, estimate *ΔH* and *ΔS* for the solution process.



(a)



(b)

Continued on next page

Visualization 11.4 *Continued*

Solution:

The solute in (a) is presumably gaseous Cl_2, while the solvent is liquid CCl_4. When Cl_2 is dissolved in CCl_4 there are only van der Waals forces between solute and solvent molecules and these are not as strong as the van der Waals forces between the molecules in CCl_4 (the forces between two CCl_4 molecules are fairly strong because of the large number of electrons). Because the Cl_2 molecules separate the CCl_2 molecules somewhat, the potential energy of the solution is higher than that of the solute and solvent and ΔH is therefore positive. The ΔS for (a) is negative because the high entropy (high disorder) of the gas is removed when the molecules enter solution and are forced to be much closer together.

The solute in (b) is methanol (CH_3OH) and the solvent is dichloromethane. The strongest intermolecular force occurs in the methanol, where the molecules are hydrogen-bonding. This interaction is reduced in solution and ΔH is therefore positive. The entropy change for this process is positive because of the mixing of the two liquids; that is, there is greater disorder in solution.

10.4 CONCENTRATIONS OF SOLUTIONS

The frequent use of solutions in the laboratory, in the industrial process facility, or around the home requires appropriate methods of describing the composition of these solutions. The compositions of saturated solutions at a specific temperature are defined by the solubility of the given solutes, but the more commonly encountered solutions, both in the laboratory and in nature, are not saturated and have a great variety of compositions. The description "a solution of sugar in water" relates *what* the components are but says nothing about *how much* of each component is present. The terms "concentrated" and "dilute" are sometimes used in this regard, but these terms are only relative; that is, a concentrated sugar solution contains more sugar per unit volume than does a dilute one.

The composition of a solution is conveniently described in terms of its **concentration**, which is simply the amount of solute in a given quantity of solvent or solution:

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solvent or solution}}$$

The amounts may be expressed in any units appropriate for the purpose. Thus, grams of solute per 100 grams of solvent, grams of solute per kilogram of solution, and milliliters of solute per liter of solution are all acceptable expressions of concentration. Some of the more commonly used expressions of concentration are summarized in Table 10.1.

TABLE 10.1 Some Common Ways of Expressing Concentrations of Solutions

NAME	ABBREVIATION	DEFINITION
Mass percentage	mass %	Parts by mass of solute per 100 parts by mass of solution
Volume percentage	vol %	Parts by volume of solute per 100 parts by volume of solution
Parts per million	ppm	Parts by mass of solute per million parts by mass of solution
Parts per million	ppm (vol)	Parts by volume of solute per million parts by volume by volume of solution
Molarity	M	Moles of solute per liter of solution
Molality	m	Moles of solute per kilogram of solvent
Mole fraction	X	Ratio of the number of moles of a component to the total number of moles in the solution
Normality	N	Number of equivalents of solute per liter of solution

Mass Percentage

The expression of concentration as a **mass percentage** (or weight percentage) is the parts by mass of solute per 100 parts by mass of solution. Examples of problems involving mass percentage are given in Problems 10.2–10.4.

Problem 10.2

A solution was prepared by dissolving 20.0 g of NaCl in 250 g of H_2O. Express the concentration of the solution in terms of the mass percentage.

Solution:

The solution has a total mass of 270 g. Therefore:

$$\frac{20.0\text{ g Na Cl}}{(20.0 + 250)\text{ g solution}} \times 100\% = 7.41\text{ mass }\%$$

Problem 10.3

What mass of HCl is present in 2.20 kg of a 35.0 mass % solution?

Solution:

$$2.20\text{ kg solution} \times 1000\text{ g/kg} \times \frac{35.0\text{ g HCl}}{100\text{ g solution}} = 770\text{ g HCl}$$

Therefore, the mass of HCl is 770 g or 0.770 kg.

Problem 10.4

Concentrated phosphoric acid, which has a density of 1.70 g/mL at 20 °C, is 85.5% H_3PO_4 by mass. What volume of the concentrated acid must be used in a reaction that requires 0.450 mol of H_3PO_4?

Solution:

$$0.450\text{ mol} \times 98.00\text{ g of phosphoric acid/mol} = 44.1\text{ g of }H_3PO_4$$

$$44.1\text{ g }H_3PO_4 \div \frac{85.5\text{ g }H_3PO_4}{100\text{ g solution}} = 51.6\text{ g of concentrated acid}$$

$$51.6\text{ g} \div 1.70\text{ g/mL} = 30.4\text{ mL of concentrated phosphoric acid}$$

Therefore, the volume required is 30.4 mL.

Volume Percentage

Although it is less commonly employed than mass percentage, **volume percentage** may be used in special cases, particularly in describing the composition of gaseous solutions. Volume percentage is defined as the parts by volume of solute per 100 parts by volume of solution.

Problem 10.5

If 25.0 L of air contains 233 mL of argon, what is the volume percentage of Ar?

Solution:

Each liter of air contains 1000 mL. Therefore,

$$\frac{233\text{ mL Ar}}{25.0\text{ L air} \times 1000\text{ mL/L}} \times 100\% = 0.932\text{ vol }\%$$

Parts per Million

For very dilute solutions, concentrations are expressed in **parts per million** (ppm); i.e., parts by mass of solute per million parts by mass of solution. The concentration of a solution expressed in parts per million is 10,000 times its concentration expressed as a mass percentage. Thus, a solute with a concentration of 0.025 wt-% also has a concentration of 250 ppm.

Just as it is sometimes convenient to express concentrations in terms of the volume percentage, the units of parts per million by volume—ppm(vol)—are also occasionally used. This concentration unit is defined as the parts by volume of solute per million parts by volume of solution.

Problem 10.6

If 150 g of orange juice contain 120 mg of ascorbic acid (vitamin C), what is the concentration of ascorbic acid expressed in ppm?

Solution:

Each gram of orange juice contains 1000 mg. Therefore,

$$\frac{120\text{ mg ascorbic acid}}{150\text{ g orange juice} \times (1000\text{ mg/1 g})} \times 10^6\text{ parts per million} = 800\text{ ppm}$$

Problem 10.7

The average concentration of carbon monoxide in the air over a certain city was 17.1 ppm(vol). How many milliliters of CO are contained in each liter of that air?

Solution:

There are 17.1 mL of CO in every one million mL of air. Therefore,

$$\frac{17.1\text{ mL of CO}}{1000000\text{ mL of air}} \times \frac{1000\text{ mL}}{1\text{ Liter}} = 0.0171\text{ mL CO per liter of air}$$

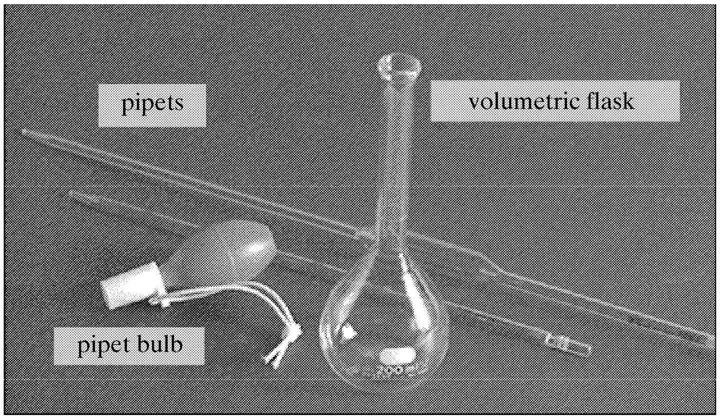


Figure 10.8 Some volumetric equipment.

Molarity

Molarity, the number of moles of solute per liter of solution, is one of the most common expressions of concentration. The most convenient way to prepare a solution of specific molarity is to use a volumetric flask (Figure 10.8). The proper amount of solute is placed in the flask, and solvent is then added with thorough mixing until the solution fills the flask exactly to the calibration mark on the neck. Volumetric flasks are available in a variety of sizes, each with its volume carefully calibrated. When a solution is prepared by diluting a sample of a solution of known concentration, a pipet is used to transfer a specific amount of the solution to a volumetric flask. Several types of pipets and a pipet bulb (used to pull the solution into the pipet) are shown in Figure 10.8.

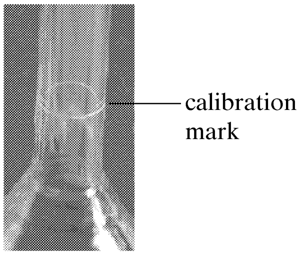


Figure 10.9 The calibration mark on the neck of a volumetric flask.

Suppose, for example, we wish to prepare 250 mL of 0.50 M $CaCl_2$ solution. One mole of $CaCl_2$ weighs approximately 111 g. Therefore, 0.50 mol weighs 55.5 g, and one liter of the solution would require 55.5 g of $CaCl_2$. However, since we wish to make only 250 mL (0.250 L), we will need 55.5 × 0.250, or 13.9 g of $CaCl_2$. We place this weight of $CaCl_2$ in a 250-mL volumetric flask and add water slowly to the flask, agitating it thoroughly to dissolve all the solute. Finally, we add enough water to bring the volume just to the calibration mark (Figure 10.9).

Some additional examples of calculations involving molarity can be found in Methodology examples 10.1–10.2 and Problems 10.8–10.9.

Solutions containing a specific concentration of a species also may be prepared from a more concentrated solution of that species through the process of dilution. This process involves accurately measuring, with a pipet (Figure 10.8), a volume of the concentrated solution whose molarity is known. This solution is then placed in a volumetric flask and water is added to the mark. Since the dilution procedure will neither create nor destroy matter, the moles of species before dilution must be equal to the moles of species present after dilution (see Methodology 10.2 and Problem 10.8).

Methodology 10.1

What mass of chloride ion is contained in 75.0 mL of 0.200 M BaCl2 solution?

How many moles of chloride ions are there in one mole of $BaCl_2$?

Two.

What is the molarity of the solution in terms of chloride ion?

Since one mole of $BaCl_2$ contains two moles of chloride ions, the solution is 0.400 *M* in chloride ion.

Continued on next page

Methodology 10.1 Continued

How many moles of chloride are in 75 mL?

Each liter of the solution contains 0.400 mol of chloride ion. Therefore 0.075 L contains

$$0.400 \text{ mol/L} \times 0.0075 \text{ L} = 0.030 \text{ mol}$$

What is the mass of 0.030 mol of chloride ion?

Each mole of chloride has a mass of 35.453 g. Therefore,

$$0.030 \text{ mol} \times 35.453 \text{ g/mol} = 1.1 \text{ g}$$

Methodology 10.2

How would one prepare 500 mL of 0.15 M $AgNO_3$ solution from a 6.0 M stock solution of $AgNO_3$?

How many moles of silver nitrate are there in 500 mL of 0.15 M silver nitrate?

The solution must contain a total of 0.075 mol of silver nitrate;

$$\frac{0.15 \text{ mol } AgNO_3}{\text{Liter of solution}} \times \frac{500 \text{ mL of solution}}{1000 \text{ mL per Liter}} = 0.075 \text{ mol}$$

How many liters of the stock solution contain 0.075 mol of silver nitrate?

The stock solution contains 6.0 moles per liter. So, in order to obtain 0.075 mol we need

$$\frac{0.075 \text{ mol}}{6.0 \text{ mol/L}} = 0.013 \text{ L}$$

How, then, is the solution prepared?

13 mL of the 6.0 M stock solution is diluted with distilled water to a volume of 500.0 mL in a 500-mL volumetric flask. The resulting solution is 0.15 M $AgNO_3$.

Problem 10.8

What is the molarity of a 20 mass % NaCl solution that has a density of 1.15 g/mL?

Solution:

Because molarity is based on volume of solution, while percentage is based on mass of solution, it is not possible to derive one of these concentration expressions from the other unless the density of the solution is known. Since 1 mL of the solution weighs 1.15 g, 1 L weighs

$$1.15 \text{ g/mL} \times 1000 \text{ mL/L}$$

The solution is 20 mass % NaCl. Therefore, the mass of NaCl in 1 L of solution is:

$$1.15 \text{ g/mL} \times 1000 \text{ mL/L} \times \frac{20 \text{ g NaCl}}{100 \text{ g solution}}$$

To find the number of moles of NaCl in 1 L (that is, the molarity), the number of grams of NaCl per liter is divided by the number of grams in one mole of NaCl. Therefore,

$$\frac{1.15 \text{ g/mL} \times 1000 \text{ mL/L} \times 0.02}{58.4 \text{ g/mol}} = 3.94 \text{ mol/L} = 3.94\ M$$

Problem 10.9

What volume of concentrated hydrochloric acid (12 *M*) is required to make 250 mL of 0.35 *M* aqueous HCl solution?

Solution:

The number of moles of HCl required to prepare the solution is:

$$\frac{0.35 \text{ mol of HCl}}{1 \text{ L of solution}} \times \frac{250 \text{ mL}}{100 \text{ mL/L}} = 0.088 \text{ mol of HCl}$$

The molarity of concentrated HCl is 12 *M*. Therefore, the required volume of concentrated HCl is:

$$0.088 \text{ mol} / 12 \text{ mol/L} = 0.0073 \text{ L or } 7.3 \text{ mL}$$

Check Point 10.1

What is the concentration of the solution prepared by diluting 7.50 mL of 0.980 *M* nitric acid to a total volume of 100.0 mL?

Solution:

0.0735 *M*

◇ ◇ ◇ ◇ ◇

Molality

Molarity is an expression of concentration based on the *volume of solution* and is therefore subject to changes in temperature. Furthermore, it does not specify the number of moles of solvent present. For some purposes it is desirable to have an expression of concentration that is not affected by temperature and that indicates the molar ratio of solute to solvent. One such expression in common use is **molality**; i.e., the number of moles of solute per kilogram of solvent. Thus, while molarity is based on the volume of solution, molality is based on the *weight of solvent.* A 2.5 molal (abbreviated 2.5 *m*) sugar solution contains sugar and water in a ratio such that 2.5 mol of sugar are present for every 1000 g of water. The volume of a solution with its concentration known only in terms of molality cannot be determined unless the density of the solution is also known.

Methodology 10.3

What is the molality of a solution prepared by dissolving 10.0 g of iodine, I_2, in 100 g of CCl_4?

What is the definition of molality?

The number of moles of solute per 1000 g of solvent.

How many moles of I_2 were dissolved in 100 g of CCl_4?

The formula weight of I_2 is 253.81 g/mol. Therefore, 10.0 g of I_2 is 0.0394 mol.

$$\frac{10.0 \text{ g of iodine}}{253.81 \text{ g/mol}} = 0.0394 \text{ mol}$$

How many moles of I_2 would there be in 1000 g of solvent?

There are 0.0394 mol of iodine in 100 g of solvent, so in 1000 g there must be

$$0.0394 \times \frac{1000 \text{ g}}{100 \text{ g}} = 0.394 \text{ mol}$$

Therefore, the molality, that is the number of moles per 1000 g of solvent, is 0.394 *m*.

Problem 10.10

What is the molality of a 20 mass % solution of glucose ($C_6H_{12}O_6$) in water?

Solution:

The solution contains 20 g of glucose per 80 g of water. The molecular weight of glucose is 180.16 g/mol. The number of moles of glucose is 20 g/180.16 g/mol and the mass of water is 0.80 kg. Therefore,

$$\frac{20\text{ g glucose}}{180.16\text{ g/mol}} \div 0.080\text{ kg} = 1.4\text{ m}$$

Problem 10.11

What is the molality of a 2.50 M H_2SO_4 solution that has a density of 1.18 g/mL?

Solution:

One liter of this solution has a mass of 1180 g. Because each liter contains 2.50 mol of H_2SO_4, the mass of H_2SO_4 per liter is 245 g.

$$2.50\text{ mol} \times 98.08\text{ g/mol} = 245\text{ g of } H_2SO_4$$

Therefore, the mass of water in one liter of the solution is 935 g (1180 − 245) or 0.935 kg, and the molality is:

$$\frac{2.50\text{ mol } H_2SO_4}{0.935\text{ kg solvent}} = 2.67\ m$$

Mole Fraction

Another useful method of expressing concentration is the **mole fraction**, which can be applied to every component of a solution, solvent as well as solutes. The mole fraction of a component in a solution is defined as the ratio of the number of moles of that component to the total number of moles of all the constituents in the solution. Thus, in a solution of A dissolved in B:

$$\text{mole fraction of A} = \frac{\text{moles of A}}{\text{moles of A} + \text{moles of B}}$$

By definition, the sum of the mole fractions of all the components of a solution is equal to one.

Problem 10.12

What is the mole fraction of glucose in a 20 mass % solution of glucose in water?

Solution:

The number of moles of glucose present is:

$$\frac{20\text{ g glucose}}{180.16\text{ g/mol}} = 0.11\text{ mol}$$

Continued on next page

Problem 10.12 *Continued*

Solution: *Continued*

The number of moles of water is:

$$\frac{80 \text{ g water}}{18.02 \text{ g/mol}} = 4.4 \text{ mol}$$

Therefore, the mole fraction of glucose is

$$\frac{0.11 \text{ mol glucose}}{0.11 \text{ mol glucose} + 4.4 \text{ mol water}} = 0.024$$

Problem 10.13

What is the mole fraction of HCl in a 10 *m* aqueous solution of HCl?

Solution:

A 10 *m* solution of HCl contains 10 mol of HCl per 1000 g of water, or 10 mol of HCl per (1000/18) mol of water. Therefore, the mole fraction of HCl is 0.15.

Normality

Another concentration expression, somewhat related to molarity, is **normality**, which is the number of **equivalents** of solute per liter of solution. Thus 1.2 *N* is read "1.2 normal" and indicates 1.2 equivalents of solute for every liter of solution. An equivalent of any substance is the mass (in grams) of the substance that in a particular chemical reaction is equivalent to (that is, will combine with, or replace, or otherwise react with) one mole of hydrogen atoms. In most cases the equivalent weight of a substance is equal to its molar mass or is some simple fraction (one-half, one-third, and so forth) of its formula weight. Unlike a mole, an equivalent of a substance is not a constant amount, but a value that depends upon the specific reaction that involves the substance.

10.5 PROPERTIES OF SOLUTIONS

Solutions have the same general characteristics as their solvents. Thus, solutions in liquid solvents show the typical behavior of liquids; they have measurable vapor pressures, surface tensions, viscosities, and so forth. However, the magnitudes of the properties—that is, the actual values of the various properties—differ between a liquid solution and the pure liquid solvent. This is to be expected, since the molecules in a liquid are in intimate contact, and the molecules of one component will be influenced by those of another.

Of particular interest are four properties of liquid solutions—vapor pressure, boiling point, freezing point, and osmotic pressure—that are dependent only on the *number* of solute particles (molecules or ions) in a given amount of solvent, not on the *nature* of the solute particles. Because these four properties are closely interrelated, they are often referred to as the **colligative properties** (from the Latin *colligare*, meaning "to bind together").

Vapor Pressure

When a nonvolatile solute (one that has a negligible vapor pressure) is dissolved in a liquid solvent, the resulting solution has a vapor pressure that is *lower* than that of the pure solvent at the same temperature. This effect can be demonstrated with two open beakers, one containing pure water and the other containing a solution of sugar in water, placed inside a tightly sealed enclosure. After a period of time, it is observed that the volume of pure water has decreased, while the volume of sugar solution has increased. Through the processes of evaporation and condensation, water has been transferred from one beaker to the other, because the vapor pressure of pure water is higher than the vapor pressure of water in the solution. If a similar experiment is performed with two sugar solutions, one more concentrated than the other, there is a net transfer of water from the less concentrated to the more concentrated solution until the solutions are the same concentration. This indicates that the extent to which the vapor pressure is lowered is dependent on the amount of solute present: the more concentrated the solution, the lower the vapor pressure.

This vapor pressure lowering can be rationalized on the molecular level as simply a matter of statistics. Since the solute is nonvolatile, only the solvent molecules escape from the solution and enter the vapor phase. Moreover, only surface molecules with sufficiently high kinetic energy can escape. The solute molecules merely "take up space" and reduce the proportion of molecules that have kinetic energy high enough to escape from the liquid surface. Thus the effect of a solute on vapor pressure is dependent only on the relative number of molecules, not on their nature. (This rationalization is based on the assumption that the solute-solute attractions are nearly the same magnitude as the attractions in the pure components, and also that the solvent and solute molecules are of comparable size.)

The quantitative relationship between vapor pressure lowering and concentration is embodied in **Raoult's Law** (Francois-Marie Raoult, 1886):

The vapor pressure (P) of a volatile component of a solution is equal to the product of the mole fraction (X) of that component and the vapor pressure of the pure component ($P°$) at the same temperature.

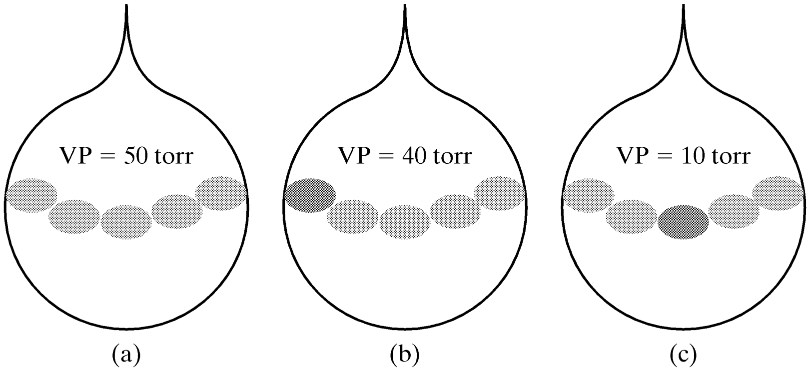
$$P = P°X$$

It is clear from this expression that as the concentration of nonvolatile solute increases, the smaller the mole fraction of solvent becomes, and the lower is the vapor pressure with respect to that of the pure solvent.

Problem 10.14 illustrates the application of Raoult's Law to predict the vapor pressures of solutions.

Visualization 10.5

The three diagrams below illustrate solvents (grey) and solutes (black) in solution, each characterized by a different vapor pressure. Which diagram is correct?



Solution:

Diagram (a) represents pure solvent; (b) and (c) contain solute in a mole ratio of 1 to 5 (0.20). Thus, the mole ratio of solvent is 0.80 and the vapor pressure due to solvent (we assume the solute to be nonvolatile) is 0.80 × 50 torr = 40 torr.

Problem 10.14

What is the vapor pressure of a 20.0 wt % glucose ($C_6H_{12}O_6$) solution in water at 29 °C? The vapor pressure of pure water at 29 °C is 30.0 torr.

Solution:

$$P^\circ = \text{the vapor pressure of water at 29 °C} = 30.0 \text{ torr}$$

$$X = \text{the mole fraction of water in the solution} = \frac{\text{number of moles of water}}{\text{total number of moles}}$$

Since there are 20 g of glucose for every 80 g of water, there are (20/180) mol of glucose for every (80/18) mol of water. Therefore:

$$X = \frac{4.44 \text{ mol } H_2O}{(4.44 + 0.111)} \text{ mol} = 0.976$$

and

$$P = 30.0 \text{ torr} \times 0.976 = 29.3 \text{ torr}$$

In the case of a solution in which the solute has an appreciable vapor pressure (for example, the solution of a liquid in a liquid), the application of Raoult's Law becomes somewhat more complex. Each component has a certain vapor pressure, which is less than that of the pure substance at the same temperature, and the vapor pressure of the solution is the sum of the vapor pressures of the components. Suppose we have a solution of two volatile liquids, A and B. According to Raoult's Law, the vapor pressure of component A is given by

$$P_A = P_A{}^0 X_A$$

where $P^\circ{}_A$ is the vapor pressure of pure A at the temperature in question and X_A is the mole fraction of A in the solution. Component B also has a vapor pressure, given by

$$P_B = P_B{}^0 X_B$$

The vapor pressure of the solution, then, is equal to $P_A + P_B$.

Problem 10.15

A solution is prepared by mixing 2.0 mol of benzene and 3.0 mol of carbon tetrachloride. The vapor pressure of pure benzene and carbon tetrachloride at 25 °C are 95.5 torr and 115.6 torr, respectively. What is the vapor pressure of the solution at 25 °C?

Solution:

The vapor pressure of the solution is the sum of the vapor pressures of the constituents. The vapor presure of each is given by Raoult's Law.

The mole fraction of benzene in the solution is

$$X = \frac{2.0 \text{ mol } C_6H_6}{(2.0 + 3.0) \text{ mol}} = 0.40$$

Therefore, the vapor pressure of benzene in the solution is

$$P_{C_6H_6} = P^0{}_{C_6H_6} X_{C_6H_6} = 95.5 \text{ torr} \times 0.40 = 38.2 \text{ torr}$$

The mole fraction of carbon tetrachloride is 0.60, and the vapor pressure of CCl_4 is

$$P_{CCl_4} = P^0{}_{CCl_4} X_{CCl_4} = 115.6 \text{ torr} \times 0.60 = 69.4 \text{ torr}$$

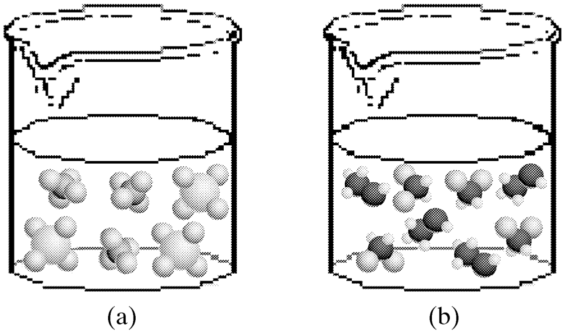
The vapor pressure of the solution, then, is

$$P_{soln} = P_{C_6H_6} + P_{CCl_4} = 38.2 + 69.4 = 107.6 \text{ torr}$$

Raoult's Law should not be considered a precise quantitative statement of the behavior of solutions. A hypothetical solution that would adhere strictly to Raoult's Law under all conditions is called an **ideal solution**; real solutions deviate from Raoult's Law to varying extents. The relationship expressed in Raoult's Law assumes that the solvent-solute attractions are of the same magnitude as the intermolecular attractions in the pure components. Actually, when they are weaker, the molecules of the component substances can escape more easily from solution than they can from the pure substance, and the solution has a higher vapor pressure than is predicted by Raoult's Law. On the other hand, if the solvent-solute attractions are stronger than the attractions between like molecules, then the molecules cannot escape as readily from the solution as from the pure substances, and the solution's vapor pressure is lower than predicted. In general, solutions of nonvolatile solutes in liquids tend to follow Raoult's Law more closely than solutions with more than one volatile component. Also, as solutions become more dilute, the solvent approaches ideal behavior more closely.

Visualization 10.6

In the beakers below are shown molecules of solute and solvent. Which solution is most likely to deviate from ideality?



Solution:

In (a) the molecules are CCl_4 and another tetrachloride, presumably $SiCl_4$. Both are tetrahedral molecules with no dipole moments and only van der Waals forces. In (b) we have a mixture of methanol and dichloromethane. The methanol has hydrogen-bonding, which is a stronger intermolecular force than the dipole-dipole and van der Waals interactions in the CH_2Cl_2. Thus, (b) is most likely to deviate from ideality.

Boiling Point

Since the normal boiling point of a liquid is a function of the liquid's vapor pressure, it is to be expected that the vapor pressure lowering caused by dissolution of a solute in a liquid will bring about a change in the liquid's boiling point. This effect is illustrated in Figure 10.10, where the vapor pressure curve for water is plotted, along with the vapor pressure curve for a solution of sugar in water. The normal boiling point of a liquid is the temperature at which its vapor pressure is equal to 1 atm (760 torr). Since dissolution of sugar in water lowers the vapor pressure of the water at any given temperature, pure water will have a vapor pressure of 1 atm at a *lower* temperature than the sugar solution will. In other words, a solution of a nonvolatile molecular solute in a liquid has a *higher* boiling point than the pure liquid does. This boiling point elevation is shown as ΔT_{bp}.

The quantitative relationship between the boiling point elevation and the concentration of solute is revealed by the following hypothetical experiment. A series of solutions of sugar in water, of various molalities, are prepared, and the boiling point of each solution is

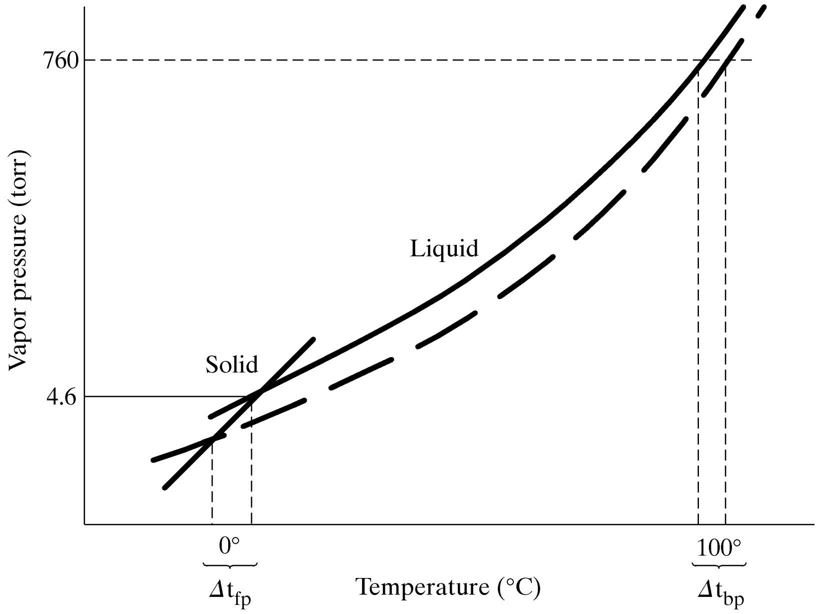


Figure 10.10 The vapor pressure curves for pure water and a sugar solution.

TABLE 10.2 Normal Boiling Points of Ideal Solutions of Various Molalities

MOLALITY	BOILING POINT (°C)
0 (pure H_2O)	100.000
0.1	100.051
0.5	100.256
1.0	100.512
2.0	101.024
3.0	101.536

determined. Assuming all solutions behave ideally, the results will show that the elevation of the boiling point is directly proportional to the molality (Table 10.2). A 1.0 *m* solution has a boiling point that is 0.512 ° higher than that of pure water, a 2.0 *m* solution boils 2 × 0.512 °, or 1.024 °, higher than water, and so on. If the experiment is repeated using any other nonvolatile, nondissociating solute, the results are the same; the boiling point of water is raised by 0.512 °C for each mole of solute per 1,000 g of water. Thus it is the *number* of molecules of solute, not the nature of those molecules, that determines the boiling point elevation. We may express this relationship for water solutions as

$$\Delta T_{bp} = 0.512\, m,$$

where *m* is the molality of the solution.

Other liquids behave the same as water does in this regard, the only difference being the amount by which the boiling point is raised. The relationship between boiling point elevation and concentration for solutions in general is given by the expression

$$\Delta T_{bp} = K_{bp} m$$

where ΔT_{bp} is the number of degrees the boiling point is raised, *m* is the molality of solute in the solution, and K_{bp} is a constant whose value is characteristic of the particular liquid solvent in question. The value of this constant, called the **molal boiling point constant**, is given in Table 10.3 and in Appendix 7 for several common solvents.

TABLE 10.3 Normal Boiling Points and Molal Boiling Point Constants of Some Liquid Solvents

LIQUID	NORMAL BOILING POINT (°C)	K_{bp} (°C-kg/mol)
Acetone	56.5	1.67
Benzene	80.1	2.53
Carbon tetrachloride	76.8	5.02
Chloroform	61.2	3.63
Ethyl alcohol	78.4	1.22
Water	100.0	0.512

Problem 10.16

Predict the boiling point of a solution made by dissolving 20.0 g of quinone ($C_6H_4O_2$) in 100.0 g of acetone.

Solution:

The molecular weight of quinone is 108. The molality of the solution is

$$\frac{20\text{ g quinone}}{108\text{ g/mol quinone}} \times \frac{1000\text{ g/kg}}{100\text{ g acetone}} = 1.85\ m$$

The molal boiling point constant for acetone is 1.67.

$$\Delta T_{bp} = K_{bp}m$$

$$\Delta T_{bp} = 1.67 \times 1.85 = 3.09\ ^\circ\text{C}$$

Since the boiling point of pure acetone is 56.5 °C, and the boiling point elevation is 3.09 °C, the boiling point of the solution will be

$$56.5 + 3.09 = 59.6\ ^\circ\text{C}$$

Freezing Point

Another property of liquids that is related to vapor pressure is the freezing point, for the freezing point is the temperature at which the vapor pressures of the solid and liquid forms of a substance are the same. Referring back to Figure 10.10, note that the vapor pressure curves of the liquid and solid forms of the solvent intersect at the freezing point. However, because the vapor pressure curve of the solution is lower than that of the pure liquid, the intersection occurs at a lower temperature. In other words, dissolving a nonvolatile solute in a liquid causes the resulting solution to have a lower freezing point than that of the pure solvent.

Illustrations of this phenomenon of freezing point lowering are encountered frequently in everyday life. The salt water of the ocean does not freeze at temperatures that freeze bodies of fresh water; we sprinkle salt on ice-covered roads to cause melting; and the water in automobile cooling systems is prevented from freezing by the addition of “antifreeze.” These are all examples of aqueous solutions having lower freezing points than pure water.

Experiments show that freezing point depression and concentration are related quantitatively by an expression very similar to that discussed for boiling point elevation. One mole of solute dissolved in one kilogram of solvent lowers the freezing point of that particular solvent by a constant amount called the **molal freezing point constant**. The value of the constant is different for each solvent but is independent of the nature of the solute, provided the solute is nonvolatile and does not dissociate in solution. Table 10.4 and Appendix 7 list the molal freezing point constants for a number of solvents.

TABLE 10.4 Freezing Points and Molal Freezing Point Constants of Some Solvents

SOLVENT	FREEZING POINT(°C)	K_{fp} (°C-kg/mol)
Acetic acid	16.6	3.90
Benzene	5.5	5.12
Camphor	179.7	39.7
Carbon tetrachloride	−22.8	29.8
Chloroform	−63.5	4.68
Naphthalene	80.2	6.80
Water	0.0	1.86

The expression for freezing point lowering is

$$\Delta T_{fp} = K_{fp} m$$

where ΔT_{fp} is the freezing point depression, K_{fp} is the molal freezing point constant, and m is the molality of the solute in the solution. The application of this relationship in predicting freezing points of solutions is illustrated in Problem 10.17.

Problem 10.17

The compound most commonly used as an automotive antifreeze is ethylene glycol ($HOCH_2CH_2OH$), a water-soluble liquid with relatively low vapor pressure. Assuming that ethylene glycol and water form an ideal solution, what is the freezing point of a 25 wt % solution of ethylene glycol?

Solution:

The solution contains 25 g of ethylene glycol for every 75 g of water. The molecular weight of ethylene glycol is 62, and therefore the molality of the solution is

$$\frac{25\text{ g ethylene glycol}}{62\text{ g/mol ethylene glycol}} \times \frac{1000\text{ g/kg}}{75\text{ g H}_2\text{O}} = 5.38\, m$$

The freezing point depression is

$$\Delta T_{bp} = 1.86 \times 5.38 = 10.0\ ^\circ\text{C}$$

The freezing point of the solution, then, is

$$fp = 0.0 - 10.0 = -10.0\ ^\circ\text{C}$$

Osmotic Pressure

Membranes of certain materials permit the passage of water molecules but not the passage of molecules or ions of solutes dissolved in water. These **semipermeable membranes** include many natural membranes, such as animal and plant cell walls and intestine coverings, as well as some artificial membranes such as parchment paper, cellophane, and certain gelatinous compounds.

An apparatus in which pure water is separated from a sugar solution by a semipermeable membrane is shown in Figure 10.11. At the start, both liquid levels are at the same height, but with the passage of time it is observed that the level of the sugar solution rises, while the level of the pure water falls. This indicates a transfer of water from the pure solvent through the membrane into the solution. This phenomenon is called osmosis (from the Greek, meaning "to thrust"). If sugar solutions are placed on both sides of the membrane, with one of the solutions being more concentrated than the other, water will pass from the less concentrated into the more concentrated solution.

A very simplified explanation of this process is as follows: Water molecules, in their constant, random motion, collide with the semipermeable membrane on both sides.

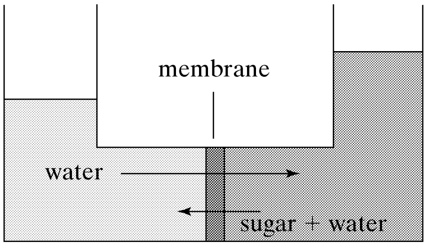


Figure 10.11 Osmosis through a semipermeable membrane.

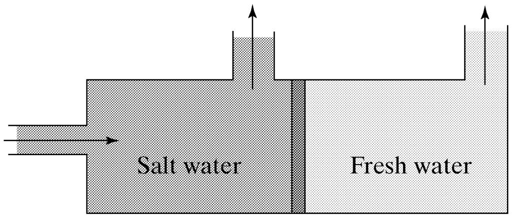


Figure 10.12 A representation of the desalinization of water by reverse osmosis.

However, the rate of these collisions is greater on the pure water (or less concentrated) side than on the solution (or more concentrated) side, simply because the concentration of water molecules is greater in pure water than in the solution. Sugar molecules also collide with the membrane, but these collisions are ineffective because the membrane will not permit the passage of the sugar molecules. The net result is that although water molecules pass through the membrane in both directions, *more* pass through per unit time from the pure water to the solution (left to right in Figure 10.11). Hence, the volume of liquid becomes larger on the right and smaller on the left.

If the open arms of the apparatus above were fitted with pistons, then it would be possible to force water through the membrane in either direction by applying sufficient pressure to the surface of the proper liquid. By applying just the right amount of pressure to the solution (the right side), the osmotic flow of water from left to right would be prevented, and the two liquid levels would be maintained at the same height. The amount of pressure necessary to accomplish this is called the **osmotic pressure** (π) of the solution. Osmotic pressure, like the other colligative properties, is dependent on the number of particles of solute, not on their nature. Like vapor pressure, it is a measure of the tendency of the solvent molecules to escape, but in inverse proportion; the lower the escaping tendency, the greater the osmotic pressure.

Quantitative investigations have shown that the osmotic pressure of a solution is proportional to the molal concentration of the solute. For dilute aqueous solutions, however, the molarity and molality are very nearly the same, and the following relationship has been found to apply:

$$\Pi = \text{Osmotic pressure} = CRT$$

where the osmotic pressure is in atmospheres, C is the concentration in moles per liter, R is the ideal gas constant, and T is the absolute temperature.

Since the walls of living cells are permeable to water and some solutes, but not permeable to others, osmosis is an extremely important process in living organisms. The absorption of soil water by plant roots and the transportation of that water up to the leaves, the passage of nutrients through the intestinal wall into the bloodstream, and the elimination of wastes by passage from the kidney cells into the urine are a few examples of osmosis in life processes.

A potentially valuable application of the phenomenon of osmosis is the production of fresh water from the oceans. If salt water is pumped under pressure into a tank fitted with a semipermeable membrane, water molecules will pass through the membrane, leaving the ions of salt behind (Figure 10.12). Here water is moving from the more concentrated side to the less concentrated side of the membrane because of the high pressure applied to the salt-water side—a process referred to as **reverse osmosis**. Although this technique has been successful on a small scale, large-scale desalinization has not yet become practical, primarily because of the lack of large, long-lasting membranes.

10.6 MOLECULAR WEIGHT DETERMINATIONS

The colligative properties of solutions provide a means of experimentally determining molecular weights. If a solution is prepared from accurately measured weights of solute and solvent and the colligative properties of that solution are measured, one can then calculate the number of moles of solute present. From the weight of solute and the number of moles of solute, it is a simple matter to calculate the weight of one mole, that is, the molecular weight. While any of the colligative properties can be employed for this purpose, osmotic pressure and freezing point can usually be measured more conveniently. The use of freezing point depression is illustrated in Methodology 10.4.

Methodology 10.4

After a sample of compound X weighing 1.286 g was dissolved in 25.00 g of benzene, the freezing point of the resulting solution was found to be 3.27 °C. What is the molecular weight of compound X?

What strategy should we employ to solve this problem?

> We know that a solution has a lower freezing point than that of the solvent and that the extent to which the freezing point is depressed is proportional to the molality of the solution. Once the molality is established, we will know how many moles of the compound are contained in 1000 g benzene. We know that 1.286 g of the compound are dissolved in 25.00 g benzene, and therefore in 1000 g of benzene there are
>
> $$1.286 \times \frac{1000}{25} = 51.44 \text{ g}$$
>
> This mass, then, will be the mass of the number of moles found to be in the solution.

What is ΔT for this solution?

> The freezing point of pure benzene is 5.50 °C. Therefore, the freezing point depression (ΔT_{fp}) is
>
> $$5.50^\circ - 3.27^\circ = 2.23\ ^\circ\text{C}$$

What is the molality of the solution?

> The molal freezing point constant (K_{fp}) for benzene is 5.12 (see Table 10.4). Therefore, the molality of the solution can be calculated as follows:
>
> $$\Delta T_{fp} = K_{fp} \bullet \text{m}$$
>
> $$m = \frac{\Delta T_{fp}}{K_{fp}} = \frac{2.23}{5.12} = 0.436\ m$$

There are, therefore, 0.436 mol in a 1000 g of benzene and this number of moles then weighs 51.44 g. Finally, we must determine the mass of one mole.

$$\frac{51.44 \text{ g}}{0.436 \text{ mol}} = 118 \text{ g/mol}$$

For molecular weight determinations of compounds of very high molecular weight (for example, proteins), the measurement of osmotic pressure provides a more satisfactory method than the measurement of the other colligative properties. This is because solutions of very low molality provide very small changes in freezing point and boiling point, making these changes difficult to measure accurately.

Problem 10.18

A sample of hemoglobin weighing 1.000 g is dissolved in water to make 50.0 mL of solution. The measured osmotic pressure of this solution is 5.90 torr at 25 °C. What is the molecular weight of hemoglobin?

Solution:

Denoting osmotic pressure by π, we can write

$$\pi = CRT = \frac{n}{V} RT$$

Continued on next page

Problem 11.08 *Continued*

Solution: *Continued*

where n is the number of moles of solute and V is the volume of the solution (in liters). But:

$$n = \frac{\text{grams of solute}}{\text{gram-molecular weight of solute}}$$

Therefore:

$$\pi = \frac{gRT}{(\text{mol wt})V}$$

Solving for molecular weight, we obtain

$$\text{Mol wt} = \frac{gRT}{\pi V} = \frac{(1.000\text{ g})\left(0.0821\ \frac{\text{L-atm}}{\text{mol-K}}\right)(298\text{ K})}{\left(\frac{590}{760}\text{ atm}\right)(0.050\text{ L})} = 63{,}000\text{ g/mol}$$

The superiority of osmotic pressure over freezing point depression for very high-molecular-weight substances is easily demonstrated. The aqueous solution of hemoglobin in Problem 11.18 is only about 3×10^{-4} molal:

$$\frac{1.000}{63{,}000} \times \frac{1000}{50} = 0.00032\ m$$

This corresponds to a freezing point depression of only 0.00059 °C:

$$\Delta T_{fp} = 1.86 \times 0.00032 = 0.00059\ ^\circ\text{C}$$

Although such a small temperature change is extremely difficult to measure, a column of mercury 5.9 mm in height is relatively easy to measure.

10.7 SOLUTIONS OF ELECTROLYTES

The structural and electrical characteristics of the water molecule give this liquid the capability of dissolving a large number of ionic and polar covalent substances. This, together with its great abundance, gives water a unique position among liquid solvents, and the nature of *aqueous* solutions deserves special emphasis.

It was recognized as early as the eighteenth century that water-soluble substances could be divided into two categories: those whose aqueous solutions conduct electric current and those whose aqueous solutions do not. The former are known as **electrolytes**; the latter are called **nonelectrolytes**. These two types of solutes may be distinguished experimentally by use of an apparatus such as that shown schematically in Figure 10.13. Two metallic electrodes are connected to a source of electricity, and some device for detecting the flow of electric current is placed in the circuit. This may be an ammeter or simply a light bulb or buzzer. When the electrodes are suspended in air, no current flows, since air is a nonconductor. Similarly, if the electrodes are immersed in pure water, there is still no flow of current, indicating that water also is not an electrical conductor. Now, when a solute is dissolved in the water, the resulting solution may or may not be a conductor. If the solute is an electrolyte, then the solution will conduct, as indicated by a flow of current through the circuit. But if the solute is a nonelectrolyte, no current will flow.

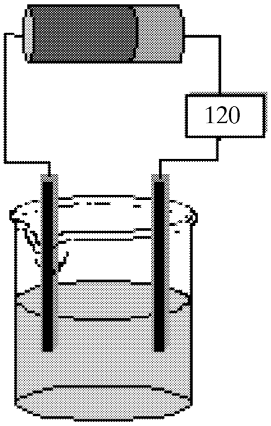


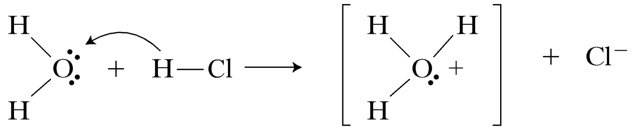
Figure 10.13 A simple apparatus to determine conductivity.

The search for an explanation of the conductivity of electrolytic solutions led Svante Arrhenius, a Swedish chemist and physicist, to formulate his **theory of electrolytic dissociation** in 1887. This theory has been modified considerably over the years as a result of increased knowledge of chemical bonding. Today we recognize that in order for a solution to conduct electricity, it must contain ions. Whereas the conductivity of an electric current by a metal is explained by the motion of the loosely bound electrons of the metallic crystal, the conductance of current by a solution—called **electrolytic conductance**—is accomplished by the motion of ions. Positive ions (cations) move through the solution toward the negative electrode (cathode), and negative ions (anions) move toward the positive electrode (anode). Although the phenomenon of electrolytic conductance involves more than just the motion of ions (as we shall see in Chapter 18), the presence of ions that are free to move is essential for the conductance of electric current by a solution. An electrolyte, then, is a substance whose aqueous solution contains ions; solutions of nonelectrolytes do not contain ions.

Classification of Electrolytes

Electrolytes may be divided conveniently into three types of compounds: acids, bases, and salts. (Compounds that do not fit into any of these categories are therefore nonelectrolytes, and include hydrocarbons, alcohols, esters, ethers, aldehydes, ketones, and so on.) There are several useful ways of defining acids, bases, and salts, depending on the purpose at hand; these various concepts will be treated at length in subsequent chapters. For our present purpose, it will be adequate to use those definitions that have been derived from the Arrhenius theory of electrolytic dissociation.

Acids are compounds that react with water to produce **hydronium ions**. These ions, generally symbolized by the formula H_3O^+, may be thought of as hydrated protons. By way of illustration, consider the compound hydrogen chloride (HCl), a covalent compound that consists of discrete molecules and exists as a gas at standard temperature and pressure. The bond between the atoms has only about 20% ionic character. However, if HCl is dissolved in water, a reaction occurs, during which the proton is transferred from the HCl molecule to a water molecule. The chlorine atom left after removal of the proton has one more electron than its normal complement and is therefore a chloride ion.



$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

Thus, while neither HCl nor H_2O alone conducts current, a solution of HCl in H_2O contains ions and is a conductor. Hydrogen chloride, therefore, is an electrolyte. Sometimes, for convenience, the water is omitted, and the equation representing this reaction is written simply as

$$HCl \longrightarrow H^+ + Cl^-$$

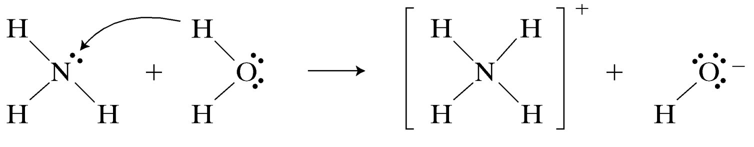
All acids, including the hundreds of known carboxylic acids, react with water in an analogous way; therefore, all acids are electrolytes.

Bases are compounds that dissolve in water to form hydroxide ions (OH^-). This group of compounds includes all the hydroxides: NaOH, $Ca(OH)_2$, and so on.

$$NaOH \longrightarrow Na^+ + OH^-$$

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2\,OH^-$$

It also includes some other compounds that do not themselves contain hydroxide ions but react with water to form these ions. Notable among these compounds are ammonia and its derivatives, the amines.



$$NH_3 + H_2O \longrightarrow NH_4{}^+ + OH^-$$

When a solution of an acid and a solution of a base are mixed together, a chemical reaction occurs in which the hydronium ion and the hydroxide ion combine to form molecules of water. This reaction is called **neutralization**.

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O$$

The anion of the acid and the cation of the base remain in solution, and if water is removed by evaporation, a compound of these two ions is obtained. This type of compound, which may be thought of as consisting of the anion of an acid and the cation of a base, is called a **salt**. Some neutralizations and the salts that are formed are illustrated in the following "molecular" equations:

$$\underset{\text{acid}}{HNO_3} + \underset{\text{base}}{NaOH} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\text{salt}}{NaNO_3}$$

$$\underset{\text{acid}}{H_2SO_4} + \underset{\text{base}}{KOH} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\text{salt}}{KHSO_4}$$

$$\underset{\text{acid}}{2\,CH_3COOH} + \underset{\text{base}}{Ca(OH)_2} \longrightarrow \underset{\text{water}}{2\,H_2O} + \underset{\text{salt}}{Ca(CH_3COO)_2}$$

Most salts are ionic compounds, and when ionic crystals dissolve in water, they are present in the solution as hydrated ions. Salts, therefore, are electrolytes, and their aqueous solutions conduct electricity.

Although they contain neither hydrogen nor hydroxide ions, the oxides of many elements are nevertheless electrolytes, for they undergo reactions with water to produce ions in aqueous solution. In general, the water-soluble oxides of nonmetallic elements dissolve in water to produce hydronium ions and may therefore be considered acids. This can be illustrated with sulfur dioxide and carbon dioxide, as follows:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + H_2O \longrightarrow H_3O^+ + HSO_3^-$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 + H_2O \longrightarrow H_3O^+ + HCO_3^-$$

In fact, many nonmetallic oxides show this relationship to specific acids. These oxides may be thought of as resulting from the removal of water from their corresponding acids, and are therefore called **acid anhydrides**. A number of common acids and their anhydrides are listed in Table 10.5.

The water-soluble oxides of metals, on the other hand, dissolve in water with the production of hydroxide ions and may therefore be considered bases.

$$\underline{CaO} + H_2O \longrightarrow Ca^{2+} + 2\,OH^-$$

$$\underline{Na_2O} + H_2O \longrightarrow 2\,Na^+ + 2\,OH^-$$

TABLE 10.5 Some Common Acids and Their Anhydrides

ACID − WATER	= ANHYDRIDE
$H_2SO_3 - H_2O$	$= SO_2$
$H_2SO_4 - H_2O$	$= SO_3$
$H_2CO_3 - H_2O$	$= CO_2$
$2\,HNO_2 - H_2O$	$= N_2O_3$
$2\,HNO_3 - H_2O$	$= N_2O_5$
$2\,HClO_4 - H_2O$	$= Cl_2O_7$
$2\,H_3PO_3 - 3\,H_2O$	$= P_2O_3$
$2\,H_3PO_4 - 3\,H_2O$	$= P_2O_5$

TABLE 10.6 Some Bases and Their Anhydrides

BASE − WATER	= ANHYDRIDE
$2\ NaOH - H_2O$	$= Na_2O$
$Ca(OH)_2 - H_2O$	$= CaO$
$Ba(OH)_2 - H_2O$	$= BaO$
$Zn(OH)_2 - H_2O$	$= ZnO$
$2\ Al(OH)_3 - 3\ H_2O$	$= Al_2O_3$

For the same reason that oxides of nonmetals are called acid anhydrides, oxides of the metals are called **basic anhydrides**; that is, they may be thought of as resulting from the removal of water from a hydroxide base, as illustrated in Table 10.6.

Strength of Electrolytes

Equivalent solutions of all electrolytes are not equally good conductors of electricity. Suppose, for example, we prepare three aqueous solutions: One is 1 *m* HCl, another is 1 *m* $HC_2H_3O_2$, and the third is 1 *m* HCN. Each of these solutions is acidic because the solute reacts with water to produce hydronium ions and anions, according to the following general equation:

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

Moreover, all three of the solutions are of the same concentration. We might expect, therefore, that each of the three will conduct electric current equally well. If, however, we test their conductance, the ammeter tells us that the HCl solution is a better conductor than the $HC_2H_3O_2$ solution, and that the $HC_2H_3O_2$ solution is, in turn, a better conductor than the HCN solution. Since the ability of a solution to conduct electricity is a function of the number of ions present, the difference in conductance of the three solutions suggests that they contain different numbers of ions, in spite of the fact that each was prepared by dissolving 1 mole of solute in 1,000 g of water.

In order to understand this difference in conductance, we must realize that (1) the reaction between the acid and water to produce ions is reversible, and (2) other things being equal, the *rate* of a reaction is proportional to the concentration of the reactants. Thus, if HX can react with H_2O to produce H_3O^+ and X^-, then H_3O^+ and X^- can also react with each other to produce HX and H_2O. This reversible reaction can be represented as

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

When molecules of HX are dissolved in water, their concentration is high at first, and the reaction producing the ions (the one going to the right in the above equation) occurs at a relatively high rate. This rate gradually decreases, however, as HX is consumed and its concentration decreases. The rate of the reaction that moves to the left, on the other hand, begins at zero and gradually increases as more and more ions are formed. Eventually the two rates must become equal, and a state of equilibrium is reached. Thus, the reaction of an acid with water does not lead to its complete conversion into ions. An aqueous solution of HX contains H_3O^+ and X^-, but it also contains undissociated molecules of HX.

The extent to which an electrolyte solution contains ions—and therefore the degree to which it conducts electric current—varies widely and depends on the **position** of the equilibrium. In the case of HCl, the equilibrium position lies far in the direction favoring ion production; in $HC_2H_3O_2$, the equilibrium mixture contains many more undissociated molecules of acid and fewer ions; and the HCN equilibrium contains even fewer ions. In other words, the HCl solution is the best conductor because it contains the most ions, and the HCN solution is the poorest conductor because it contains the fewest ions. The extent to which an electrolyte yields ions in aqueous solution is referred to as its **strength**. Thus, of the three electrolytes considered in our illustration, HCl is the strongest, $HC_2H_3O_2$ is intermediate in strength, and HCN is the weakest.

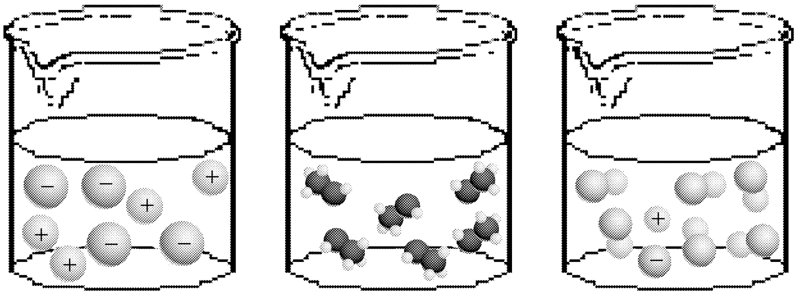
Since the relative strengths of electrolytes vary over a wide range, it is often convenient to divide electrolytes qualitatively into two categories: strong and weak. An electrolyte that is so greatly dissociated into ions in aqueous solution that, for all practical purposes, the dissociation may be considered complete is by definition a **strong electrolyte**. All others are **weak electrolytes**. Hence, a solution of the strong electrolyte nitric acid (HNO_3) may be considered to contain only H_2O, H_3O^+, and NO_3^-, with no molecules of HNO_3. But the weak electrolyte nitrous acid (HNO_2) contains HNO_2 molecules as well as H_2O, H_3O^+, and NO_2^-.

In recognizing which common electrolytes are strong and which are weak, the following generalizations are useful:

Acids:	HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 are strong electrolytes. Nearly all other acids are weak.
Bases:	The hydroxides of the Group IA metals and the Group IIA metals (except Be) are strong electrolytes. Most other hydroxides, the compound NH_3, and the amines are weak.
Salts:	Nearly all common salts are strong electrolytes. A few, such as the halides of Zn, Cd, and Hg(II), are weak.

Visualization 10.7

Classify the following aqueous solutions as nonelectrolytes, weak electrolytes, or strong electrolytes. The water molecules are not shown.



(a) (b) (c)

Solution:

(a) strong electrolyte
(b) nonelectrolyte
(c) weak electrolyte (only a small fraction of the molecules have dissociated to form ions).

Check Point 10.2

How would you classify CO_2?

Solution:

weak electrolyte

◇ ◇ ◇ ◇ ◇

Colligative Properties of Electrolytic Solutions

The previous discussion of the colligative properties of solutions was confined to those solutions in which the solute remains undissociated, so that the number of dissolved particles is directly proportional to the number of moles of solute used. When the solute is an electrolyte, the formation of ions results in a higher concentration of particles than the concentration based on the number of moles of solute dissolved, and the quantitative application of colligative properties becomes more complex. For example, suppose we prepare a 1 *m* solution of the weak electrolyte HX by dissolving exactly 1 mol of HX in exactly 1 kg of water. The solute, upon dissolving, reacts with water to form ions, and a state of equilibrium is reached between the undissociated molecules and the ions:

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

The equilibrium concentration of undissociated HX is less than 1 molal, but for each molecule dissociated, two ions have been formed. Since the concentration of solute particles is the sum of the concentrations of HX, H_3O^+, and X^-, the molality of the particles is greater than one. As a result, the freezing point of this solution will be lowered more than 1.86 °C and the boiling point will be raised more than 0.512 °C. Similarly, the vapor pressure will be lowered by an amount greater than is predicted by Raoult's Law, and the osmotic pressure will also be greater than predicted. The extent to which the colligative properties are affected by dissociation depends on the degree to which dissociation occurs for the specific electrolyte in question; that is, it depends on the strength of the electrolyte. In fact, the degree of dissociation of an electrolyte can be estimated by measuring the colligative properties of its solutions, as illustrated in Problem 10.19.

Problem 10.19

A 1.00 *m* solution of the weak acid HX in water has a freezing point of −2.05 °C. What is the degree of dissociation of the acid in this solution?

Solution:

The relationship between the freezing point lowering and the concentration for an aqueous solution is:

$$\Delta T_{fp} = 1.86\, m$$

Since the freezing point of this solution has been lowered 2.05°, we can calculate the molality of the total number of particles in the solution.

$$2.05 = 1.86\, m$$

$$m = \frac{2.05}{1.86} = 1.10\, m \text{ (total number of particles)}$$

If we now let x equal the number of moles of acid dissociated at equilibrium, then the molal concentrations of the various particles are as follows:

$$\underset{(1-x)}{HX} + H_2O \rightleftharpoons \underset{(x)}{H_3O^+} + \underset{(x)}{X^-}$$

and the molality of the total number of particles is

$$(1 - x) + x + x = 1 + x$$

Therefore:

$$1 + x = 1.10$$

and

$$x = 1.10 - 1 = 0.10$$

Thus, of the number of moles of HX dissolved in the solution, one-tenth are dissociated at equilibrium. In other words, the electrolyte is 10% dissociated.

On the basis of the foregoing discussion, one might logically conclude that dissolution of a strong electrolyte (one that is known to be 100% in ionic form) such as NaCl would have exactly twice the effect on colligative properties that a nondissociated solute

TABLE 10.7 Freezing Points (Actual and Predicted) of 0.1 *m* Solutions of Some Electrolytes

ELECTROLYTE	NUMBER OF IONS	PREDICTED FREEZING POINT	ACTUAL FREEZING POINT
NaCl	2	−0.372	−0.348
NaOH	2	−0.372	−0.348
$MgCl_2$	3	−0.558	−0.494
K_2SO_4	3	−0.558	−0.432
$K_3[Fe(CN)_6]$	4	−0.744	−0.530

has. Since a 1 *m* solution of NaCl is 2 *m* in ions (1 *m* in Na^+ and 1 *m* in Cl^-), one would expect the freezing point to be lowered 2 × 1.86°, or 3.72 °C, and the boiling point to be raised 2 × 0.512°, or 1.024 °C. Similarly, a salt such as $BaCl_2$, which yields three moles of ions per mole of compound, would be expected to lower the freezing point 3 × 1.86°, or 5.58 °C, and so forth.

Experiment reveals, however, that while these strong electrolytes do affect colligative properties to an extent close to that predicted on the basis of the number of ions, the effect is always less than the whole-number multiple expected. This is demonstrated in Table 10.7, where the experimentally determined freezing points of 0.1 *m* aqueous solutions of several strong electrolytes are compared with the predicted freezing points. The same relationship holds for the other colligative properties as well. The differences between the measured colligative properties of strong electrolyte solutions and the predicted whole-number values decrease as the solutions become more dilute, as illustrated in Table 10.8.

The deviations exhibited by ionic solutes may be explained as follows: Because of the electrical charges on ions, each ion tends to be attracted to ions of opposite sign. These interionic attractions restrain the ions somewhat in their freedom of motion, so that they are not as independent of one another as uncharged molecules in solution. The result is that the effectiveness of the ions is decreased, and the solution behaves as if there were fewer particles present. As a solution becomes more dilute, the ions are spread farther and farther apart, so that their influence on one another decreases. In extremely dilute solutions, the ions behave essentially independently. This explanation is a very simplified version of what is known as the **Debye-Hückel Theory.**

TABLE 10.8 Observed Freezing Point Depressions Compared with Calculated Values of Some NaCl Solutions

MOLAL CONCENTRATION	FREEZING POINT DEPRESSIONS	
	OBSERVED (°C)	CALCULATED (°C)
1	3.46	3.72
0.1	0.348	0.372
0.01	0.0360	0.0372
0.001	0.00366	0.00372

10.8 COLLOIDS

The statement has been made earlier in this chapter that the fundamental difference between homogeneous mixtures (solutions) and heterogeneous mixtures lies in the *size* of the dispersed particles. In a true solution the dispersed particles of solute are individual molecules or ions, and these submicroscopic particles will not "settle out" no matter how long the solution is kept standing. In a heterogeneous mixture, on the other hand, the particles are relatively large aggregates of atoms, visible under a microscope, if not to the naked eye, and large enough to be separated by gravity. Thus, for example, if fine sand is shaken with water, the sand particles will remain distributed throughout the water for only a short period of time; they will quickly "settle out." This mixture obviously consists of two distinguishable phases.

There is a type of mixture intermediate between these two extremes, wherein the dispersed particles are considerably larger than most molecules, yet not large enough to be visible or to be separated by gravity. These mixtures are called **colloidal dispersions**, or simply **colloids**.

It is not possible to state precisely the range of particle sizes that represents colloidal dispersions, but this range is generally considered to be between about 1 nm and 500 nm in diameter. Most molecules have diameters of less than 1 nm, and particles larger than 500 nm can be seen under an ordinary microscope and usually do not remain colloidally dispersed. It should be noted that the size of the particle does not define its makeup. Colloidal particles may be aggregates of atoms, ions, or molecules; in the case of some very large molecules, such as starch, proteins, and other polymers, they also may be single molecules.

Although colloidal particles are too small to be visible to the naked eye, they are large enough to reflect light, a fact that can sometimes be used to distinguish between colloids and true solutions. When a narrow beam of bright light is directed through a colloidal dispersion, the dispersed particles will scatter the light; the path of the light beam can be observed by viewing the system at right angles to the beam. This phenomenon has been named the **Tyndall effect**, after its discoverer, the English physicist John Tyndall. A true solution does not display this effect because the dispersed solute particles are too small to reflect light from their surfaces.

Colloids can be classified into several different types, the most important of which are aerosols, emulsions, sols, and gels. An **aerosol** is a dispersion of either a solid or a liquid in a gas. Smoke is a common example of the former; clouds, mists, and fogs are examples of the latter. Many commercial aerosol sprays, such as insecticides, deodorants, and hair sprays, are colloidal dispersions of liquids in air.

Emulsions are colloids in which one liquid is dispersed in another liquid. Milk, cream, and mayonnaise are examples of fats or oils dispersed in water. Colloidal dispersions of liquids in solids are sometimes called **solid emulsions**. Examples include pearls, which are suspensions of water in $CaCO_3$, and opals, which are suspensions of water in SiO_2.

A colloidal dispersion of a solid in a liquid is called a **sol**. The dispersed particles may be fragments of the crystalline lattice of the solid—as in colloidal dispersions of gold, sulfur, and silver iodide in water—or they may be single, large molecules such as starch, protein, and gums.

Gels are somewhat different from the other types of colloids in that both phases are continuous. A solid is arranged in a fine network, interlacing a liquid. Jellies, gelatin desserts, and gelatinous precipitates are common examples of gels.

The properties of colloids are more complex and more difficult to quantify than the properties of true solutions. In general, solid-in-liquid colloids have vapor pressures, boiling points, and freezing points that differ very little from those of the pure solvents. The colligative relationships that have been discussed for solutions do not apply to colloidal dispersions.

CHAPTER SUMMARY

This chapter has dealt with the following major topics:

1. **The general process of solution formation, including the rate of solution, solubility, and the energetics of the solution process**. You should master the terminology introduced and achieve a thorough understanding of the forces involved and the various factors that influence both solution rate and solubility. (Be sure that you can distinguish between rate of solution and solubility.) Since the concept of solubility involves equilibrium, you may find it helpful to

review the discussion of vapor pressure in Chapter 8. Also, in studying the energetics of solution, you might review the concepts of enthalpy, entropy, and free energy in Chapter 9.

2. **Concentrations of solutions.** You should be thoroughly familiar with the various ways of expressing concentration—weight percentage, volume percentage, parts per million, molarity, molality, and mole fraction—and you should be able to apply their mathematical relationships to solve a variety of problems.
3. **Colligative properties: vapor pressure, boiling point, freezing point, and osmotic pressure.** The relationships between these properties and concentration will enable you to solve various types of useful problems, including the experimental determination of molecular weights. Be sure that you understand and can apply these calculations.
4. **Electrolytic solutions.** Substances can be divided into two categories, electrolytes and nonelectrolytes, based on whether or not their aqueous solutions contain ions. Electrolytes, whose aqueous solutions do contain ions, are of three types: acids, bases, and salts. Although these compounds and their reactions with one another will be covered in detail in later chapters, it is important that you learn this classification now and that you understand the difference between **strong** and **weak electrolytes**.

TERMS

Following are some of the important terms introduced in this chapter:

Saturated solution A solution in which the dissolved solute is in equilibrium with the undissolved solute. A solution that contains less solute than the equilibrium amount is **unsaturated**; a solution that contains more solute than the equilibrium amount is **supersaturated**.

Ion-dipole attraction The attractive force between an ion and a polar molecule.

Solvation The attachment of solvent molecules to ions or to molecules of the solute. If the solvent is water, the term **hydration** is used.

Solubility A description of the composition of a saturated solution. Solubility is usually expressed in terms of the amount of dissolved solute in a given amount of solvent or as the amount of solute in a given amount of solution.

Le Châtelier's Principle If a stress is applied to a system in equilibrium, the system will readjust in such a way as to relieve the stress and establish a new equilibrium state. Stated alternatively, if the conditions of a system in equilibrium are changed, the process that tends to restore the original conditions will be favored.

Henry's Law The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution.

Molality (m) The number of moles of solute per kilogram of solvent.

Mole fraction The mole fraction of one component of a solution is the ratio of the number of moles of that component to the total number of moles of all the constituents of the solution.

Colligative properties Those properties of solutions that depend only on the number of solute particles and not on the nature of the solute. Specifically, these properties are vapor pressure, boiling point, freezing point, and osmotic pressure.

Raoult's Law The vapor pressure (P) of a volatile component of a solution is equal to the product of the mole fraction (X) of that component and the vapor pressure of the pure component (P^0) at the same temperature, or $P = P^0 X$. If the solution contains more than one volatile component, then each of those components has a vapor pressure in accordance with Raoult's Law ($P_A = P_A{}^0 X_A$; $P_B = P_B{}^0 X_B$; and so on), and the vapor pressure of the solution is the sum of the vapor pressures of all its volatile components ($P = P_A + P_B + \cdots$).

Ideal solution A hypothetical solution that would adhere strictly to Raoult's Law under all conditions.

Molal boiling point constant (K_{bp}) The elevation in the boiling point (°C) of a given solvent produced by the presence of one mole of solute per kilogram of solvent, assuming an ideal solution. This relationship is expressed as DTbp 5 Kbpm. Each solvent has its own specific Kbp.

Molal freezing point constant (K_{fp}) The number of degrees Celsius that the freezing point of a solvent is lowered by the presence of one mole of solute per kilogram of solvent, or $\Delta T_{fp} = K_{fp}m$.

Semipermeable membrane Any membrane that permits the passage of water molecules but does not permit the passage of molecules or ions of solutes dissolved in the water.

Osmosis The process whereby water molecules pass from a less concentrated solution through a semipermeable membrane into a more concentrated solution.

Osmotic pressure A measure of the tendency for osmosis to occur in a given system. Osmotic pressure is the pressure that would have to be applied to the solution on the more concentrated side of the membrane to prevent osmosis from occurring. Osmotic pressure is related to the concentration in moles per liter (C), to the ideal gas constant (R), and to the absolute temperature (T) by the expression, **osmotic pressure** $= CRT$.

Electrolyte Any substance that, when dissolved in water, yields a solution that conducts electric current. This electrical conductivity is due to the presence of ions in the solution. Any substance whose aqueous solution does not conduct electric current is called a **nonelectrolyte**. Electrolytes are of three types: acids, bases, and salts. They may also be classified as **strong** and **weak**. Strong electrolytes are so greatly dissociated into ions in aqueous solution that the dissociation may be considered complete. All other electrolytes are classified as weak.

Acids, bases, and salts *Acids* are compounds that react with water to produce hydronium ions (H_3O^+). **Bases** are compounds that dissolve in water to form hydroxide ions (OH^-). **Salts** are compounds that consist of the cation of a base and the anion of an acid. These definitions, based on the **Arrhenius theory of electrolytic dissociation**, apply only to aqueous solutions.

Neutralization A reaction between an acid and a base.

Acid anhydride An oxide of a nonmetallic element, which may be thought of as resulting from the removal of water from an acid. For example, SO_2 is the anhydride of H_2SO_3; N_2O_5 is the anhydride of HNO_3, and so on.

Basic anhydride An oxide of a metallic element that results from the removal of water from a base. (For example, Na_2O is the anhydride of NaOH; CaO is the anhydride of $Ca(OH)_2$.)

Colloid A mixture in which the dispersed particles are too large to yield a true solution yet too small to be visible or to "settle out." Some types of colloids are aerosols, emulsions, gels, and sols.

PROBLEMS

1. Indicate clearly the difference between the terms in each of the following pairs:
 (a) solute and solvent
 (b) solubility and rate of solution
 (c) saturated solution and unsaturated solution
 (d) molarity and molality
 (e) electrolyte and nonelectrolyte
 (f) strong electrolytes and weak electrolytes
 (g) acid anhydrides and basic anhydrides
 (h) solution and colloid

2. Predict whether each of the following compounds will have greater solubility in water or in benzene:
 (a) potassium nitrate
 (b) butanone
 (c) ethyl ether
 (d) oxalic acid
 (e) n-hexane
 (f) iodine
 (g) chloroform (trichloromethane)

3. The solubility of pure N_2 in water at a pressure of one atmosphere and a temperature of 30 °C is 0.0162 g/L. If dry air is bubbled through one liter of water at a temperature of 30 °C and a pressure of 742 torr, what weight of N_2 will dissolve in the water? [air is 78.09 volume % N_2]

4. From the following thermodynamic data (at 25 °C), calculate the free energy of solution for silver fluoride and for silver chloride at 25 °C. On the basis of your answers, comment on the relative solubilities of the two compounds.

For AgF: Lattice energy = 967 kJ/mol
 Heat of hydration = 987 kJ/mol
 Entropy of solution = −19.8 J/mol-K
For AgCl: Lattice energy = 918 kJ/mol
 Heat of hydration = 852 kJ/mol
 Entropy of solution = +31.7 J/mol-K

5. If 100 g of ammonium nitrate are dissolved in 100 mL of water contained in a beaker sitting in a pan of water, ice will form on the outside of the beaker. Explain.

6. In how many grams of H_2O must 25.0 g of NaCl be dissolved to yield a 10.0 wt % solution?

7. A solution is found to contain 42.5 ppm of riboflavin. How many grams of riboflavin are there in 25.0 g of the solution?

8. Assume that 5.00 mL of ethanol are dissolved in enough water to make 1.00 L of solution. Express the concentration in terms of (a) volume percentage and (b) parts per million by volume.

9. If 1.50 g calcium nitrate are dissolved in 20.0 mL of solution, what is the molarity of the solution?

10. How many milliliters of water must be added to 100 mL of 3.0 M HCl in order to make a solution that is 0.65 M HCl?

11. Explain how you would prepare each of the following aqueous solutions:
 (a) 1.00 L of 0.50 *M* KNO_3 solution from solid KNO_3
 (b) 250 mL of 0.25 *M* NaCl solution from a 1.0 *M* NaCl stock solution
 (c) 500 mL of a solution that is 0.15 *M* in Cl_2 from solid $CaCl_2 \cdot 2H_2O$
 (d) At least 1 L of 0.50 *M* $NaC_2H_3O_2$ from solid $NaC_2H_3O_2$
 (e) At least $\frac{1}{2}$ L of a 15 wt % solution of NaOH from solid NaOH

12. What is the molarity of water at 25.0 °C if its density is 0.997 g/mL?

13. What weight of metal ion is contained in each of the following aqueous solutions?
 (a) 100 mL of 0.20 *M* $AgNO_3$
 (b) 20 mL of 0.75 *M* $CuSO_4$
 (c) 3.0 L of 1.2×10^{-3} *M* $MgCl_2$
 (d) 500 mL of a 5.0 wt % $Hg(NO_3)_2$ solution, which has a density of 1.06 g/mL

14. Tell how to prepare each of the following test solutions with concentrations of 1.0 mg metal ion per milliliter of solution.
 (a) 500 mL $AgNO_3$ from 0.5 *M* $AgNO_3$ solution
 (b) 500 mL $AgNO_3$ from solid $AgNO_3$
 (c) 1 L $CuSO_4$ from solid $CuSO_4 \cdot 5H_2O$
 (d) 1 L $CuSO_4$ from 0.05 *M* $CuSO_4$ solution
 (e) 250 mL $AlCl_3$ by dissolving solid Al in HCl
 (f) 2 L Na_2CO_3 from solid Na_2CO_3

15. Commercial concentrated hydrochloric acid contains 36.5 wt % HCl and has a density of 1.185 g/mL. Express the concentration of this solution in terms of the (a) molarity, (b) molality, and (c) mole fraction of HCl.

16. A 9.00 wt % stock solution of potassium hydroxide has a density of 1.082 g/mL. How would you prepare 1 L of a 1.0 *M* solution of KOH from the stock solution?

17. A solution of 1.86 *M* sulfuric acid has a density of 1.115 g/mL. Calculate the molality of the solution.

18. A solution was prepared by dissolving 4.35 g of $CaCl_2$ in 75.0 g of distilled water. The density of the solution was 1.05 g/mL.
 (a) What is the weight % concentration of calcium chloride in this solution?
 (b) What is the molarity (M) of this solution?
 (c) What is the mole fraction of calcium chloride in the solution?

19. Sodium carbonate is a base which is sold commercially as an aqueous solution that is 10.0% sodium carbonate by mass. The solution has a density of 1.10 g/mL. The density of water is 0.997 g/mL. Determine its concentration in the following units:
 (a) solubility (g/100 g)
 (b) g/L
 (c) mole fraction
 (d) molarity
 (e) molality

20. Calculate the percentage composition by weight of nitric acid in a 2.0 *M* HNO_3 solution.

21. How many milliliters of 47.0% hydrobromic acid (density 1.50 g/mL) are needed to prepare 1 L of a 0.156 *M* solution?

22. The solubility of oxygen in water at 25 °C and 1 atm is 0.0393 g per liter of solution. What is the molarity of a saturated aqueous solution of oxygen at this temperature and pressure?

23. A solution is prepared by dissolving 25.0 g of methanol (CH_3OH) in 100 g of water. Express the concentration of this solution as the (a) weight percentage, (b) molality, and (c) mole fraction of methanol.

24. The solubility of $CaSO_4$ in water at 10 °C is 1.063 g per liter of solution. Calculate the molarity of a saturated $CaSO_4$ solution of 10 °C.

25. A 20.0 wt % solution of $Na_2S_2O_3$ in water has a density of 1.10 g/mL. Calculate (a) the molarity and (b) the molality of the solution.

26. A mixture of 60.0 g of chloroform and 80.0 g of carbon tetrachloride is prepared. Calculate the mole fraction of each constituent of the resulting solution.

27. At 20°C the solubility of lead chloride is 0.99 g per 100 mL of solution. At 100 °C the solubility is 3.14 g per 100 mL of solution.
- (a) Calculate the molarity of saturated solutions of $PbCl_2$ at the two temperatures.
- (b) Is the solution process endothermic or exothermic?

28. An aqueous solution contains 20.0% HCl and has a density of 1.05 g/mL.
- (a) Calculate the molarity of this solution.
- (b) Calculate the molality of this solution.
- (c) Calculate the mole fraction of the HCl in this solution.
- (d) Calculate the volume of this solution that should be used to make 500 mL of a 0.20 M HCl solution.
- (e) Calculate the weight of the solution required to react with 10 g Na_2CO_3 to produce H_2CO_3 and NaCl.

29. Calculate the vapor pressure at 25 °C of an aqueous solution containing 100 g of glycerine ($C_3H_8O_3$) in 150 g of water. The vapor pressure of pure water at 25 °C is 23.8 torr. (Assume glycerine to be nonvolatile.)

30. A commercial de-icer spray that you may have used on your car's windshield contains ethyl alcohol. How does it work?

31. Methanol is sometimes used as an antifreeze. Calculate (a) the number of moles and (b) the number of grams of methanol that must be added to 10.0 L of water to lower the freezing point to −10.0 °C.

32. The alcohol content of whiskey is often measured in units of proof. The proof of an alcoholic liquid is twice the volume percent of ethanol it contains. Thus, 100 proof is 50% ethanol by volume. Given that the densities of pure ethanol and pure water are 0.789 g/mL and 0.997 g/mL, respectively, at 25 °C, calculate the vapor pressure of 90 proof whiskey at 25 °C. At this temperature the vapor pressures of pure ethanol and pure water are 65.0 torr and 23.8 torr, respectively.

33. A solution of an unidentified nonelectrolyte was prepared by dissolving 0.125 g of the compound in enough water to make 250.0 mL of solution at 15 °C. The osmotic pressure of the solution was 12.8 torr. What is the molecular weight of the unknown compound?

34. Calculate the temperature at which a solution of antifreeze ($C_2H_6O_2$ dissolved in water) will freeze if its concentration is 46% $C_2H_6O_2$ by mass, $K_f = 1.86$ °C·kg/mol.

35. A solution was prepared by dissolving 2.35 g of CCl_4 in 15.0 g of cyclohexane at room temperature. The freezing point of this solution was −14 °C. The melting point of cyclohexane is 6 °C. Determine K_f for cyclohexane.

36. Explain the fact that freshly boiled water freezes at a higher temperature than unboiled tap water.

37. A solution of 4.785 g of mercury(II) chloride in 60 g of water is found to boil at 100.152 °C. Is mer-cury(II) chloride dissociated in water solution?

38. A certain nonvolatile, molecular compound has a molecular weight of 75.2. If 1.00 g of this compound is dissolved in 10.00 g of pure benzene, what is the vapor pressure of the solution at 25 °C? (The vapor pressure of pure benzene at 25 °C is 95.5 torr.)

39. At 23 °C the vapor pressures of chloroform and carbon tetrachloride are 178 torr and 100 torr, respectively. Calculate the vapor pressure of the solution in Problem 20.

40. A solution is prepared by dissolving 10 g of solid *para*-dichlorobenzene ($C_6H_4Cl_2$) in enough carbon tetrachloride to make a total of 350 mL of solution. The density of the resulting solution is 1.60 g/mL.
- (a) Calculate the molarity of the solution.
- (b) Calculate the weight percent *para*-dichlorobenzene of the solution.
- (c) Calculate the molality of the solution.
- (d) Calculate the mole fraction of the solute.
- (e) At 23 °C the vapor pressure of CCl_4 is 100 mm. Calculate the vapor pressure of the solution at this temperature.
- (f) When a different solution of $C_6H_4Cl_2$ is prepared it is found to have a boiling point of 78.6 °C. Given that $K_b = 5.0$ °C-kg/mol and the boiling point of pure CCl_4 is 76.6 °C, calculate how many grams of solute are present in 100 grams of CCl_4.

41. A solution is prepared by dissolving 1.28 g of naphthalene, $C_{10}H_8$, in 10.0 g of benzene.
- (a) By how much is the freezing point of benzene lowered?
- (b) What is the freezing point of the solution?
- (c) What is the mole fraction of benzene in the solution?
- (d) The vapor pressure of pure benzene is 100 mm at room temperature. What is the vapor pressure of this solution at the same temperature?
- (e) What is the boiling point of the solution?

42. When 0.532 g of a certain solid organic compound was dissolved in 16.8 g of urethane, whose freezing point was 49.50 °C, the freezing point of the solution was lowered to 48.32 °C. Chemical analysis showed this compound to be 69.5% C, 7.25% H, and 23.25% O. Determine the true formula of this compound. (K_f for urethane = 5.14).

43. A solution was prepared by dissolving 12.21 g of $CaCl_2$ in enough water at 25 °C to make 50.00 mL of solution. The density of the solution was 1.19 kg/L.
- (a) What is the molar concentration (*M*) of this solution?
- (b) What is the concentration of $CaCl_2$ in mass-percent?

(c) What is the vapor pressure of this solution at 100 °C?
(d) At what temperature will this solution begin to freeze?

44. 2.5 g of calcium iodide (CaI_2) were dissolved in enough water to make 750.0 mL of solution, which had a density of 1.003 g/mL.
(a) Calculate the molarity (M) of the solution.
(b) Calculate the mass % of calcium iodide in the solution.

45. A solution is made by dissolving 10.0 g C_6H_5COOH in 95.0 g water. This solution has a volume of 100.0 mL. For this solution determine:
(a) the weight percent of C_6H_5COOH
(b) the density
(c) the molarity
(d) the molality
(e) the mole fraction of C_6H_5COOH
(f) the boiling point of the solution [Kb for H_2O = 1.86].
(g) the vapor pressure of the solution at 25 °C [vapor pressure of H_2O at 25 °C = 25 mm Hg].
(h) the reaction that occurs between C_6H_5COOH and H_2O

46. The change in enthalpy (ΔH^0) for the spontaneous dissolution of sodium nitrate at 25 °C is +20 kJ/mol.
(a) Is the dissolution process exothermic or endothermic?
(b) An estimated value of $\Delta S_{\text{solution}}$ for $NaNO_3$ at 25° C is 170 J/mol-K. Is this value consistent with the experimental observations? Explain.

47. A 100-g sample of water at 273 K dissolves 4.89 mL of O_2, 2.35 mL of N_2, and 5.6 mL of Ar when each gas is at a pressure of 1 atm. Calculate the freezing point of water that is saturated with air at 1 atm pressure and 273 K. [Air contains 78.09% N_2, 20.94% O_2, and 0.93% Ar by volume]

48. When human blood is mixed with distilled water, the red corpuscles swell and burst. Explain.

49. The vapor pressure of pure benzene at 25 °C is 95.5 torr. When 10.0 g of compound X are dissolved in 90.0 g of C_6H_6, the vapor pressure of the solution is 94.8 torr. Calculate the molecular weight of compound X.

50. If 50.0 g of a compound of molecular weight 92 are dissolved in 100.0 g of water, what is the normal boiling point of the solution?

51. When 40.0 g of compound Y are dissolved in 500.0 g of benzene, the resulting solution has a normal boiling point of 81.4 °C. Calculate the molecular weight of compound Y.

52. What is the freezing point of a 0.50 m aqueous sugar solution?

53. A sample of otherwise pure camphor contains an impurity of a solid hydrocarbon, $C_{10}H_8$, to the extent of 1.0 g of the hydrocarbon for every 100 g of camphor. What is the melting point of the camphor sample?

54. When 1.00 g of compound A is dissolved in 10.00 g of benzene, the resulting solution has a freezing point of −1.3 °C. Calculate the molecular weight of compound A.

55. When 0.650 g of a certain compound is dissolved in 27.80 g of diphenyl, the freezing point of the solution is 68.44 °C. The freezing point of pure diphenyl is 70.00 °C, and the molal freezing point constant is 8.00. Calculate the molecular weight of the compound.

56. A solution consisting of 0.100 g of a certain compound and 10.00 g of cyclohexane freezes at 1.00 °C. Calculate the molecular weight of the compound. (Cyclohexane has a freezing point of 6.00 °C and a molal freezing point constant of 20.0.)

57. A compound has a composition of 93.75 wt % carbon and 6.25 wt % hydrogen. When 0.320 g of this compound is dissolved in 10.0 g of benzene, the solution has a freezing point of 4.20 °C. Calculate (a) the empirical formula, (b) the molecular weight, and (c) the molecular formula of the compound.

58. Complete and balance the following:
(a) $K_2O(s) + H_2O \rightarrow$
(b) $CO_2(g) + H_2O \rightarrow$
(c) $SO_2(g) + H_2O \rightarrow$
(d) $MgO(s) + H_2O \rightarrow$
(e) $N_2O_5(s) + H_2O \rightarrow$
(f) $B_2O_3(s) + H_2O \rightarrow$

59. Designate each of the following compounds as a strong electrolyte, weak electrolyte, or nonelectrolyte:
(a) KBr
(b) NH_4Cl
(c) CH_3NH_2
(d) HCN
(e) CO_2
(f) $NaC_2H_3O_2$
(g) HCOOH
(h) $HClO_4$
(i) C_6H_{12}
(j) CaO
(k) NaOH
(l) CH_3COCH_3
(m) CH_3CH_2OH
(n) SO_2
(o) $NH_4C_2H_3O_2$
(p) CH_3OCH_3
(q) $CH_3CH_2CO_2CH_3$
(r) MgI_2
(s) HF
(t) CH_3CH_2Cl

60. Characterize each of the following as non (N), weak (W), or strong (S) electrolytes:
a. methanol
b. acetone (propanone)
c. ferric chloride
d. ammonia
e. carbon dioxide
f. propanoic acid
g. sulfuric acid
h. nitrous acid

61. A 0.10 m solution of a certain weak acid freezes at −0.245 °C. Calculate the percentage dissociation of the weak acid.

62. A 0.50 m solution of NaCl freezes at −1.70 °C. What is the *apparent* percentage of dissociation of NaCl?

63. What concentration of sodium chloride in water is needed to produce an aqueous solution which has the same osmotic pressure as blood does at 25 °C? The osmotic pressure of blood is 7.70 atm.

64. A solution of 4.785 g of mercury(II) chloride in 60 g of water is found to boil at 100.152 °C. Is mercury(II) chloride dissociated in water solution?

65. Explain the following experimental observations:
(a) The freezing point depression per mole of potassium chloride is greater in a 0.010 m solution than in a 1.0 m solution.
(b) The vapor pressure of the solvent over a solution of nonvolatile solute is less than the vapor pressure of the pure solvent.

66. A solution was prepared by dissolving 12.21 g of $CaCl_2$ in enough water at 25 °C to make 50.00 mL of solution. The density of the solution was 1.19 kg/L.

(a) What is the molar concentration (M) of this solution?
(b) What is the concentration of $CaCl_2$ in mass-percent?
(c) What is the vapor pressure of this solution at 100 °C?
(d) At what temperature will this solution begin to freeze?

67. Inorganic salts are commonly used to melt ice on the roadways. Several different kinds are sold under the brand names Halite (NaCl), Runway (KCl), and Dry-Rite ($CaCl_2$). If 10 kg of each of these inorganic salts were available, which one should be used to be the most effective at melting ice on roadways on a cold winter's day?

68. Assuming complete dissociation, calculate the moles of calcium chloride needed to lower the freezing point of 10.0 L of water to −10.0 °C. Why is $CaCl_2$ not used as an automotive antifreeze?

69. Multiple-choice questions

1. Which of the following would be a good solvent for dissolving ethyl amine?
   (a) benzene (b) cyclohexane
   (c) methanol (d) carbon tetrachloride
2. Which of the following aqueous solutions has the lowest vapor pressure at 20 °C?
   (a) 0.1 m glucose (b) 0.1 m NaCl
   (c) 0.1 m $MgCl_2$ (d) 0.01 m glucose
3. The solubility of Li_2CO_3 in water decreases with increasing temperature. Therefore:
   (a) Li_2CO_3 will dissolve more rapidly at 10 °C than at 25 °C
   (b) ΔG for the solution process is positive
   (c) ΔH for the solution process is negative
   (d) ΔH must be smaller than ΔS for the solution process
4. In which of the following liquids does sodium nitrate have the greatest solubility?
   (a) methanol (b) diethyl ether
   (c) carbon tetrachloride (d) benzene
5. Which of the following aqueous solutions has the lowest freezing point?
   (a) 0.1 m NH_3
   (b) 0.1 m $HC_2H_3O_2$
   (c) 0.1 m $NH_4C_2H_3O_2$
   (d) all have the same freezing point
6. Which one of the following is a nonelectrolyte?
   (a) HNO_2 (b) CO_2 (c) CH_3OH (d) KF
7. Which of the following solutions has the highest molality?
   (a) 20% NaCl (b) 20% NaOH
   (c) 20% HCl (d) 20% $NaNO_3$
8. Which one of the following is a weak electrolyte?
   (a) H_2SO_3 (b) $(NH_4)_2SO_3$
   (c) CH_3F (d) Na_2SO_3
9. If liquid A has a vapor pressure of 40 torr and liquid B has a vapor pressure of 80 torr, then the vapor pressure of a solution made from 1 mol of A and 1 mol of B will have a vapor pressure of:
   (a) 40 torr (b) 60 torr
   (c) 80 torr (d) 120 torr
10. If a solution consists of 0.1 mol of A, 0.2 mol of B, and 0.3 mol of C, then the mole-fraction of B in the solution is:
    (a) 0.200 (b) 0.333 (c) 0.500 (d) 0.600

11

Stoichiometry

The combination of particles in specific whole number ratios is a fundamental concept in chemistry. Protons, electrons, and neutrons are combined in a certain ratio to obtain an isotope of an element, elements may be combined in a specific relationship to form chemical species such as molecules, and these molecules may then undergo chemical reactions, which are simply rearrangements of the combinations, to give new compounds. Knowledge of the various ratios, calculations involving these ratios, and conversions using these ratios is essential in learning chemistry. The area of calculations dealing with these weight relationships in matter and its reactions is called **stoichiometry**, from the Greek expression meaning "measurement of elements." This chapter provides an introduction to chemical formulas, reaction stoichiometry, and the analysis of materials using gravimetric, volumetric, and combustion methods.

11.1 CHEMICAL EQUATIONS

Consider the simple reaction in which carbon and oxygen combine to form a third substance, carbon dioxide. This process is described in words as: carbon **plus** oxygen **yields** carbon dioxide. The equation for the reaction is derived as follows. Since carbon is an elementary substance, it is designated by its symbol, C. The elementary substance oxygen, however, does not exist in its normal state as a collection of individual atoms, but rather as diatomic molecules, and we must indicate this fact by writing O_2. The compound carbon dioxide is designated by its formula, CO_2. Using an arrow to replace the word "yields" in our description, we write the equation as follows:

$$C + O_2 \longrightarrow CO_2$$

This chemical equation is more informative than the word description because it tells us not only what substances are involved in the reaction, but also the composition of these substances. Furthermore, the equation tells us the ratio (of atoms or molecules) in which the various substances react; that is, one atom of carbon reacts with one molecule of oxygen to form one molecule of carbon dioxide. We can also visualize the reaction at the atomic level in a simplistic way (Figure 11.1).

In any chemical equation, all substances consumed in the reaction, called the **reactants**, are placed to the left of the arrow, and all substances produced in the reaction,

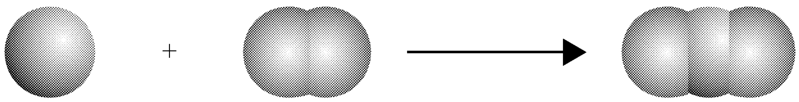


Figure 11.1 Visualizing the reaction of carbon atoms with oxygen molecules at the atomic level.

called the **products** of the reaction, are placed to the right of the arrow. An equal sign is sometimes used in place of the arrow.

Chemical reactions are simply rearrangements of atoms (as Dalton observed, atoms are neither created nor destroyed), and this fact must be observed in writing chemical equations. In other words, the same number of atoms of each element must appear in the products as in the reactants. (Thus, in the equation for the reaction of carbon and oxygen, one carbon atom and two oxygen atoms appear on each side of the arrow). If this condition is not met by simply writing the symbols and formulas for the reactants and products, then the statement is not truly an equation, and further steps must be taken.

As an illustration, consider the combustion of methane, in which methane and oxygen react to form carbon dioxide and water. Writing the proper formulas for the substances involved results in the following statement:

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

This statement is not really an equation—an expression of equality—for, of the three elements involved, only carbon has the same number of atoms on both sides of the arrow. (An expression of this kind is sometimes referred to as a **skeletal**, or **unbalanced**, equation.) In order to remedy this situation, we must supply the proper numerical coefficients. Since four hydrogen atoms appear on the left side of our statement and only two on the right, we may assume that one molecule of methane will give rise to two molecules of water, and we write

$$CH_4 + O_2 \longrightarrow CO_2 + 2\,H_2O$$

Now both the carbon and hydrogen are balanced, but the oxygen is not; there are four oxygen atoms on the right-hand side, but only two on the left. If we place a 2 in front of the formula for oxygen, the statement will then read

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

We now have achieved a **balanced equation**, which states that one molecule of methane reacts with two molecules of oxygen to form one molecule of carbon dioxide and two molecules of water (Figure 11.2).

It should be noted that in obtaining a balanced equation one may not change any numerical subscripts, which indicate the composition of a substance. For example, we may not balance the hydrogen atoms in the above illustration by changing CH_4 to CH_2. Nature has decreed that the substance we call methane has a composition represented by the formula CH_4, and a substance with the formula CH_2, if it did exist, would not be methane but a different compound with entirely different properties.

Methodology 11.1 and Problems 11.1–11.2 further illustrate the balancing procedure.

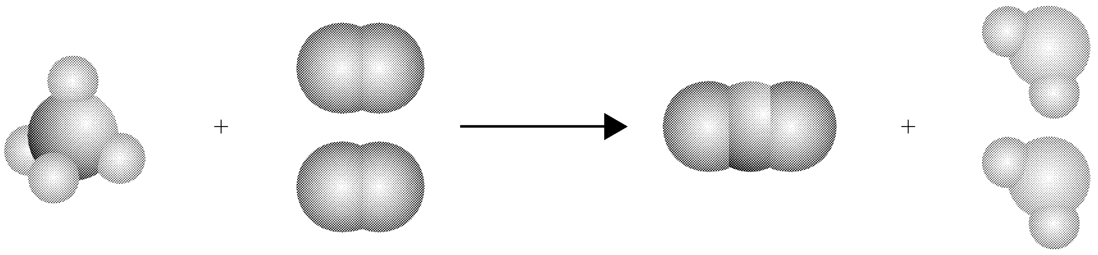
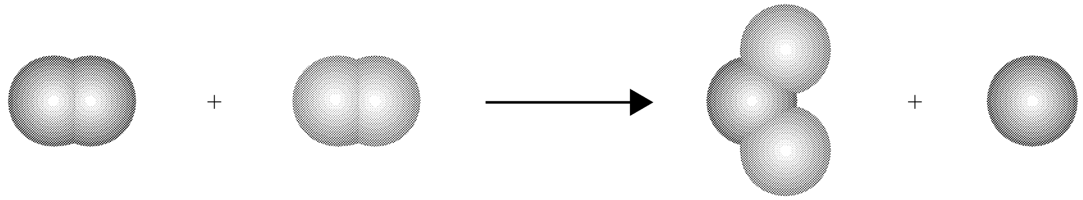


Figure 5.2 Visualizing the reaction of methane with oxygen molecules.

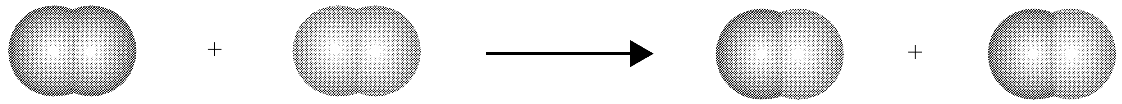
Visualization 11.1

Which of the following does not describe an equation on the molecular level?

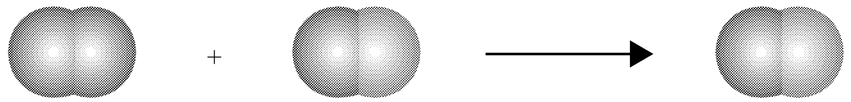
a.



b.



c.



Solution:

In reactions (a) and (b) there are the same numbers of nitrogen (dark) and oxygen (light) atoms on both sides of the equation. In (c) there are two nitrogens and two oxygens on the left, but only one nitrogen and one oxygen on the right.

Methodology 11.1

Balance the equation

$$C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$$

Balancing the equation means placing coefficients in front of the reagents so that there are equal numbers of each elements on both sides of the equation. How should we begin?

The most obvious starting point is perhaps with the carbon atoms. Since there are six carbon atoms on the left, there must be six on the right, so we place a 6 before CO_2:

$$C_6H_6 + O_2 \longrightarrow 6\,CO_2 + H_2O$$

There is only one reagent on each side of the equation that contains hydrogen so we continue by balancing the hydrogens.

Giving H_2O a coefficient of 3 will balance the hydrogens:

$$C_6H_6 + O_2 \longrightarrow 6\,CO_2 + 3\,H_2O$$

The only element remaining to be balanced is oxygen.

Since we have 15 oxygen atoms on the right and only 2 on the left, we need a coefficient of $7\frac{1}{2}$ for O_2:

$$C_6H_6 + 7\tfrac{1}{2}O_2 \longrightarrow 6\,CO_2 + 3\,H_2O$$

Continued on next page

Methodology 11.1

The equation is now balanced. However, if we wish to think of an equation as representing numbers of molecules involved in the reaction, then fractional coefficients should be avoided.

This can be accomplished by multiplying each coefficient by 2, resulting in the following balanced equation:

$$2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O$$

Problem 11.1

Balance the equation

$$PCl_3 + H_2O \longrightarrow HCl + H_3PO_3$$

Solution:

Probably the simplest starting point is to balance the chlorine atoms:

$$PCl_3 + H_2O \longrightarrow 3\,HCl + H_3PO_3$$

Phosphorus and chlorine are now balanced; hydrogen and oxygen are not. By giving H_2O a coefficient of 3, the equation is completely balanced:

$$PCl_3 + 3\,H_2O \longrightarrow 3\,HCl + H_3PO_3$$

Problem 11.2

Balance the equation

$$Ba(OH)_2 + HNO_3 \longrightarrow Ba(NO_3)_2 + H_2O$$

Solution:

The nitrogen atoms may be balanced by placing a 2 in front of HNO_3:

$$Ba(OH)_2 + 2\,HNO_3 \longrightarrow Ba(NO_3)_2 + H_2O$$

Giving H_2O a coefficient of 2 balances both the oxygen and hydrogen, and results in a balanced equation:

$$Ba(OH)_2 + 2\,HNO_3 \longrightarrow Ba(NO_3)_2 + 2\,H_2O$$

It is sometimes desirable to have a chemical equation convey additional information about the reaction. In particular, it is often important to indicate the physical state of a reactant or product. This is accomplished by writing in parentheses after the formula the letters *g*, *l*, or *s*, indicating gas, liquid, or solid, respectively. For example

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

Similarly, a reactant or product in aqueous solution (a solution in which the substance is dissolved in water) may be so designated by use of the abbreviation aq:

$$Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Whether heat is absorbed or evolved may be shown by simply writing the word "heat" as if it were a reactant or a product. Alternatively, the symbol Δ may be used for heat:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + \text{heat}$$

11.2 REACTION STOICHIOMETRY

As we have seen, the coefficients in a balanced chemical equation tell us the relative **number of molecules** (or atoms or ions) of each substance consumed or produced in the reaction. Because a mole of any substance contains the same number of molecules as a mole of any other substance, the coefficients also tell us the relative **number of moles** of each substance involved in the reaction. Furthermore, since a mole of a substance is equal to the formula weight of that substance in grams, chemical equations are expressions of the weight relationships between substances in a chemical reaction. Since matter is conserved in a chemical reaction, the number of moles and total weight of an element in the reactants must equal the number of moles and total weight of the element in the products.

Mole-Mole Relationships

Since the coefficients in a chemical equation indicate the relative numbers of moles of substances reacting or produced in the reaction, they can be used to determine the number of moles of each substance involved in the reaction if the number of moles of any one reactant or product is known. In these problems, the molar ratios provide a "bridge" allowing one to convert amounts of one species to amounts of another.

Consider the equation for the combustion of benzene:

$$2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O$$

The coefficients of benzene and CO_2 reveal that every time a molecule of benzene reacts with oxygen, six molecules of CO_2 are formed. Generally, we prefer to operate with moles rather than molecules and therefore we can also say that six moles of water are formed from the reaction of two moles of benzene (or, three moles of water are formed from one mole of benzene). In some cases it is helpful to divide all of the coefficients by the coefficient of a substance involved in a problem. For example, if we want to know how many moles of CO_2 will be produced from the reaction of 0.25 mol of O_2, the relationship between O_2 and CO_2 can be seen by dividing all coefficients by the coefficient of O_2. The equation then becomes

$$\frac{2}{15}C_6H_6 + O_2 \longrightarrow \frac{12}{15}CO_2 + \frac{6}{15}H_2O$$

It is clear then that the reaction of one mole of O_2 will produce 12/15 mol of CO_2. If we want to know how many moles of CO_2 are formed from 0.25 mol of O_2, we need only multiply 0.25 by 12/15:

$$0.25\text{ mol }O_2 \times \frac{12\text{ mol }CO_2}{15\text{ mol }O_2} = 0.20\text{ mol }CO_2$$

Methodology 11.2

Determine how many moles of CO_2 are produced from the complete combustion of 3.20 mol of benzene.

What coefficients appear in front of benzene and CO_2?

The balanced equation indicates that C_6H_6 and CO_2 are related by the molar ratio 2:12 (2 mol of C_6H_6 yields 12 mol of CO_2).

Determine this relationship by dividing all of the coefficients by the coefficient in front of benzene:

$$\frac{2}{2}C_6H_6 + \frac{15}{2}O_2 \longrightarrow \frac{12}{2}CO_2 + \frac{6}{2}H_2O,$$

Continued on next page

Methodology 11.2 Continued

or

$$C_6H_6 + \frac{15}{2} O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$$

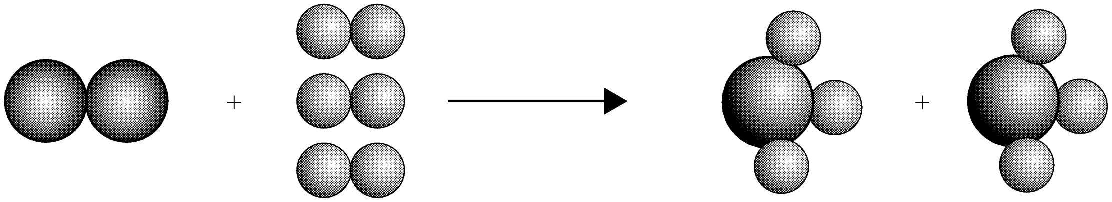
What ratio do we multiply 3.20 mol of benzene by in order to get the number of moles of CO_2?

3.20 mol of C_6H_6 will yield

$$3.20 \text{ mol } C_6H_6 \times \frac{12 \text{ mol } CO_2}{2 \text{ mol } C_6H_6} = 19.2 \text{ mol } CO_2$$

Visualization 11.2

Given the following molecular process:



(a) How many moles of NH_3 will be formed if 2 mol of N_2 are consumed?

(b) How many moles of H_2 are required to react with 0.30 mol of N_2?

Solution:

(a) $2 \text{ mol } N_2 \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2} = 4 \text{ mol of } NH_3$

(b) $0.30 \text{ mol } N_2 \times \frac{3 \text{ mol } H_2}{1 \text{ mol } N_2} = 0.90 \text{ mol } H_2$

Through the use of Avogadro's number, the relationship between moles can be extended to molecules (Problem 11.3).

Problem 11.3

Using the equation for the combustion of benzene given in the previous example, how many molecules of water are produced from the reaction of 0.20 mol of C_6H_6?

Solution:

From the balanced equation, we see that 2 mol of C_6H_6 yields 6 mol of H_2O; therefore, 0.20 mol of C_6H_6 will react to produce

$$\left(0.20 \times \frac{6}{2}\right) \text{ mol of } H_2O$$

Since one mole contains 6.022×10^{23} molecules, the number of water molecules produced is

$$0.20 \text{ mol } C_6H_6 \times \frac{6 \text{ mol } H_2O}{2 \text{ mol } C_6H_6} \times \frac{6.022 \times 10^{23} \text{ molecules } H_2O}{1 \text{ mol } H_2O} = 3.6 \times 10^{23} \text{ molecules of } H_2O$$

Limiting Reactant

Often one or more reactants are in excess of that required for complete reaction with the remaining reactant. This leads to a situation where the chemical reaction is limited by the amount of one of the reactants which, when its supply is exhausted, will stop the formation of products and halt the reaction; this is called the limiting reactant. Since the moles of product formed and moles of reactant used are determined by the reaction stoichiometry, it is *not* always the case that the reactant present in the smallest quantity is the limiting reactant. The molar ratios involved in the reaction must be taken into consideration. The concept of a limiting reactant is further illustrated in Methodology 11.3 and Problem 11.4.

Methodology 11.3

Using the equation for the combustion of benzene given in the Methodology 5.2, if we have 6 mol of oxygen and 1 mol of benzene, which reactant limits the reaction and how much of the other reactant will remain unreacted?

We always start with the balanced equation:

$$2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O$$

How much oxygen is required to react completely with one mole of benzene?

From the balanced equation, we see that 1 mol of C_6H_6 would require 15/2 as much O_2, or 7.5 mol of O_2.

Are 7.5 mol of O_2 available?

No, we have only 6 mol of O_2, so the oxygen supply will be exhausted first and will limit the reaction.

How much benzene is necessary to react with 6 mol of O_2?

If all 6 mol of the O_2, are consumed, we would need

$$6\text{ mol } O_2 \times \frac{2\,C_6H_6}{15\,O_2} = 0.8\text{ mol } C_6H_6$$

Is 0.8 mol benzene available?

We started with 1.0 mol of benzene and therefore 0.8 mol will react with the oxygen and 0.2 will remain when the reaction is complete. Consequently, we say that the benzene is in excess and the O_2 is the limiting reagent.

Problem 11.4

Given the following reaction,

$$C_2H_2 + 2\,Cl_2 \longrightarrow C_2H_2Cl_4$$

how many moles of $C_2H_2Cl_4$ can be produced from 4.0 mol C_2H_2 and 5.0 mol Cl_2?

Solution:

If all of the Cl_2 reacts, we would use

$$5.0\text{ mol } Cl_2 \times \frac{1\,C_2H_2}{2\,Cl_2} = 2.5\text{ mol } C_2H_2\ (1.5\text{ mol } C_2H_2 \text{ remains unreacted})$$

so Cl_2 is the limiting reactant. The moles of $C_2H_2Cl_4$ formed can be found from the reaction stoichiometry which shows a 1:1 ratio of C_2H_2 reacted to $C_2H_4Cl_4$ formed, so 2.5 mol of $C_2H_2Cl_4$ will form.

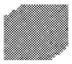
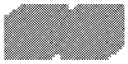
Mass-Mass Relationships

By combining the mole ratios given in the equation with the relationship between the mole and the formula weight, one can calculate the masses of substances reacting with, or produced from, a given mass of any substance involved in the reaction (Methodology examples 11.4 and 11.5 and Problem 11.5). Again, one of the reactants may serve to limit the reaction.

Visualization 11.3

Given the general equation

$$A + 3\,B \longrightarrow 2\,C$$

and assuming that  is one mole of A and that  is one mole of B, what quantity of B is required to react with  of A?

Solution:

The equation tells us that 3 mol of B are required to react with 1 mol of A. Therefore, six moles of B  will be required to react with two moles of A.

Methodology 11.4

In the hydrolysis of phosphorus trichloride, what mass of HCl can be produced from the reaction of 15.0 g of PCl_3 with excess H_2O? The equation for the reaction is

$$PCl_3 + 3\,H_2O \longrightarrow 3\,HCl + H_3PO_3$$

First express the amount of PCl_3 in terms of moles.

The formula weight of PCl_3 is approximately 137. Therefore:

$$\text{Number of moles of } PCl_3 \text{ reacted} = \frac{15.0\text{ g } PCl_3}{137\text{ g } PCl_3/\text{mol } PCl_3}$$

Use the equation to determine how many moles of HCl would be formed when one mole of PCl_3 is consumed.

The equation for the reaction shows that for every mole of PCl_3 consumed, 3 mol of HCl are formed.

How many moles of HCl will actually be formed from the 15 g of PCl_3?

$$\text{Moles of HCl produced} = \frac{15.0\text{ g } PCl_3}{137\text{ g } PCl_3/\text{mol } PCl_3} \times \frac{3\text{ mol HCl}}{1\text{ mol } PCl_3}$$

Now convert from moles of HCl to grams of HCl.

To convert the number of moles of HCl to the number of grams of HCl, we need only multiply by the number of grams in one mole:

$$\frac{15.0\text{ g } PCl_3}{137\text{ g } PCl_3/\text{mol } PCl_3} \times \frac{3\text{ mol HCl}}{1\text{ mol } PCl_3} \times \frac{36.5\text{ g HCl}}{1\text{ mol HCl}} = 12.0\text{ g HCl}$$

Problem 11.5

What mass of aluminum is required to produce 3.0 g of hydrogen according to the following equation?

$$2\,\mathrm{Al} + 3\,\mathrm{H_2SO_4} \longrightarrow \mathrm{Al_2(SO_4)_3} + 3\,\mathrm{H_2}$$

Solution:

$$\frac{3.0\text{ g H}_2}{2.0\text{ g H}_2\text{/mol H}_2} \times \frac{2\text{ mol Al}}{3\text{ mol H}_2} \times \frac{27.0\text{ g Al}}{1\text{ mol Al}} = 27\text{ g Al}$$

Methodology 11.5

Given the reaction in Problem 5.12, what mass of hydrogen would be formed from the reaction of 40 g Al and 40 g of H_2SO_4?

What do we do first?

Always start by writing the equation for the reaction:

$$2\,\mathrm{Al} + 3\,\mathrm{H_2SO_4} \longrightarrow \mathrm{Al_2(SO_4)_3} + 3\,\mathrm{H_2}$$

Can we assume that the aluminum controls the reaction?

No, we must find the limiting reactant by converting mass to moles and looking at the molar ratio in the reaction stoichiometry.

Determine how many moles of Al and H_2SO_4 we have.

$$\text{moles Al} = \frac{40\text{ g AL}}{27\text{ g/mol Al}} = 1.5\text{ mol Al}$$

$$\text{moles H}_2\text{SO}_4 = \frac{40\text{ g H}_2\text{SO}_4}{98\text{ g/mol H}_2\text{SO}_4} = 0.41\text{ mol H}_2\text{SO}_4$$

Which is the limiting reactant?

If we react all of the H_2SO_4, we would require

$$0.41\text{ mol H}_2\text{SO}_4 \times \frac{2\text{ Al}}{3\text{ H}_2\text{SO}_4} = 0.27\text{ mol Al}$$

We have much more than this amount (1.5 mol), so the H_2SO_4 limits the reaction.

What is the mole ratio between H_2SO_4 and H_2?

The equation shows that 3 mol of H_2 are produced when 3 mol of H_2SO_4 are consumed. In other words, the number of moles H_2 formed would be the same as the number of moles H_2SO_4 reacted (1 : 1 stoichiometry).

How many moles of H_2 will be formed?

We have already established that we have 0.41 mol of H_2SO_4 and thus 0.41 mol H_2 would be formed.

Now convert 0.41 mol H_2 to grams.

$$0.41\text{ mol H}_2 \times \frac{2.0\text{ g}}{\text{mol H}_2} = 0.82\text{ g H}_2$$

Check Point 11.1

If 2.7 g Al are consumed in the following reaction

$$2\,\mathrm{Al} + 3\,\mathrm{H_2SO_4} \longrightarrow \mathrm{Al_2(SO_4)_3} + 3\,\mathrm{H_2}$$

how many grams of H_2 are produced?

Solution:

0.30 g

◇ ◇ ◇ ◇ ◇

Stoichiometry of Solutions

Frequently chemists are interested in reactions in which one or more of the reactants is in solution form.

When a solution whose concentration is expressed as a weight or volume percentage is used in a chemical reaction, stoichiometric calculations involving the weight of solution offer no particular difficulty (Problems 11.6 and 11.7).

Problem 11.6

Consider the laboratory production of hydrogen by the following reaction:

$$H_2SO_4(aq) + Zn(s) \longrightarrow ZnSO_4(aq) + H_2(g)$$

What weight of a 20.0 wt-% aqueous solution of H_2SO_4 would be required to completely react with 3.00 g of zinc?

Solution:

The weight of pure H_2SO_4 required is calculated by the same process as was used in the preceding examples. Since for every 20 g of pure H_2SO_4 required, 100 g of solution must be used, the weight of pure H2SO4 must then be multiplied by the factor 100 g solution/20.0 g H_2SO_4:

$$\frac{3.0\text{ g Zn}}{65.38\text{ g Zn/mol Zn}} \times \frac{1\text{ mol }H_2SO_4}{1\text{ mol Zn}} \times \frac{0.98\text{ g }H_2SO_4}{1\text{ mol }H_2SO_4} \times \frac{100\text{ g solution}}{20.0\text{ g }H_2SO_4} = 22.5\text{ g solution}$$

Problem 11.7

An aqueous solution that is 32.0% by weight HCl has a density of 1.16 g/mL. What weight of Cl_2 can be prepared from 375 mL of this solution, according to the following equation?

$$MnO_2(s) + 4\ HCl(aq) \longrightarrow MnCl_2(aq) + 2\ H_2O(l) + Cl_2(g)$$

Solution:

We first determine the weight of pure HCl in 375 mL of the solution:

$$375\text{ mL} \times 1.16\text{ g/mL} \times \frac{32.0\text{ g HCl}}{100\text{ g solution}} = 139\text{ g HCl}$$

Then, referring to the equation, we complete the solution:

$$\frac{139\text{ g HCl}}{36.5\text{ g HCl/mol HCl}} \times \frac{1\text{ mol }Cl_2}{4\text{ mol HCl}} \times \frac{70.9\text{ g }Cl_2}{1\text{ mol }Cl_2} = 67.5\text{ g }Cl_2$$

The concentration expression most frequently used by chemists is **molarity**, or the **number of moles of solute per liter of solution**.

Expressing the concentration of solutions in terms of molarity offers some advantages over other concentration expressions. Molarity relates the mass of solute to the **volume** of solution, without requiring that the density of the solution be known. Furthermore, since chemical equations describe **molar** ratios of reactants and products, the use of molarity permits direct stoichiometric calculations involving solution volumes, as illustrated in Problems 11.8 and 11.9.

Problem 11.8

Copper is dissolved by a dilute nitric acid (HNO3) solution by the following reaction:

$$3\ Cu(s) + 8\ HNO_3(aq) \longrightarrow 3\ Cu(NO_3)_2(aq) + 2\ NO(g) + 4\ H_2O(l)$$

How many milliliters of 3.00 M HNO_3 solution are required to react with 10.0 g of Cu?

Solution:

The number of moles of HNO_3 required is

$$\frac{10.00\ \text{g Cu}}{63.5\ \text{g Cu/ mol Cu}} \times \frac{8\ \text{mol HNO}_3}{3\ \text{mol Cu}} = \text{no. of moles of HNO}_3$$

The HNO_3 is provided in the form of 3.00 M solution; that is, each liter of solution contains 3.00 mol of HNO_3. The number of liters of solution required, then, is

$$\frac{\text{no. of mol HNO}_3}{3.00\ \text{mol HNO}_3\text{/L}} = \text{no. of liters}$$

Finally, since one liter equals 1,000 mL, we have

$$\text{no. of L} \times 1{,}000\ \text{mL/L} = \text{no. of milliliters}$$

Therefore, the volume of solution required is

$$\frac{10.00\ \text{g Cu}}{63.5\ \text{g Cu/ mol Cu}} \times \frac{8\ \text{mol HNO}_3}{3\ \text{mol Cu}} \times \frac{1000\ \text{mL/L}}{3.00\ \text{mol HNO}_3\text{/L}} = 140\ \text{mL}$$

Problem 5.9

What weight of $BaCl_2$ can be prepared from 50.0 mL of 0.800 M HCl by the following reaction?

$$BaCO_3(s) + 2\ HCl(aq) \longrightarrow BaCl_2(aq) + H_2O(l) + CO_2(g)$$

Solution:

The number of moles of HCl used is

$$\frac{50.0\ \text{mL}}{1000\ \text{mL/L}} \times 0.800\ \text{mol HCl/L} = \text{no. of moles of HCl}$$

According to the equation, two moles of HCl are required to produce one mole of $BaCl_2$, Therefore:

$$\frac{50.0\ \text{mL}}{1000\ \text{mL/L}} \times \frac{0.800\ \text{mol HCl}}{1\ \text{L}} \times \frac{1\ \text{mol BaCl}_2}{2\ \text{mol HCl}} \times \frac{208\ \text{g BaCl}_2}{1\ \text{mol BaCl}_2} = 416\ \text{g BaCl}_2$$

11.3 CALCULATION OF YIELD

When a compound is prepared by means of a chemical reaction (either in the laboratory or on a larger, commercial scale), the amount of product obtained—the **yield**—is, of course, of major importance. From the equation for the reaction and the stoichiometric relationships considered previously, one can calculate the yield that ought to be obtained on the basis of the quantity of reactants used. In practice, however, the amount of product obtained—the **actual yield**—is nearly always less than the calculated amount—the **theoretical yield**. This difference may be due to a number of reasons. Many reactions do not go to completion; that is, equilibrium is established with a large amount of the reactants still present. In some cases, side reactions may occur—reactions that are not described by the equation and that lead to unexpected products. Furthermore, a considerable fraction of the product may be lost during the process of separating it in pure form from the reaction mixture.

The "efficiency" of a reaction as a preparative method may be indicated by the **percentage yield**. This is the ratio of the actual yield to the theoretical yield, expressed as percentage.

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

It is important to remember to calculate the limiting reactant when obtaining the theoretical yield.

Methodology 11.6

The explosive TNT (trinitrotoluene) is made from toluene (C_7H_8) and nitric acid (HNO_3). The equation for the reaction is

$$C_7H_8 + 3\,HNO_3 \longrightarrow C_7H_5(NO_2)_3 + 3\,H_2O$$

When 100.0 g of C_7H_8 and 150.0 g of HNO_3 were mixed together, 122.5 g of $C_7H_5(NO_2)_3$ was obtained. Calculate (a) the theoretical yield and (b) the percentage yield.

Part (a): We must first determine which is the limiting reactant—100.0 g of C_7H_8 or 150.0 g of HNO_3:

$$100.0\text{ g } C_7H_8 = \frac{100.0\text{ g } C_7H_8}{92.13\text{ g/mol } C_7H_8} = 1.085\text{ mol } C_7H_8$$

$$150.0\text{ g } HNO_3 = \frac{150.0\text{ g } HNO_3}{63.01\text{ g/mol } HNO_3} = 2.381\text{ mol } HNO_3$$

The equation indicates that C_7H_8 and HNO_3 react in the ratio 1:3. Thus, the number of moles of HNO_3 required to react with 1.085 mol of C_7H_8 is 3.255 mol. Hence, the 2.381 mol of HNO_3 are not enough to react with all the C_7H_8. In other words, C_7H_8 is in excess, and the 150.0 g of HNO_3 is the limiting reactant

How much $C_7H_5(NO_2)_3$ is produced from 150.0 g HNO_3?

The theoretical yield, then, is

$$\frac{150.0\text{ g } HNO_3}{63.01\text{ g } HNO_3/\text{mol } HNO_3} \times \frac{1\text{ mol } C_7H_5(NO_2)_3}{3\text{ mol } HNO_3} \times \frac{227.1\text{ g } C_7H_5(NO_2)_3}{1\text{ mol } C_7H_5(NO_2)_3} = 180.2\text{ g } C_7H_2(NO_2)_3$$

Part (b): The actual yield is 122.5 g and the theoretical yield, as calculated, is 180.2 g. How do we obtain the percentage yield?

$$\frac{122.5}{180.2} \times 100\% = 67.98\%$$

Check Point 11.2

The reaction

$$C_4H_6 + 2\,H_2 \longrightarrow C_4H_{10}$$

produces 6.0 g of C_4H_{10} from 10.0 g C_4H_6 and excess H_2. What is the percent yield?

Solution:

56%

◇ ◇ ◇ ◇ ◇

11.4 CHEMICAL ANALYSIS

Chemical analysis is the general term applied to procedures used in determining the composition of matter. The determination of what elements or compounds are present is called **qualitative** analysis. **Quantitative** analysis involves the determination of the proportions in which the various elements or compounds are present. Many of the common quantitative analytical methods employ the principles of stoichiometry.

Gravimetric Analysis

One general method of determining the percentage of a specific constituent in a sample of matter involves the following procedure:

1. A sample of the matter under investigation is accurately weighed (usually to 0.1 mg).
2. The weighed sample is dissolved to form an aqueous solution. (Depending on the nature of the sample, water alone may dissolve it, or other reagents may have to be added.)
3. A substance that reacts with the constituent to form a precipitate is added to the solution. All of the constituent in the original sample must end up in this precipitate.
4. The precipitate is removed from the liquid by filtration, using either a filter crucible (see Figure 11.3) or "ashless" filter paper in a funnel. In either case, the liquid passes through and the precipitate is retained.
5. The precipitate is washed to remove adhering impurities and is then dried to constant weight. Some precipitates can be thoroughly dried at relatively low temperatures; in those cases a filter crucible is used for the filtration, and the crucible and its contents are heated in a laboratory oven until no further weight loss occurs. Some other precipitates require such high temperatures for drying that

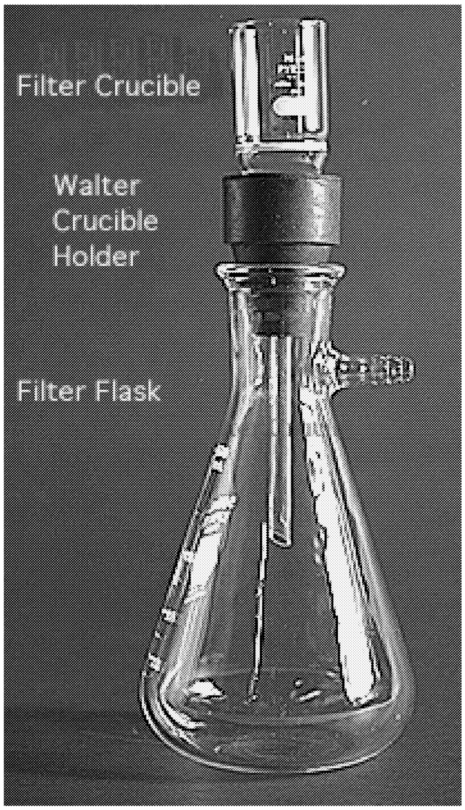


Figure 11.3 Filter crucible used for gravimetric analyses.

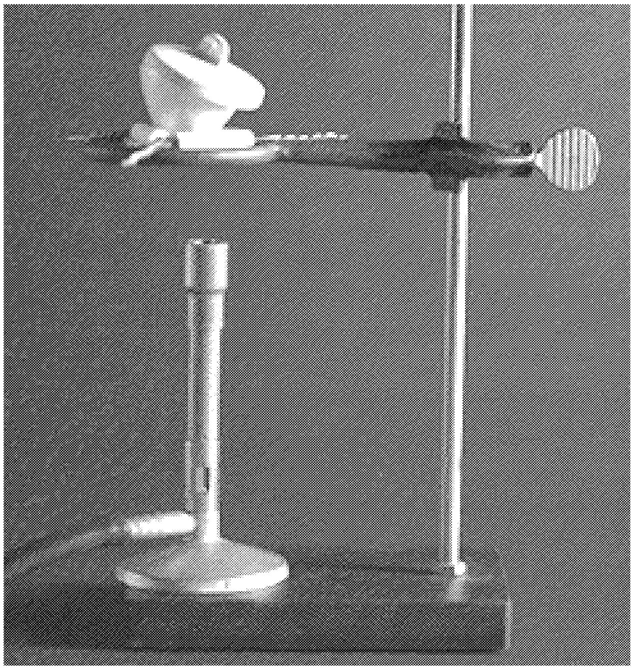


Figure 11.4 Ignition of the contents of a crucible.

an oven cannot be used. These are filtered through ashless paper. The paper is then folded and placed in a porcelain crucible. In a process called **ignition** (see Figure 11.4), the crucible is heated in a flame, whereupon the paper burns, leaving only the precipitate in the crucible. The crucible and its contents are then weighed.

This analytical procedure, in which the only measurements required are weighings, is called **gravimetric analysis** (from the Latin *gravis* meaning "heavy," and *metricus*, meaning "measurement").

In this method of analysis, the only information required for calculating the percentage of the constituent in the sample is (a) the accurate mass of the sample being analyzed, (b) the accurate mass of the precipitate being weighed, and (c) the correct formula of the precipitate (Methodology 11.7).

Methodology 11.7

The percentage of Sb in an antimony ore is determined by dissolving a sample of the ore and precipitating all the antimony as Sb_2S_3. This precipitate is then dried and weighed. A sample of ore weighing 0.6875 g yielded a precipitate of Sb_2S_3 weighing 0.3127 g. What is the percentage of Sb in the ore?

First, find the number of moles of Sb_2S_3 from the weight of Sb_2S_3:

$$\frac{0.3127\text{ g } Sb_2S_3}{339.68\text{ g/mol } Sb_2S_3} = \text{no. of moles of } Sb_2S_3$$

Next, find the number of moles of Sb.

Each mole of Sb_2S_3 contains two moles of Sb; therefore the number of moles of Sb in the precipitate is

$$\frac{0.3127\text{ g } Sb_2S_3}{339.68\text{ g/mol } Sb_2S_3} \times \frac{2\text{ Sb}}{1\text{ } Sb_2S_3} = \text{no. of moles of Sb}$$

Continued on next page

Methodology 11.7 Continued

How is this number of moles of Sb in the precipitate related to the number of moles of Sb in the ore sample?

Since all the Sb in the ore sample was converted to Sb_2S_3, this is also the number of moles of Sb in the sample.

Now, convert the number of moles of Sb to the mass of Sb in the ore sample.

By multiplying the number of moles by the mass of one mole, we obtain the mass of Sb in the sample:

$$\frac{0.3127\text{ g }Sb_2S_3}{339.68\text{ g/mol }Sb_2S_3} \times \frac{2\text{ Sb}}{1\text{ }Sb_2S_3} \times \frac{121.75\text{ g Sb}}{\text{mol Sb}} = \text{no. of grams of Sb}$$

Finally, determine the percentage of Sb in the sample.

To find the percentage of Sb in the sample, we simply divide the mass of Sb by the mass of the sample and multiply by 100%:

$$\frac{0.3127\text{ g }Sb_2S_3}{339.68\text{ g }Sb_2S_3/\text{mol }Sb_2S_3} \times \frac{2\text{ mol Sb}}{1\text{ mol }Sb_2S_3} \times \frac{121.75\text{ g Sb/mol Sb}}{0.6875\text{-g sample}} \times 100\% = 32.60\%\text{ Sb}$$

In some gravimetric analyses, the precipitate undergoes a chemical change in the ignition process. In this case the formula of the original precipitate does not enter into the calculation. Only the formula and mass of the substance **actually weighed** are required. For example, magnesium may be determined gravimetrically by precipitation of $MgNH_4PO_4$. When this compound is ignited, the following reaction occurs:

$$2\,MgNH_4PO_4(s) \longrightarrow Mg_2P_2O_7(s) + 2\,NH_3(g) + H_2O(g)$$

Thus, when the crucible is weighed after ignition, it does not contain the substance precipitated, but only $Mg_2P_2O_7$. (NH_3 and H_2O escape as gases.) This calculation is illustrated in Problem 11.10.

Problem 11.10

A sample of limestone weighing 1.5805 g yielded 0.8765 g of $Mg_2P_2O_7$. Calculate the percentage of Mg in the limestone.

Solution:

$$\frac{0.8765\text{ g }Mg_2P_2O_7}{222.6\text{ g }Mg_2P_2O_7/\text{mol }Mg_2P_2O_7} \times \frac{2\text{ mol Mg}}{1\text{ mol }Mg_2P_2O_7} \times \frac{24.305\text{ g Mg/mol Mg}}{1.5805\text{-g sample}} \times 100\%$$

$$= 12.11\%\text{ Mg}$$

Volumetric Analysis

Another widely used quantitative analytical method is called **volumetric analysis**. As the name implies, this method involves the measurement of volume. The general procedure is as follows:

1. A solution is prepared from an accurately weighed sample of the material to be analyzed.
2. A substance is chosen that will react rapidly and completely with the constituent that is to be determined, and a standard solution of this substance is prepared. (A standard solution is one of accurately-known concentration, usually expressed in terms of molarity with a precision of ±0.0001 M.)

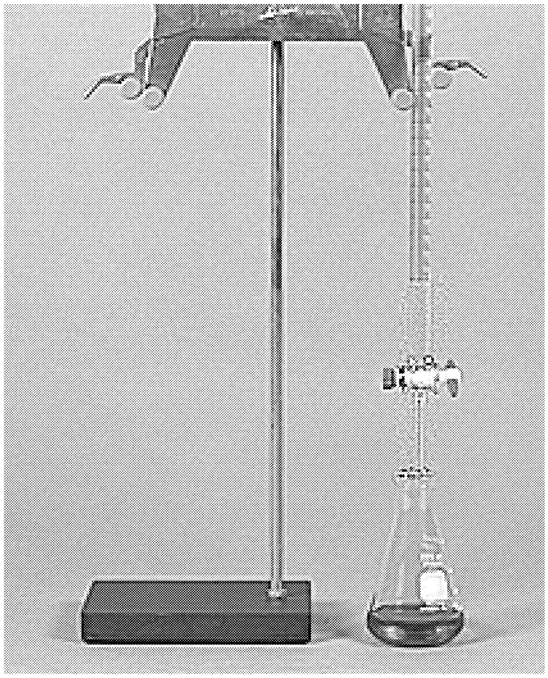


Figure11.5 Titration using a buret.

3. Some of the standard solution is poured into a buret, which is a long tube with a stopcock at the bottom. The tube is graduated (usually in tenths of a milliliter) so that the volume of solution that passes through the stopcock can be accurately measured (see Figure 11.5).
4. The standard solution is slowly added from the buret to the "unknown" solution, allowing a reaction to occur. This process is known as **titration**, and the solution in the buret is called the **titrant**. The titration is continued until the reaction is complete, that is, until the amount of reactant added is exactly the amount required to react with all of the constituent that is being determined. At this point (called the **equivalence point**), the titration is stopped.

   There must be some way for the analyst to know when the equivalence point is reached. This is accomplished by adding an **indicator** to the "unknown" solution before the titration is begun. An indicator is a substance that gives a visible change at, or very near to, the equivalence point; most commonly, it is a change in color. The particular indicator that is used depends on the specific reaction involved.
5. From buret readings before and after the titration, the exact volume of standard solution required can be measured. Since the molarity of the standard solution is known, the number of moles of titrant can be calculated. Furthermore, from a knowledge of the stoichiometry of the equation, the number of moles of constituent present in the sample can also be calculated.

As an illustration of a volumetric analysis, let us suppose we have a sample of soda ash (impure Na_2CO_3) and we wish to determine its purity; that is, we wish to determine the percentage of Na_2CO_3 in the sample. Further, assume we know that Na_2CO_3 will react rapidly and completely with HCl and that the equation for the reaction is

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2$$

Therefore, we choose a standard solution of HCl as our titrant, and we proceed as follows.

First we weigh a sample of the soda ash on the analytical balance and dissolve it in water. After pouring this solution into an Erlenmeyer flask, we add a few drops of a suitable indicator.

The next step is to partially fill the buret with a standard solution of HCl and record the reading. The stopcock of the buret must then be opened so that the HCl solution will run slowly into the soda ash solution, which should be constantly stirred to promote mixing. When the indicator changes color, we stop the titration by closing the stopcock, and we again record the buret reading.

Let us assume we obtained the following measured values and use them to calculate the percentage of Na_2CO_3 in the soda ash:

Mass of soda ash sample:	0.2749 g
Concentration of HCl solution:	0.1254 M
Buret reading at start:	2.72 mL
Buret reading at finish:	35.25 mL

The volume of HCl solution used was

$$35.25 - 2.72 = 32.53 \text{ mL}$$

Therefore, the number of moles of HCl used was

$$0.1254 \text{ mol HCl/L} \times \frac{32.53 \text{ mL}}{1000 \text{ mL/L}} = \text{no. of moles of HCl}$$

The equation for the reaction indicates that one mole of Na_2CO_3 reacts with two moles of HCl; therefore, the number of moles of Na_2CO_3 in the sample was

$$\frac{0.1254 \text{ mol HCl}}{\text{L}} \times \frac{32.53 \text{ mL}}{1000 \text{ mL/L}} \times \frac{1 \text{ mol } Na_2CO_3}{2 \text{ mol HCl}} = \text{no. of moles of } Na_2CO_3$$

Multiplying the number of moles by the formula weight of Na_2CO_3 (106.0 g/mol) gives the number of grams of Na_2CO_3 in the sample. Finally, dividing this weight by the weight of the sample and multiplying by 100% gives the percentage of Na_2CO_3 in the soda ash:

$$\frac{0.1254 \text{ mol HCl}}{\text{L}} \times \frac{32.53 \text{ mL}}{1000 \text{ mL/L}} \times \frac{1 \text{ mol } Na_2CO_3}{2 \text{ mol HCl}} \times \frac{106.0 \text{ g } Na_2CO_3/\text{mol } Na_2CO_3}{0.2749\text{-g sample}} \times 100\% = 78.62\% \ Na_2CO_3$$

Some additional illustrations of volumetric calculations appear in Problems 11.11–11.13.

Problem 11.11

The antiseptic tincture of iodine is a solution of iodine and KI in ethyl alcohol. When a sample of tincture of iodine weighing 5.000 g is diluted with water and titrated with 0.1500 M $Na_2S_2O_3$ solution, 19.75 mL of the latter is required. The reaction is:

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow 2\,NaI + Na_2S_4O_6$$

What is the weight percentage of I_2 in the sample?

Solution:

$$\frac{0.1500 \text{ mol } Na_2SO_3}{\text{L}} \times \frac{19.75 \text{ mL}}{1000 \text{ mL/L}} \times \frac{1\ I_2}{2\ Na_2SO_3} \times \frac{253.8 \text{ g } I_2/\text{mol}}{5.000\text{-g sample}} \times 100\% = 7.519\% \ I_2$$

Problem 11.12

When 25.00 mL of 0.2468 M KOH solution was titrated with a certain HCl solution, 42.50 mL was required to reach the equivalence point. What was the molarity of the HCl solution?

$$\mathrm{KOH + HCl \longrightarrow KCl + H_2O}$$

Solution:

The equation indicates that one mole of HCl is required for each mole of KOH titrated. Therefore, there are the same number of moles of HCl in 42.50 mL of solution as the number of moles of KOH in 25.00 mL of the KOH solution.

$$\frac{0.2468\ \text{mol KOH}}{\text{L}} \times \frac{25.00\ \text{mL}}{1000\ \text{mL/L}} \times \frac{1000\ \text{mL/L}}{42.50\ \text{mL}} = 0.1452\ \text{mol/L} = 0.1452\ \text{M HCl}$$

Problem 11.13

A sample of pure $H_2C_2O_4$ weighing 0.2244 g is dissolved in water and the solution is titrated with a certain NaOH solution. The reaction that occurs is

$$\mathrm{H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O}$$

If 30.12 mL of the NaOH solution is required, what is the molarity of that solution?

Solution:

$$\frac{0.2244\ \text{g}\ H_2C_2O_4}{90.04\ \text{g/mol}\ H_2C_2O_4} \times \frac{2\ \text{NaOH}}{H_2C_2O_4} \times \frac{1000\ \text{mL/L}}{30.12\ \text{mL}} = 0.1654\ \text{mol/L} = 0.1654\ \text{M NaOH}$$

Combustion Analysis

The percentage of carbon and of hydrogen in compounds is usually determined by a procedure called **combustion analysis**, using the apparatus shown in Figure 11.6. A weighed sample of the compound is placed in the combustion tube, which is then positioned in a furnace. As the furnace heats the sample, a stream of oxygen is passed through the combustion tube. Complete combustion of the compound occurs, converting the carbon and the hydrogen **quantitatively** to carbon dioxide (CO_2) and water vapor (H_2O). These gases are carried along in the oxygen stream through two detachable absorbent tubes. One of the tubes contains a material that absorbs the CO_2 and the other contains an absorbent for the H_2O. Each of the tubes is weighed prior to the combustion and then again after the combustion is complete. The gain in weight is a measure of the weight of CO_2 and of H_2O produced by the combustion. Using these two weights and the weight of the original sample, the principles of stoichiometry are applied to calculate the percentages of carbon and hydrogen in the compound (Problem 11.14).

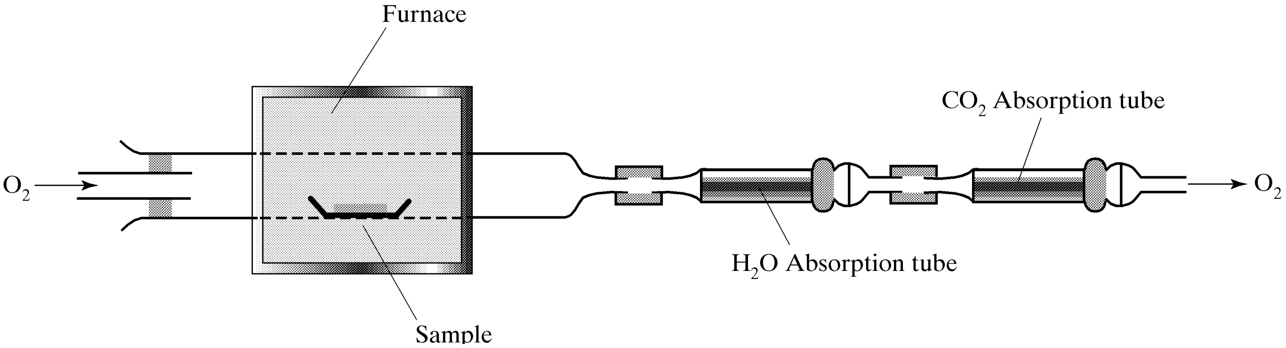


Figure 11.6 A combustion train.

Problem 11.14

A sample of a compound weighing 0.1012 g was subjected to combustion analysis, yielding 0.1501 g of CO_2 and 0.0717 g of H_2O. What are the percentages of carbon and hydrogen in the compound?

Solution:

Since the carbon and hydrogen in the compound are converted completely into CO_2 and H_2O, the weight of carbon in the sample is the weight of carbon in 0.1501 g of CO_2, and the weight of hydrogen in the sample is the weight of hydrogen in 0.0717 g of H_2O:

$$0.1501 \text{ g } CO_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g } CO_2} \times \frac{1}{0.1012\text{-g sample}} \times 100\% = 40.48\% \text{ C}$$

$$0.0717 \text{ g } H_2O \times \frac{(2 \times 1.008) \text{ g H}}{18.02 \text{ g } H_2O} \times \frac{1}{0.1012\text{-g sample}} \times 100\% = 7.93\% \text{ H}$$

Often, a combination of these methods of analysis are employed to determine empirical formulas as illustrated in the Problem 11.15.

Problem 11.15

A compound containing only carbon, hydrogen, and chlorine is analyzed in two separate experiments. In the first experiment, the compound is subjected to combustion analysis. A 3.00-g sample of the compound generated 6.19 g CO_2 and 2.79 g H_2O. In the second experiment, a gravimetric procedure was employed to determine the amount of chlorine in the sample. A 5.00-g sample was dissolved in water and treated with a solution of $AgNO_3$ to form the insoluble AgCl precipitate. The precipitate was filtered, washed, and dried. Its weight was determined to be 6.72 g. Determine the empirical formula of the compound.

Solution:

The combustion analysis provides information that will allow us to calculate the number of moles C and H in 3.00 g of the compound:

$$\text{C: } \frac{6.19 \text{ g } CO_2}{44.0 \text{ g/mol } CO_2} = 0.141 \text{ mol } CO_2 \times \frac{1 \text{ C}}{1 \text{ } CO_2} = 0.141 \text{ mol H}$$

$$\text{H: } \frac{2.79 \text{ g } H_2O}{18.0 \text{ g/mol } H_2O} = 0.155 \text{ mol } H_2O \times \frac{2 \text{ H}}{1 \text{ } H_2O} = 0.310 \text{ mol H}$$

The gravimetric procedure will allow us to calculate the number of moles Cl in 5.00 g of the compound:

$$\frac{6.72 \text{ g AgCl}}{143.3 \text{ g/mol AgCl}} = 0.0469 \text{ mol AgCl} \times \frac{1 \text{ Cl}}{1 \text{ AgCl}} = 0.0469 \text{ mol Cl}$$

In order to combine the information above and obtain the molar ratios, we must correct for the fact that two different sample sizes were used in the experiments. In the case of C and H, we had 3.00 g. For the Cl determination, we had 5.00 g. Since the moles of C and H were determined from only 3/5 the amount of sample used in the Cl analysis, and since molar ratios are directly proportional to mass, we can multiply the moles of C and H by 5/3 which should allow direct comparison with the Cl determination:

$$\text{C: } \frac{5}{3} \times 0.141 \text{ mol C} = 0.235 \text{ mol C}$$

$$\text{H: } \frac{5}{3} \times 0.310 \text{ mol H} = 0.517 \text{ mol H}$$

$$\text{Cl: } 0.0469 \text{ mol Cl}$$

The molar ratio is then found by dividing through by 0.0469, giving $C_{5.01}H_{11.02}Cl_{1.00}$, which, within experimental error, provides an empirical formula of $C_5H_{11}Cl$.

CHAPTER SUMMARY

The contents of this chapter lie at the heart of any discussion of a chemical reaction. Reactions are written as equations which express: a) the formulas of the compounds involved as reactants and products, and b) the relative number of moles of each reactant and product consumed or produced in the reaction. Each equation must be balanced; that is, must have the same number of atoms of each element on both sides of the arrow. It is the coefficients in front of each reactant or product which express the ratio of moles of the elements. For example, in the reaction of nitrogen with hydrogen to form ammonia:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

the coefficients tell us that when one mole of N_2 reacts with three moles of H_2, two moles of ammonia will form. If we want to know how many moles of N_2 will be consumed in order to make 0.40 mol of ammonia, we look to the coefficients to tell us that one mole of N_2 must be consumed in order to obtain two moles of ammonia. Therefore:

$$0.40 \text{ mol } NH_3 \times \frac{1 \text{ mol } N_2}{2 \text{ mol } NH_3} = 0.20 \text{ mol } N_2$$

After we know the mole relationships between reactants and products we can also calculate masses, use solutions as reactants and products, or calculate, using the ideal gas equation, the volume of a gas consumed or produced.

Of course, not all reactions go to completion. When we carry out a synthesis we generally express the extent of the reaction in terms of its percent yield. This requires that we first determine how much product would be formed from the specific masses of reactant (this frequently requires that we determine which reactant is the limiting reactant). We then divide the actual yield of the synthetic process by the theoretical yield. This division produces the percent yield.

The last part of the chapter utilizes these mole-mole relationships in several different types of classical analytical procedures.

TERMS

Important terms include:

Stoichiometry The mole relationships between the reactants and products as expressed by the coefficients in a balanced equation.

Reactants The substances on the left hand side of the arrow. These are usually the starting materials for the reaction.

Products The substances of the right hand side of the arrow. These are usually the substances the chemist wants to produce.

Limiting Reactant The reactant that would be totally consumed in the reaction if it went to completion. This number of moles of this reactant determines the amount of product that can be obtained in the reaction.

Yield The extent of the reaction expressed by the amount of a product actually produced divided by the theoretical yield.

Gravimetric Analysis A type of analytical procedure in which the weight of a precipitate is used to determine how much of one of the elements or ions in the precipitate was present in the unknown.

Volumetric Analysis A type of analysis in which the volume of a solution required to react with the substance being analyzed is used to calculate the amount of some substance in the original sample.

Combustion Analysis The combustion (complete reaction with oxygen) of some compounds, especially those that produce CO_2 and water, can be used to determine the percent carbon and hydrogen in a sample.

PROBLEMS

1. What is the mass of aluminum in 1.0 kg of each of the following compounds?
   (a) $AlCl_3$ (b) $KAl(SO_4)_2 \cdot 12H_2O$
2. How many grams of boron are contained in 6.00 g of borax, $Na_2B_4O_7 \cdot 10H_2O$?
3. Determine the percentage composition of the following compounds:
   (a) LiBr (b) FeF_3 (c) K_2CO_3
4. Calculate the empirical formulas of compounds with the following percentage compositions:
   (a) 46.68% N, 53.32% O
   (b) 85.62% C, 14.38% H
   (c) 75.92% C, 6.37% H, 17.70% N
   (d) 58.53% C, 4.09% H, 11.38% N, 25.99% O
5. A certain compound has an empirical formula of CH_2O and a molecular weight of approximately 90. How many moles and how many molecules are there in 50.0 g of the compound? How many carbon atoms are there in 50.0 g of the compound?
6. Determine the molecular formula of the following compound: 40.00% C, 6.72% H, 53.29% O, molecular weight = 180
7. Elemental analysis of sulfathiazole, a sulfa drug, gave the following results: 42.35% carbon, 3.53% hydrogen, 16.48% nitrogen, 12.55% oxygen, and 25.18% sulfur. Calculate the empirical formula for sulfathiazole.
8. A sample of chloroform ($CHCl_3$) weighing 150 g contains
   (a) how many moles of $CHCl_3$?
   (b) how many chloroform molecules?
   (c) what weight of carbon?
   (d) how many chlorine atoms?
   (e) how many moles of hydrogen?
9. How much do one million carbon monoxide (CO) molecules weigh?
10. Balance the following equations:
    (a) $SO_2 + O_2 \rightarrow SO_3$
    (b) $Na + H_2O \rightarrow NaOH + H_2$
    (c) $Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$
    (d) $C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$
    (e) $H_3PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$
    (f) $AgNO_3 + Cl_2 \rightarrow AgCl + N_2O_5 + O_2$
    (g) $Mg_3As_2 + HCl \rightarrow AsH_3 + MgCl_2$
    (h) $Ag_2S + KCN \rightarrow KAg(CN)_2 + K_2S$
    (i) $Pb + Na + C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + NaCl$
    (j) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + H_2O$
11. Consider the complete combustion of 10.0 g of acetylene according to the following equation:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O$$

    (a) How many moles of CO_2 are produced?
    (b) What weight of H_2O is produced?
    (c) How many molecules of O_2 are consumed?
12. The fermentation of sucrose (cane sugar) to produce ethyl alcohol and carbon dioxide can be represented by the following equation:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4\,C_2H_5OH + 4\,CO_2$$

    (a) What is the theoretical mass of ethyl alcohol produced from the fermentation of 450 g of sucrose?
    (b) What weight of CO_2 gas will be liberated during the fermentation of one pound of sucrose?
13. What weight of magnesium metal is required to prepare 100 g of magnesium nitride according to the equation below?

$$2\,NH_3 + 3\,Mg \longrightarrow Mg_3N_2 + 3\,H_2$$

14. The following reaction, carried out at high temperature, is an important step in the commercial preparation of nitric acid:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

    (a) What weight of NO can be produced theoretically from 50 kg of NH_3?
    (b) What weight of O_2 will be consumed in reacting with 10 mol of NH_3?
    (c) What weight of water is produced from the reaction of 10 mol of NH_3?
    (d) How many moles of O_2 will react with 1.0 kg of NH_3?
15. How many grams of SO_2 would be formed by burning 1.00 kg of coal that contains 5.0% sulfur as an impurity? (Assume that SO_2 is the only product formed from the sulfur.)
16. The SO_2 formed in the preceding problem is passed through a suspension of finely ground limestone in water. This is a process used to remove SO_2 from smokestack gases; the reaction is

$$CaCO_3(s) + SO_2(g) \longrightarrow CaSO_3(s) + CO_2(g)$$

    (a) How many grams of $CaSO_3$ are formed?
    (b) How many moles of CO_2 are formed?
17. An 18.0% by weight solution of sugar (sucrose, $C_{12}H_{22}O_{11}$) in water has a density of 1.07 g/mL.
    (a) What volume does 100 g of the solution occupy?
    (b) How many grams of sucrose are present in one liter of solution?
    (c) How many moles of sugar are needed to prepare 150 mL of solution?
18. The elementary substance bromine can be prepared from an aqueous solution of NaBr by reaction with Cl_2:

$$2\,NaBr(aq) + Cl_2 \longrightarrow 2\,NaCl(aq) + Br_2$$

    Sea water contains about 0.0070% by weight NaBr. How many kilograms of sea water are required to produce 1.0 kg of Br_2?
19. If 10.0 g of $CHCl_3$ are dissolved in 1.00 L of ethyl ether ($C_4H_{10}O$; density = 0.708 g/mL), what is the weight percentage of $CHCl_3$ in the resulting solution?

20. A solution containing 20.0% HNO_3 (by weight) has a density of 1.12 g/mL. What volume of this solution contains exactly one mole of HNO_3?

21. Commercial hydrochloric acid contains 36% HCl by weight and has a density of 1.18 g/mL. What volume of this acid solution is required to produce 25.0 g of H_2S by the following reaction?

$$FeS(s) + 2\,HCl(aq) \longrightarrow FeCl_2(aq) + H_2S(g)$$

22. Describe how you would prepare each of the following aqueous solutions:

(a) 500 mL of 0.25 M $CaCl_2$
(b) 2.0 L of 1.30 M Na_2CO_3
(c) 100 mL of 0.102 M KOH

23. How many grams of H_3PO_4 are contained in 27.0 mL of 0.859 M H_3PO_4 solution?

24. What volume of 6.0 M HCl solution would be required to prepare 50.0 g of Cl_2 by the following reaction?

$$4\,HCl + MnO_2 \longrightarrow Cl_2 + MnCl_2 + 2\,H_2O$$

25. The reaction that occurs when current is drawn from a lead storage battery is described by the following equation:

$$Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$$

What volume of 5.0 M H_2SO_4 solution is required to produce 10.0 g of $PbSO_4$?

26. What weight of $FeSO_4$ will be obtained from 50 kg of FeS_2 according to the following equation, if the process gives a 78% yield?

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \longrightarrow 2\,FeSO_4 + 2\,H_2SO_4$$

27. What weight of acetylene (C_2H_2) can be obtained from 2.25 g of calcium carbide, if the CaC_2 is only 92% pure?

28. If 20.0 g of PCl_5 react with an excess of water to give an 89% yield of H_3PO_4, what weight of H_3PO_4 is obtained? The reaction is

$$PCl_5 + 4\,H_2O \longrightarrow H_3PO_4 + 5\,HCl$$

29. If 100 g of Ag and 100 g of S are heated together, what is the theoretical yield of Ag_2S, according to the following equation?

$$2\,Ag + S \longrightarrow Ag_2S$$

30. Copper (II) phosphide (Cu_3P_2) may be prepared by reaction of phosphine with an aqueous solution of copper sulfate, according to the following equation:

$$3\,CuSO_4 + 2\,PH_3 \longrightarrow Cu_3P_2 + 3\,H_2SO_4$$

When 10.0 g of PH_3 were added to a solution containing 50.0 g of $CuSO_4$, 20.0 g of Cu_3P_2 were obtained. Calculate (a) the theoretical yield and (b) the percentage yield.

31. How much iron can be obtained from 100 kg of an iron ore containing 42.25% hematite (Fe_2O_3)?

32. Hardware brass is dissolved in nitric acid, and then H_2SO_4 is added to the solution to precipitate $PbSO_4$. A 1.6841-g sample of brass yielded 0.4671 g of $PbSO_4$. Calculate the percentage of lead in hardware brass.

33. A sample of the mineral witherite ($BaCO_3$) was dissolved in hydrochloric acid and the barium ion precipitated as barium sulfate. If a 0.4324-g sample of the witherite yielded 0.4705 g of $BaSO_4$, calculate (a) the percentage of barium in the sample and (b) the percentage purity of the witherite.

34. A sample of aluminum ore weighing 0.6036 g was dissolved and the aluminum precipitated as $Al(OH)_3$. Ignition gave 0.2105 g of Al_2O_3. What was the percentage of Al in the ore?

35. Calculate the percentage purity of the mineral chalcopyrite ($Cu_2S{\cdot}Fe_2S_3$) if a 1.0230-g sample yielded 0.8530 g of SO_3. (All the sulfur in the mineral was converted into SO_3.)

36. When 50.00 mL of a H_2SO_4 solution were titrated with 0.2000 M NaOH solution, 38.20 mL of the latter were required. What was the molarity of the H_2SO_4 solution? The equation for the reaction is

$$H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$$

37. A sample of pure NaCl weighing 0.2500 g was dissolved in water, and the resulting solution was titrated with a $AgNO_3$ solution. If 32.85 mL of the $AgNO_3$ solution were required, what was the molarity of that solution?

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

38. A sample of pure $K_2C_2O_4$ weighing 0.3030 g was dissolved in water, an excess of H_2SO_4 was added, and the solution was titrated with a solution of $KMnO_4$. The equation for the reaction is

$$2\,KMnO_4 + 5\,K_2C_2O_4 + 8\,H_2SO_4 \longrightarrow 6\,K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O$$

If 46.50 mL of the $KMnO_4$ solution were required to reach the endpoint, what was the molarity of that solution?

39. A sample of iron ore weighing 4.3128 g was dissolved and treated to convert the iron quantitatively into $FeSO_4$. An excess of H_2SO_4 was added, and the solution was then titrated with 0.08000 M $K_2Cr_2O_7$ solution, of which 28.25 mL were required. The equation is

$$6\,FeSO_4 + 7\,H_2SO_4 + K_2Cr_2O_7 \longrightarrow 3\,Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7\,H_2O$$

What was the percentage of Fe in the ore?

40. A 25.00-mL sample of H_2O_2 solution required 32.50 mL of 0.2714 M $KMnO_4$ solution for titration by the following reaction:

$$5\,H_2O_2 + 2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow 2\,MnSO_4 + K_2SO_4 + 5\,O_2 + 8\,H_2O$$

The H_2SO_4 was present in excess. What was the molarity of the H_2O_2 solution?

41. A sample of impure $Ca(OH)_2$ (slaked lime) weighing 0.2194 g required 42.42 mL of 0.1200 M HCl solution when titrated, using the reaction

$$Ca(OH)_2 + 2\,HCl \longrightarrow CaCl_2 + 2\,H_2O$$

What was the percentage of $Ca(OH)_2$ in the sample?

42. Combustion analysis of a 0.1020-g sample of a compound yielded 0.2736 g CO_2 and 0.0672 g H_2O. What was the percentage of carbon and hydrogen in the compound?

43. One method for determining the percentage of nitrogen in a compound involves its quantitative conversion into nitrogen gas (N_2), which is collected and measured. A 0.1000-g sample of a compound yielded 11.5 mL of N_2. The density of N_2 at the temperature and pressure at which the measurement was made was 1.11 g/L. Calculate the percentage of nitrogen in the compound.

44. A sample of nicotine, a compound containing only carbon, hydrogen, and nitrogen, was subjected to combustion analysis. A 0.2340-g sample of nicotine yielded 0.1826 g of H_2O and 0.6329 g of CO_2.

(a) Calculate the percentage composition of nicotine.
(b) What is the empirical formula of nicotine?

45. The alkaloid strychnine, a compound containing carbon, hydrogen, nitrogen, and oxygen, was submitted for elemental analysis. Combustion of a 0.3432-g sample in oxygen gave 0.2032 g H_2O and 0.9483 g CO_2. A 0.4932-g sample yielded 36.5 mL of nitrogen gas, with a density of 1.13 g/L. The molecular weight of the compound was found to be 334. Calculate (a) the percentage composition, (b) the empirical formula, and (c) the molecular formula.

12

Rates of Reaction

A chemical equation is a concise statement about a reaction that describes the reactants, the products into which they are converted, and the molar ratios pertaining to this conversion. It does not communicate anything about the speed with which the conversion takes place. Yet knowledge of the speed of a reaction—called the **reaction rate**—is often of great importance if we want to use the reaction as a preparative process or gain an understanding of the mechanism by which the reaction proceeds.

In general, the rate of any process is measured in terms of a quantity per unit of time. The rate at which an automobile travels is measured in miles per hour, and the rate of the flow of water from a pipe may be measured in gallons per minute. The rate of a chemical reaction is usually measured in terms of the change in concentration of a reactant or a product per unit of time, and the most commonly used concentration expression is that of molarity. Thus, for example, in the hypothetical reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

the rate might be expressed as the number of moles per liter of A (or B) consumed per minute or as the number of moles per liter of C (or D) produced per minute. For this case,

$$\text{Rate} = \frac{-\Delta[\mathrm{A}]}{\Delta t} = \frac{-\Delta[\mathrm{B}]}{\Delta t} = \frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{\Delta[\mathrm{D}]}{\Delta t}$$

where the symbol Δ represents a change* for either a concentration (brackets are used to designate concentration in moles per liter) or a time. If the stoichiometric coefficients of reactants or products have values other than one, then the rate must be defined to accommodate these values. For example, if the reaction is

$$\mathrm{A} + 3\,\mathrm{B} \longrightarrow 2\,\mathrm{C}$$

then the rate may be defined as

$$\text{Rate} = \frac{-\Delta[\mathrm{A}]}{\Delta t} = \frac{-\Delta[\mathrm{B}]}{3\Delta t} = \frac{\Delta[\mathrm{C}]}{2\Delta t}$$

The division by three for reactant B is required because it is consumed three times faster than reactant A is consumed, and the division by 2 for product C is necessary because it is produced at twice the rate of the consumption of reactant A.

For any given reaction, the rate is greatly influenced by the specific conditions imposed upon it. Furthermore, for most reactions the rate is not constant with time but is a maximum at the start of the reaction and gradually decreases with time. Therefore, a reaction rate is a measure of the speed with which reactants are converted into products *at a given instant under a given set of conditions*. The study of reaction rates and the factors that influence them is known as **chemical kinetics**.

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* A minus sign in front of Δ[A] means that the concentration of A decreases per unit time.

Reactions are divided into two categories: homogeneous and heterogeneous. **Homogeneous reactions** take place in a single phase; that is, the reaction mixture is a solution. Some examples are

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

In the reaction of hydrochloric acid and sodium hydroxide, which produces an aqueous salt solution, everything occurs in water, the solvent. In the given ammonia synthesis, all reaction steps are completed in the gas phase. In **heterogeneous reactions**, however, the reaction mixture consists of more than one phase, and reaction occurs at a phase boundary. The following equations illustrate this category:

$$Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$

In the first example, aqueous hydrochloric acid reacts on the surface of zinc metal to give aqueous zinc chloride and hydrogen gas. In the second heterogeneous example, gaseous carbon dioxide reacts with solid calcium oxide to produce another solid, calcium carbonate.

12.1 FACTORS THAT DETERMINE REACTION RATE

Nature of the Reactants

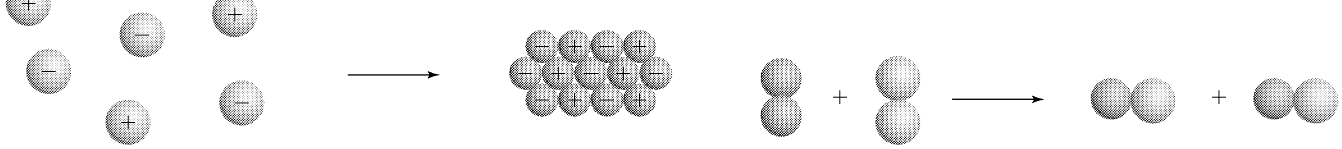
Since chemical reactions are processes involving the making and breaking of bonds, the rate of a reaction depends on the specific bonds formed and broken, and therefore on the specific structure and composition of the reactants. The reaction rates observed for different reactants vary widely from very slow to extremely fast.

Most reactions involving the combination of ions—for example, aqueous acid-base neutralization, or precipitation of an ionic solid from aqueous solution—occur very rapidly (see Figure 12.1a). Most nonionic reactions occur at considerably lower rates, and require minutes or hours to reach completion (see the reaction of N_2 with O_2 to form NO in Figure 12.1b). The rates of some very slow reactions (such as the rusting of iron) might be measured more conveniently in terms of months or years.

Concentration of the Reactants

For homogeneous chemical reactions, the reaction rate depends (for the most part) on the concentrations of the reactants. The precise relationship between concentration and rate for any particular reaction is not predictable from the equation and must be determined experimentally. In general, however, the rate of a homogeneous reaction is proportional to the product of the molar concentrations of the reactants, each raised to some power. Thus, for the generalized reaction

$$aA + bB + \cdots \longrightarrow$$



(a) (b)

Figure 12.1 The Rates of Reactions Depend Upon the Nature of the Reactants. Reactions involving ions (a) are generally faster than those involving uncharged molecular species (b).

the reaction rate and the concentrations of reactants are related by the following expression:

$$\text{Rate} \propto [\text{A}]^m[\text{B}]^n \cdots$$

The bracket pair around a chemical symbol or formula is the conventional notation for molar concentration. By using a proportionality constant, k, this expression may be converted into a mathematical equation:

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \cdots$$

This equation is called the **rate law** for the particular reaction in question, because it expresses the relationship between reaction rate and concentration of reactants under a specified set of conditions. The constant k is called the **specific rate constant** and is characteristic of that reaction at those specified conditions. Once the value of k has been determined for a particular reaction, the reaction rate can be predicted for any stated initial concentrations of A and B, provided the specified conditions are maintained.

The exponents m and n in the generalized rate law are often referred to as the **order** of the reaction; m is the order with respect to substance A, n is the order with respect to B, and the sum $m + n$ is the overall order of the reaction. Thus, a hypothetical reaction for which the rate law is

$$\text{Rate} = k[\text{X}][\text{Y}]^2$$

is first order with respect to X, second order with respect to Y, and third order overall.

The values of m and n in the generalized rate equation cannot be predicted from the stoichiometry of the chemical equation; they must be determined experimentally. It is erroneous to assume that the coefficients of the balanced equation are the exponents in the rate law, although this is true when the reaction occurs in a single step. However, most reactions proceed by a mechanism that involves several steps, that is, several successive reactions. Each of these steps proceeds at its own rate, and each rate is dependent on the concentrations of the substances that are the reactants for that step. Thus, a chemical equation describes the stoichiometry of the overall reaction; it implies nothing about the stoichiometry of the individual steps involved.

Although the values of m and n are usually positive integers, they may be fractions, negative, or even zero. Again, this is the result of the fact that the overall rate of a reaction is often the summation of a multistep process. The relationship of reaction rate to reaction mechanism is discussed further later in this chapter.

Table 12.1 lists a few simple homogeneous reactions and their experimentally determined rate laws. Note that in some cases the exponents are the same as the coefficients of the equations; in other cases they are not.

The reaction of nitrogen oxide with oxygen is described by the following equation:

$$2\,\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\,\text{NO}_2(g)$$

For this reaction at 500 °C the experimental rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

TABLE 12.1 The Rate Laws of Some Homogeneous Reactions

REACTION	RATE LAW
$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$	$r = k[N_2O_5]$
$2\,N_2O \rightarrow 2\,N_2 + O_2$	$r = k[N_2O]^2$
$CH_3CHO \rightarrow CH_4 + CO$	$r = k[CH_3CHO]^2$
$2\,NO + O_2 \rightarrow 2\,NO_2$	$r = k[NO]^2[O_2]$
$F_2 + 2\,ClO_2 \rightarrow 2\,FClO_2$	$r = k[F_2][ClO_2]$
$2\,H_2 + 2\,NO \rightarrow 2\,H_2O + N_2$	$r = k[H_2][NO]^2$

When the concentrations of NO and O_2 are each 0.50 mol/L, the rate of formation of NO_2 is 0.010 M/min (or mol/L-min).

From these data the specific rate constant, k, at 500 °C can be calculated by rearranging the expression for the rate law and inserting the corresponding values. That is

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{\left(\dfrac{0.010\ \text{mol}}{\text{L-min}}\right)}{\left(\dfrac{0.50\ \text{mol}}{1\ \text{L}}\right)^2\left(\dfrac{0.50\ \text{mol}}{1\ \text{L}}\right)}$$

or

$$k = \left(\frac{0.010\ \text{mol}}{\text{L-min}}\right)\left(\frac{1\ \text{L}}{0.50\ \text{mol}}\right)^2\left(\frac{1\ \text{L}}{0.50\ \text{mol}}\right)$$

Evaluation of this equation gives the rate constant:

$$k = 0.080\,\frac{\text{L}^2}{\text{mol}^2\text{-min}} \quad \text{or} \quad k = 0.080\ \text{M}^{-2}\ \text{min}^{-2}$$

Now that the value of the rate constant is known, the rate of production of NO_2 at 500 °C can be determined for various concentrations of the reactants. For example, if the concentration of NO is 0.10 mol/L and the concentration of O_2 is 0.30 mol/L, the rate of NO_2 formation is obtained by inserting these values into the rate law equation.

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

Therefore,

$$\text{Rate} = \left(\frac{0.080\ \text{L}^2}{\text{mol}^2\text{-min}}\right)\left(\frac{0.10\ \text{mol}}{1\ \text{L}}\right)^2\left(\frac{0.30\ \text{mol}}{1\ \text{L}}\right)$$

and solving for the rate gives

$$\text{Rate} = 2.4 \times 10^{-4}\,\frac{\text{mol}}{\text{L-min}} \quad \text{or} \quad 2.4 \times 10^{-4}\ \text{M/min}$$

The effect of concentration on reaction rate cannot be stated so simply for heterogeneous reactions. In a heterogeneous reaction, the reactants are not components of the same solution, and therefore the relative amount of reactants present cannot be expressed meaningfully in terms of molarity. The reaction between metallic zinc and hydrochloric acid is a good example:

$$\text{Zn}(s) + 2\ \text{HCl}(aq) \longrightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$$

The concentration of HCl in the solution may be described in terms of molarity, but because the zinc is not dissolved in the solution, an expression of its concentration is meaningless. Because the reaction takes place at the boundary between the solid and the liquid phases, the area of contact between the two phases influences the reaction rate. More finely divided zinc, with its greater surface area, yields a faster reaction. The

Problem 12.1

Use Table 12.1 to calculate the rate of formation of CH_4 from acetaldehyde given that k = 0.010 $M^{-1}min^{-1}$ and $[CH_3CHO]$ = 0.50 M.

Solution:

$$\begin{aligned}\text{Rate} &= k\,[\text{CH}_3\text{CHO}]^2 = 0.010\ \text{M}^{-1}\text{min}^{-1}(0.50\ \text{M})^2 \\ &= 0.0025\ \text{M/min}\end{aligned}$$

effect of particle size on reaction rate applies to heterogeneous reactions in general, where one or more of the reactants is a solid.

The effect of particle size has been strikingly illustrated by numerous coal mine explosions resulting from the ignition of bituminous dust. A lump of coal requires a high temperature for ignition, and once ignited, it burns slowly and quietly. In contrast, finely divided coal dust suspended in air may be ignited by a match with explosive violence. Similar disasters have occurred in factories and mills from the ignition of fine dusts of other combustible materials.

✓ Check Point 12.1

The rate law for a given reaction is

$$\text{Rate} = k[\text{A}][\text{B}]^3$$

What is the order of the reaction with respect to A?
What is the order of the reaction with respect to B?
What is the overall order of the reaction?

Solution:

first
third
fourth

◇ ◇ ◇ ◇ ◇

Temperature

The effect of temperature on reaction rates is summarized very simply: reaction rates increase with increasing temperature. This relationship holds for both endothermic and exothermic reactions. What it means in terms of the rate law is that an increase in temperature increases the specific rate constant k, and a decrease in temperature decreases k. The effect is quite marked. Generally, for each 10 °C rise in temperature, the reaction rate is approximately doubled. (This rough approximation should not be used in quantitative calculations.) The actual magnitude of the temperature effect must be determined experimentally for each reaction.

Catalysis

The rates of some chemical reactions are increased by the presence of certain substances that are not consumed in the overall reactions and therefore do not appear as reactants or products in the chemical equations. These substances are called **catalysts**, and their rate-increasing effect is called **catalysis**. Any reaction whose rate is increased by a catalyst is said to be **catalyzed**.

Several important facts concerning catalysts should be emphasized. First, a catalyst does not *cause* a reaction to occur. If a reaction is thermodynamically impossible under a specified set of conditions, then that reaction will not take place with or without a catalyst. The catalyst merely increases the *rate* of the reaction by providing an alternate path—a different mechanism—by which the reaction can proceed. Second, a catalyst does not speed up a chemical reaction by its mere presence; it plays an active role. Although the catalyst is not consumed in the overall reaction and may be recovered unchanged from the reaction mixture, it may undergo chemical change during some of the steps of the process. The catalyst may be used up in one step and regenerated in a later step, so that it reacts over and over again without undergoing any net change. This characteristic is illustrated by a proposed mechanism for the decomposition of hydrogen peroxide, for which iodide ion is a catalyst:

$$\begin{array}{rcll}
H_2O_2 + I^- & \longrightarrow & H_2O + IO^- & \text{(catalyst consumed)} \\
H_2O_2 + IO^- & \longrightarrow & H_2O + O_2 + I^- & \text{(catalyst regenerated)} \\
\hline
2\,H_2O_2 & \longrightarrow & 2\,H_2O + O_2 & \text{(overall reaction)}
\end{array}$$

In the reaction of a carboxylic acid with an alcohol, the presence of the hydrogen ion (the catalyst) increases the rate of the reaction tremendously and makes this reaction a feasible synthetic path for the preparation of *esters*. An ester has the generic formula RCOOR′ where R′ cannot be H. The mechanism given in Figure 12.2 shows the role of the hydrogen ion in the reaction:

A third important aspect of catalysis lies in the fact that whatever effect a given catalyst has on a specific reaction, its effect on the reverse of that reaction is the same. Thus, if a catalyst doubles the rate at which A and B react to form C and D, then that same catalyst will also double the rate at which C and D react to form A and B, given the same set of conditions.

When the catalyst is in the same phase as the reactants and products of the reaction—such as the iodide ion in the aqueous decomposition of hydrogen peroxide just cited—the catalysis is **homogeneous**. Catalysis in which the catalyst is in a separate phase from the reactants and the reaction occurs at the catalytic surface is called **heterogeneous** or **surface catalysis**. An example is the gaseous hydrogenation of an alkene using finely divided platinum as a catalyst:

$$CH_2{=}CH_2 \longrightarrow CH_3CH_3$$

In some instances, the presence of a substance in a reaction mixture may bring about a *decrease* in the reaction rate. Such a substance, which is called a **negative catalyst**, or **inhibitor**, functions by interfering with the normal mechanism of the uncatalyzed reaction.

Catalysis is a common phenomenon in nature. Nearly all of the multitude of complex chemical reactions that occur in living organisms are catalyzed by highly specific catalysts called **enzymes**. These enzymes, most of which are very high-molecular-weight protein molecules, permit vital reactions to occur at high rates in spite of the low concentrations and low temperatures that exist in living cells. The breakdown of complex nutrient molecules (fats, carbohydrates, and proteins) and the subsequent synthesis of nucleic acids, vitamins, hormones, lipids, and a host of other vital substances (including enzymes themselves) involve enzyme-catalyzed reactions. Moreover, unlike most chemical reactions performed in a laboratory, enzyme-catalyzed reactions give 100% yield; that is, there are no side reactions and no unwanted by-products.

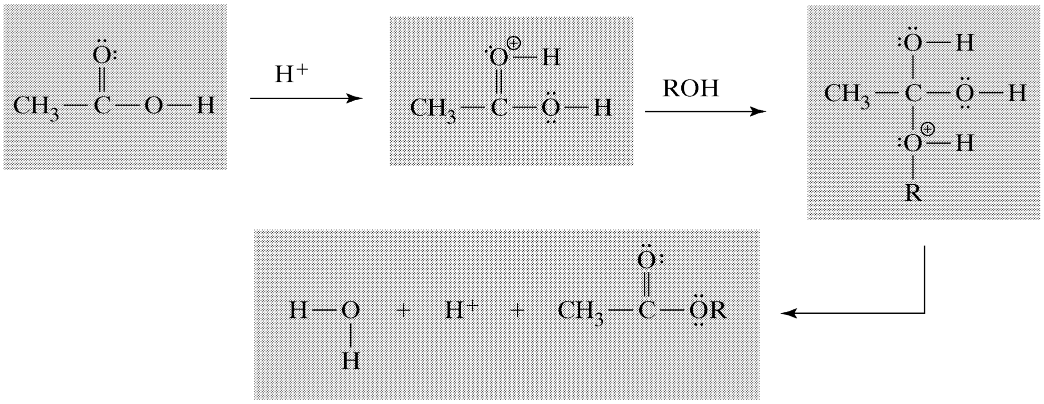


Figure 12.2 A mechanism for esterification reactions.

12.2 THEORY OF REACTION RATES

The foregoing discussion has been largely a reporting of observed facts that describe the influence of various conditions on the rate of chemical reactions. In order to explain this body of facts, a model has been developed that can be used to interpret the described behavior on the molecular level.

Collision Theory

The **collision theory**, which is an extension of the kinetic molecular theory of gases, holds as its basic assumption that in order for a reaction to occur, the reacting particles (molecules, atoms, or ions) must collide. For compounds A and B to react with each other, molecules of A must undergo collision with molecules of B in such a way that electrons and atoms are rearranged, leading to the formation of new substances. The greater the frequency of these collisions, the greater the rate of reaction. Therefore, any change of conditions that increases the frequency of collisions will also increase the reaction rate.

Although collisions are essential, not every collision between reactants results in reaction. By calculation from the kinetic molecular theory, the number of collisions between molecules in one liter of gas at STP is between 10^{31} and 10^{32} collisions per second. Obviously, if every collision resulted in reaction, all reactions would occur instantaneously. Therefore, the total number of collisions must be distinguished from the number of *effective* collisions (i.e., those that result in a reaction). Many reactions have such a low reaction rate that the number of effective collisions per unit of time must be a very small fraction of the total number of collisions occurring during that time.

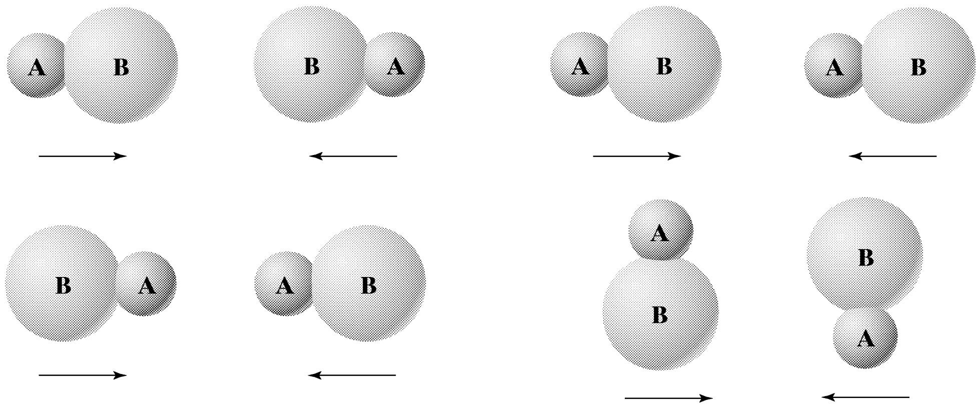
The fact that some collisions are ineffective may be explained by considering two factors. The first of these is the orientation of the colliding reactants. Most molecules are not simple spheres; therefore colliding molecules will have a large variety of different positions, relative to one another, at the instant of collision. Many of these positions will be unfavorable for the breaking and making of bonds necessary to the reaction. Only certain orientations can lead to effective collisions. This condition for reaction is illustrated in Figure 12.3 for the simple reaction

$$2\ AB \longrightarrow A_2 + B_2$$

which proceeds in a single step by direct collision of two molecules of AB.

A second, more significant factor in determining the effectiveness of collision is the kinetic energy of the colliding molecules. Recall that the molecules of a gas are in constant linear motion and that, because of their velocity and their mass, they possess kinetic energy. At any given instant, the molecules in a gas sample have a wide range of velocities and therefore a wide range of kinetic energies. As a result of random collisions, the instantaneous velocities of some molecules will be very low, while other molecules will have very high velocities because momentum was transferred to them through collisions. Thus, the kinetic energy of any individual molecule is constantly changing with time. However, in a measurable sample of gas, such a large number of molecules is present that at any one time the number of molecules with a particular velocity will be essentially constant. A very small fraction of the molecules will have extremely high or low kinetic energies, while most of the molecules will have kinetic energies close to some average value. This statistical distribution, shown graphically in Figure 12.4, is called a **Maxwell-Boltzmann distribution curve**; it has been predicted theoretically and confirmed experimentally. Note that the curve is not symmetrical, since it is limited to zero at the low-energy end while the high-energy end is limitless. The maximum in the curve represents the most probable kinetic energy; that is, a larger fraction of the molecules possess that kinetic energy than any other. Because the curve is skewed, the average kinetic energy is somewhat higher than the most probable kinetic energy.

Collisions between the reactant molecules occur with a wide range of total kinetic energies. Because the electron clouds surrounding molecules produce a force of repulsion, if



Ineffective collision: no reaction

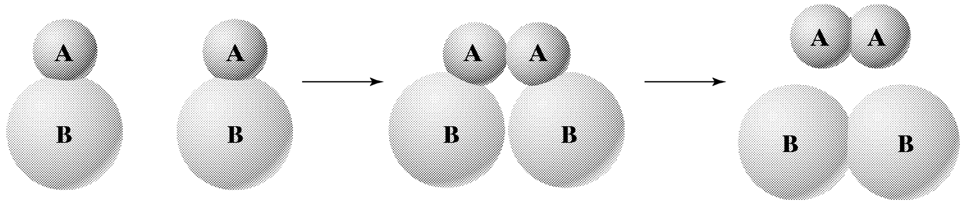


Figure 12.3 The effect of orientation on reaction rate.

two molecules with low kinetic energy collide, then the repulsion between the electron clouds will cause them to rebound without any reaction. For a collision to be effective, the colliding molecules must have sufficiently high kinetic energy to overcome the mutual repulsion of the electron clouds. Only then can the molecules penetrate each other far enough to permit the rearrangement of electrons that constitutes the making and breaking of bonds.

For each reaction, therefore, the colliding reactants must possess some minimum amount of energy in order for the collision to be effective. This minimum amount is called the **activation energy**, symbolized E_a. As the Maxwell-Boltzmann distribution curve reveals, not all molecules will possess sufficient energy, and therefore only a fraction of the total collisions will be effective.

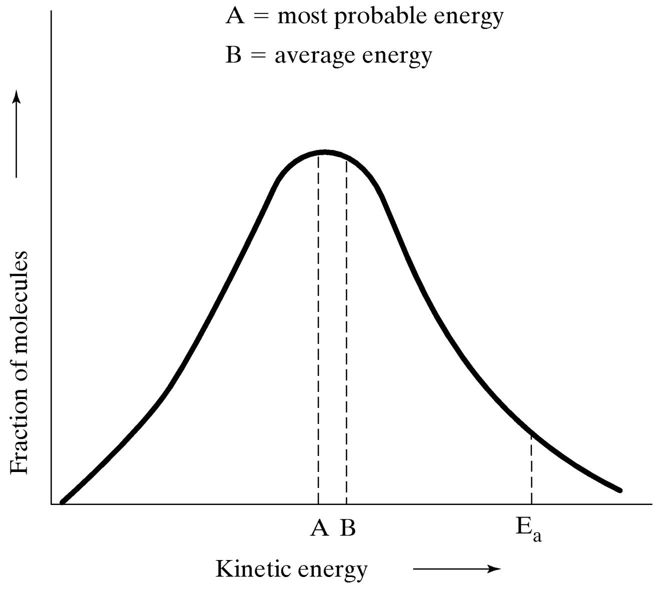
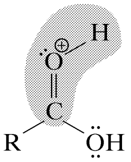


Figure 12.4 The Maxwell-Boltzmann distribution of kinetic energy.

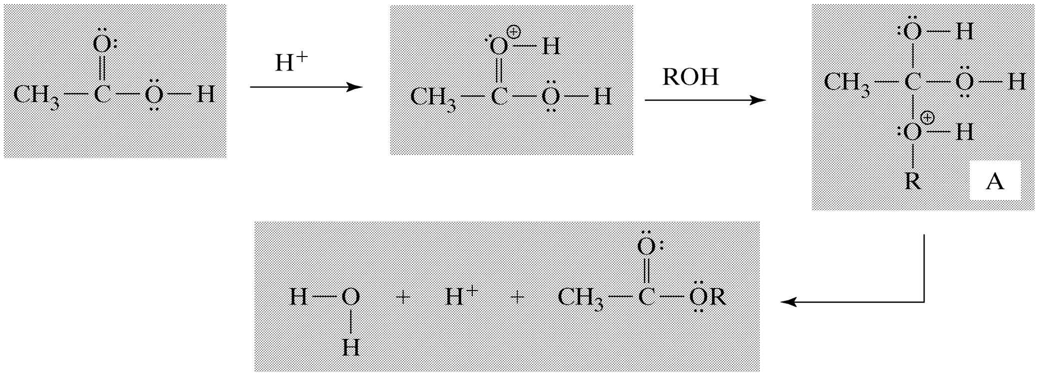
Visualization 12.1

Examine the diagram below, in which the gray depicts electron density, and explain how the hydrogen ion affects E_a in the esterification reaction shown previously:



Solution:

After we learn more about mechanisms, we can explain the effect of the hydrogen ion more carefully; but for now a sufficient rationalization points to the fact that the hydrogen ion forms a bond with one of the lone pairs on the carbonyl oxygen of the acid, thereby giving that oxygen a formal positive charge. Electron density is thereby removed from the carbon and the carbon has a partial positive charge. The carbon is therefore more attracted to the lone pair of electrons of the incoming alcohol. The energy (E_a) required to form the intermediate is consequently reduced (In the equation below, some reagents are shown above the arrow. This procedure helps to direct attention to the most important species in the reaction.):



The three major aspects of collision theory—i.e., collision rate, collisional orientation and kinetic energy—may be combined into one expression for the rate constant, k:

$$k = pZe^{-E_a/RT}$$

In this expression Z is the collision number, and it is directly related to the frequency of collisions. The probability that the reactants have an appropriate orientation when they collide is given by p. The value of p may be rather small; for example, in the reaction of atomic bromine with diatomic hydrogen, $p \sim 0.1$. The exponential term in the equation (E_a/RT) is related to the fraction of molecules that have sufficient energy (E_a) to react at a given temperature (T).

Although the discussion of molecular energy and molecular collisions has been based on the gaseous state, the same considerations apply, in general, to reacting species in liquid solution.

Problem 12.2

At 50 °C the rate constant of a particular reaction is $2.6 \times 10^{-4}\ \mathrm{M^{-1}\,s^{-1}}$. The energy of activation is 109 kJ/mol, and the collision number is $4 \times 10^{16}\ \mathrm{M^{-1}s^{-1}}$. What is the probability that colliding reactant molecules will have the appropriate orientation to react?

Solution:

From collision theory, $k = pZe^{-E_a/RT}$, therefore:

$$2.6 \times 10^{-4}\ \mathrm{M^{-1}\,s^{-1}} = (p)(4 \times 10^{16}\ \mathrm{M^{-1}\,s^{-1}})e^{-(109{,}000\ \mathrm{J/mol})/((8.314\ \mathrm{J/mol\text{-}K})\ (323\ \mathrm{K}))}$$

$$2.6 \times 10^{-4}\ \mathrm{M^{-1}\,s^{-1}} = (p)(4 \times 10^{16}\ \mathrm{M^{-1}\,s^{-1}})(2.36 \times 10^{-18})$$

$$p = 0.003$$

Thus, about 0.3% of all collisions have the appropriate orientation. Note: The value of p has only one significant figure because the collision number (Z) has only one significant figure.

Transition State Theory

An extension of the collision theory, known as the **transition state theory**, is aimed at a more detailed description of the collision process and the relation of this process to the activation energy. The basic postulate of this theory is that an effective collision between reactant molecules results in the formation of an unstable, transitory intermediate species called the **transition state**, or **activated complex**. As the two colliding molecules contact each other, some bonds become longer and weaker, and some new bonds begin to form. Therefore, the activated complex may be visualized as being held together by "partial" bonds. Although this activated complex does not represent a substance that can be observed or isolated, it is considered to have many of the same properties as real molecules, such as molecular weight, bond lengths and angles, and energy. The formation of the activated complex and its relationship to the reactants and products of the reaction are illustrated in Figure 12.5 for the simple hypothetical reaction

$$2\ \mathrm{AB} \longrightarrow \mathrm{A_2} + \mathrm{B_2}.$$

As its name implies, the activated complex is at a relatively high energy level; it possesses greater energy than either the reactants or the products. This relationship is shown graphically in Figure 12.6, where the potential energy of the system is plotted against the reaction coordinate (a measure of how far the reaction has proceeded). The reactants have some average potential energy, E_1. When a collision occurs between reactant molecules, work must be done on the system to overcome the mutual repulsion of the electron clouds. In other words, the potential energy must increase. This increase in potential energy is accomplished by conversion of some of the kinetic energy of the colliding molecules into potential energy. In order for a collision to be effective (that is, in order for the activated complex to be formed), the potential energy must reach E_2. The collision of molecules of low kinetic energy may provide an amount of potential energy somewhere between E_1 and E_2, but not enough to result in formation of the activated complex. These molecules move apart unchanged. (In terms of the energy diagram, this situation corresponds to moving partially up the hill and then sliding back down.) However, if the total

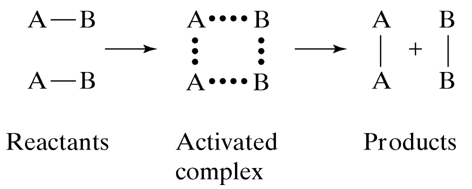


Figure 12.5 Formation of the activated complex.

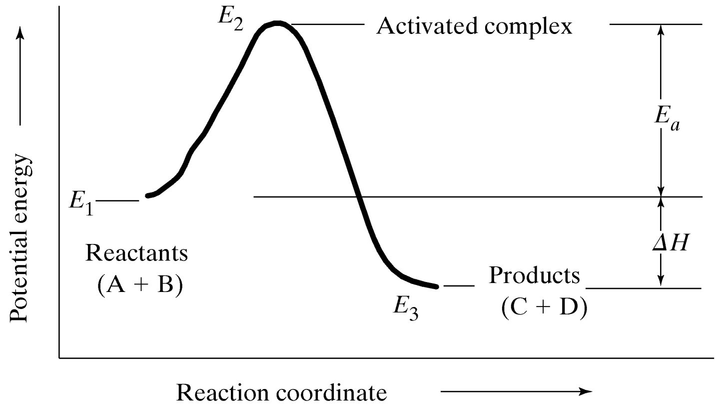


Figure 12.6 The energy of the system as a function of the progress of the reaction: a reaction profile.

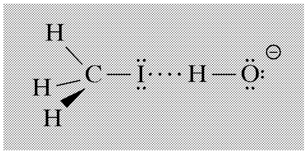
kinetic energy of the colliding molecules is sufficiently great, the necessary potential energy, E_2, will be reached and the activated complex will be formed. The potential energy barrier that must be overcome to form the activated complex—that is, the difference between the potential energy of the activated complex (E_2) and that of the reactants (E_1)—is the activation energy (E_a). Once the activated complex is formed, it "splits apart" and forms the products, and the potential energy decreases to E_3. (The system slides down the other side of the hill in the energy diagram.)

Visualization 12.2

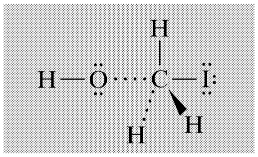
For the single-step reaction

$$CH_3I + OH^- \longrightarrow CH_3OH + I^-$$

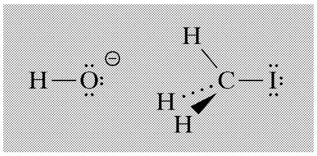
which of the following is most likely to be the transtion state for the reaction?



(a)



(b)



(c)

Solution:

Diagram (b) shows the hydroxide forming a bond to the carbon to which it ultimately (in the product) becomes attached. Diagram (a) shows the iodine and hydrogen forming a bond, which presumably would lead to the formation of HI (which is not a product). Diagram (c) shows the hydroxide ion approaching the methyl iodide, but it has not yet begun to form a bond to the carbon. It therefore is not a transition state. The correct answer is (b).

The energetics of the reverse reaction can also be interpreted in terms of Figure 12.7. The diagram represents the general reaction

$$A + B \longrightarrow C + D$$

The reverse reaction is then

$$C + D \longrightarrow A + B$$

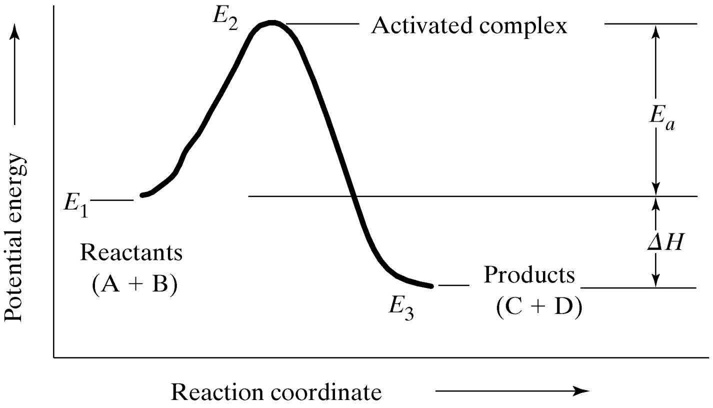


Figure 12.7 The potential energy change during an exothermic reaction.

In this reverse reaction, the activated complex formed is the same as that formed in the forward reaction, but now the reaction coordinate in the diagram is proceeding from right to left. Energetically, the system must move up and over the hill from right to left. Thus, the activation energy is $E_2 - E_3$.

It should be noted that Figure 12.7 represents an *exothermic* reaction, for the products possess less energy than the reactants. The difference between the average energy of the products and the average energy of the reactants ($E_3 - E_1$) is the energy released in the reaction (labeled ΔH in Figure 12.7). The magnitude of ΔH is dependent only on the reactants and the products, not on the pathway, and it is therefore not related to either the rate or the activation energy. For comparison, a similar energy diagram of an *endothermic* reaction is given in Figure 12.8. Note that in this case, ΔH represents the energy absorbed in the reaction, which is also independent of rate and activation energy.

For any reaction that occurs in a single step (or any single step in a multistep reaction), the rate of formation of the activated complex determines the rate of the reaction. Moreover, other conditions being equal, the lower the activation energy is, the higher the fraction of collisions that will be effective and the greater the reaction rate will be.

12.3 RATIONALIZATION OF RATE-DETERMINING FACTORS

Taken together, the two theories just described provide a satisfactory model for explaining many of the known facts regarding reaction rates. Let us now return to the four factors that determine the rate of a chemical reaction—nature of the reactants, concentration of the reactants, temperature, and catalysis—and apply our model to the explanation of their effects.

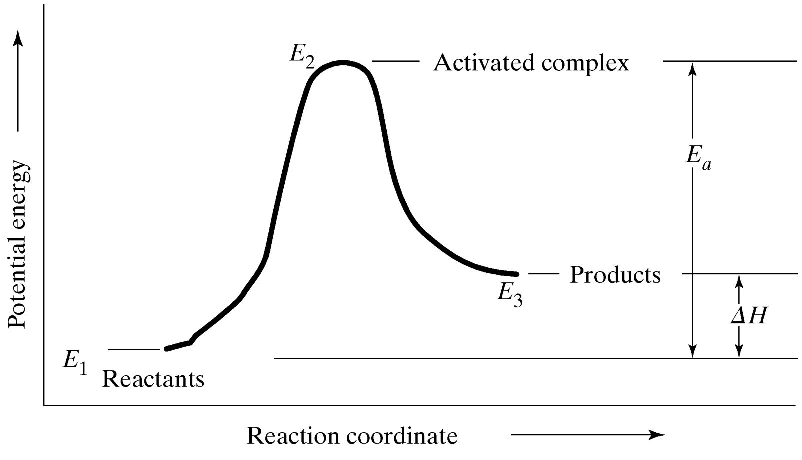


Figure 12.8 A potential energy diagram for an endothermic reaction.

Nature of the Reactants

The fact that different reactions occur at widely different rates, even though the same set of conditions is maintained, can be explained on the basis of a difference in activation energy. The nature of the reactants determines the nature of the activated complex and therefore the activation energy. In general, very fast reactions have low activation energies; slower reactions have higher activation energies.

Concentration of the Reactants

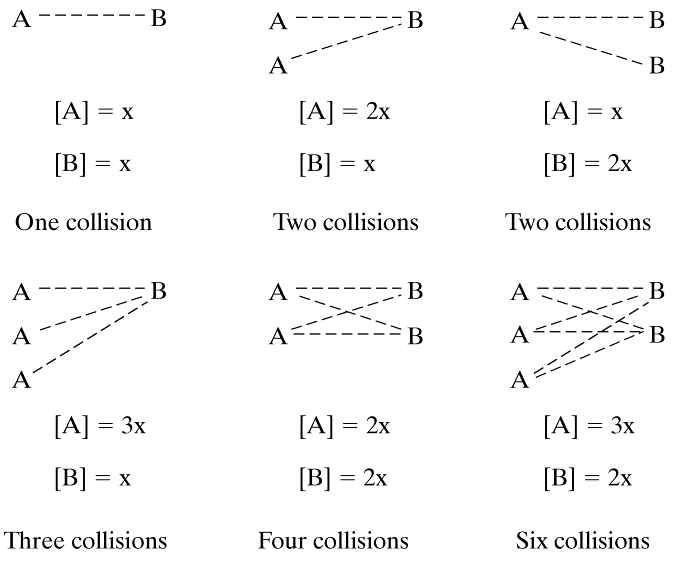
The effect of concentration on reaction rate can be explained simply on the basis of frequency of collisions. If the number of molecules per unit of volume is increased, then the number of molecular collisions occurring per unit of time is also increased.

Consider again the simple hypothetical example of the one-step reaction between A and B, for which the rate law is $r = k[\mathrm{A}][\mathrm{B}]$. The effect of concentration on the number of collisions is shown in Figure 12.9. If we assume a volume so small that it contains only one molecule of A and one of B, then only one collision is possible. When the number of molecules of A in the same volume is doubled, the number of possible A–B collisions is doubled. Similarly, with one molecule of A and two of B, two A–B collisions are possible. In short, the number of collisions per unit of time is directly proportional to the concentrations of both A and B, and this result is in agreement with the rate law.

Although changing the concentration of a reactant changes the *total* number of collisions per unit of time, the change does not have any effect on the fraction of the total collisions that result in reaction. This fraction can be changed only by a change in temperature or by use of a catalyst. However, because increasing the concentration increases the total number of collisions, it must also increase the number of *effective* collisions per unit of time. For example, if one-tenth of all collisions are effective and if there are 1,000 collisions, then 100 of these will result in reaction. If the concentration is increased sufficiently to cause 2,000 collisions, while keeping other conditions constant, the number of effective collisions will be one-tenth of 2,000, or 200. Thus, doubling the total number of collisions also doubles the number of effective collisions.

Temperature

In accounting for the increase in reaction rate caused by an increase in temperature, consideration must be given to two different aspects of the effect of temperature on molecular energy. First, because the kinetic energy of a molecule is directly proportional to the



$[\mathrm{A}] = \mathrm{x}$
$[\mathrm{B}] = \mathrm{x}$
One collision

$[\mathrm{A}] = 2\mathrm{x}$
$[\mathrm{B}] = \mathrm{x}$
Two collisions

$[\mathrm{A}] = \mathrm{x}$
$[\mathrm{B}] = 2\mathrm{x}$
Two collisions

$[\mathrm{A}] = 3\mathrm{x}$
$[\mathrm{B}] = \mathrm{x}$
Three collisions

$[\mathrm{A}] = 2\mathrm{x}$
$[\mathrm{B}] = 2\mathrm{x}$
Four collisions

$[\mathrm{A}] = 3\mathrm{x}$
$[\mathrm{B}] = 2\mathrm{x}$
Six collisions

Figure 12.9 Possibilities for collisions between A and B as a function of concentration.

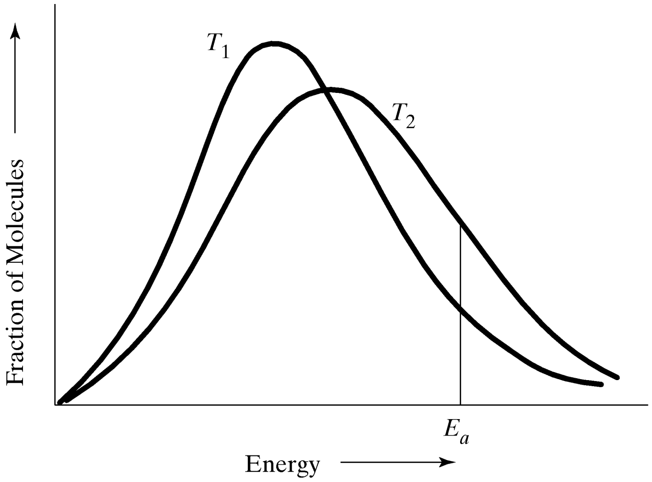


Figure 12.10 The distribution of molecular energies at two temperatures.

temperature, raising the temperature must cause an increase in the average velocity of the molecules, and this change, in turn must cause an increase in the total number of collisions per unit of time. Thus, a higher temperature should result in a higher reaction rate simply because the frequency of collisions is increased. However, it can be shown by calculation from the kinetic molecular theory that an increase in temperature of 10 °C increases the frequency of collision of gas molecules by only about 2 or 3 percent. As mentioned earlier, for many reactions an increase of 10 °C approximately doubles the reaction rate; that is, it increases the rate by about 100%. Therefore, the effect of temperature on rate cannot be explained adequately by increased frequency of collisions alone.

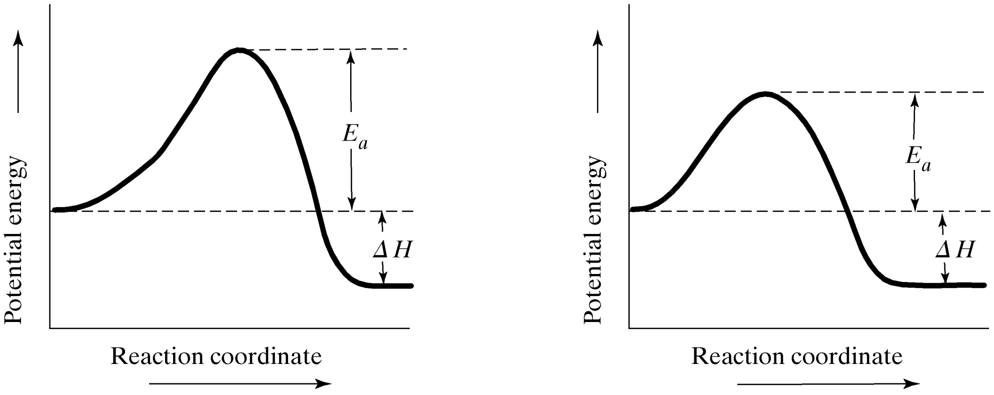
A more important factor in accounting for the temperature-rate relationship lies in the fact that a rise in temperature increases the fraction of molecules that will have sufficient energy to react. This trend can be readily understood by consideration of the effect of temperature on the Maxwell-Boltzmann distribution curve. Figure 12.10 shows the distribution of molecular energies at two different temperatures, T_1 and T_2, where T_2 is greater than T_1. E_a is the activation energy—the minimum energy necessary to form the activated complex and therefore the minimum energy necessary to lead to reaction. At both temperatures the number of molecules that possess at least that amount of energy is only a fraction of the total number of molecules in the sample. However, at the higher temperature, T_2, that fraction is larger than at the lower temperature, T_1. In other words, raising the temperature increases the proportion of collisions that are effective. Or, stating it another way, at the higher temperature, more of the collisions have sufficient energy to get to the top of the hill in the energy diagrams in Figure 12.7 and Figure 12.8.

Catalysis

The role of a catalyst in increasing reaction rate is explained by the model in terms of the catalyst's effect on the activation energy. A catalyst provides a different and "easier" pathway for the reaction to take. The activated complexes formed in the presence of the catalyst are different from, and of lower energy than, the activated complex formed in the uncatalyzed reaction. Thus, the catalyzed reaction has a lower activation energy than the uncatalyzed reaction. Because the activation energy is lower, at any given temperature more collisions have sufficient energy to form the activated complex, thereby increasing the reaction rate. This effect is illustrated schematically in Figure 12.11 with energy diagrams comparing the catalyzed and the uncatalyzed reaction.

12.4 DETERMINATION OF RATE LAWS

One method for determining a rate law is to run a series of experiments for the reaction in question, using different initial concentrations of one or more of the reactants. For example, consider the hypothetical reaction between substances A and B to form C



(a) Uncatalyzed

(b) Catalyzed

Figure 12.11 The effect of a catalyst on activation energy.

(A + B → C). Suppose a reaction mixture has equal concentrations (e.g., 0.100 M) of reactants A and B, and the reaction proceeds for some convenient period of time. The reaction mixture is analyzed to determine the concentration of C present (or, if it is more convenient, the concentration of A or B remaining may be determined). After exactly 10 minutes, say, the concentration of C is 0.015 mol/L. The reaction rate, then, is 0.015 M ÷ 10 min = 1.5×10^{-3} mol/L-min. The experiment is repeated several times under identical conditions, except that in each run different initial concentrations of A and/or B are employed. Hypothetical experimental results are tabulated in Table 12.2.

The results of experiments 1, 2, and 3 (in which the initial concentration of B is constant) indicate that the rate is directly proportional to the molar concentration of A. In other words, doubling [A] doubles the rate and tripling [A] triples the rate. Similarly, experiments 1, 4, and 5 (where the initial concentration of A remains constant) show that the rate is also proportional to the molar concentration of B. Experiment 6 is in agreement with these conclusions, since doubling both [A] and [B] increases the rate fourfold. Therefore,

$$\text{Rate} \propto [\text{A}][\text{B}]$$

and the rate law for this reaction is

$$\text{Rate} = k[\text{A}][\text{B}]$$

As a further illustration of this procedure, Table 12.3 presents rate data for the hypothetical reaction X + Y → Z + W. In this case, the rate is directly proportional to [X] (experiments 1, 2 and 3), but doubling [Y] increases the rate by a factor of four and tripling [Y] increases the rate by a factor of nine (experiments 1, 4, and 5). That is, the rate is proportional to $[\text{Y}]^2$. The rate law, therefore, is

$$\text{Rate} = k[\text{X}][\text{Y}]^2$$

TABLE 12.2 Reaction Rate Data for the Hypothetical Reaction A + B → C

EXPERIMENT (mol/L) NUMBER	INITIAL CONCENTRATIONS A	B	CONCENTRATION of C AFTER 10 MIN of C (mol/L)	RATE OF PRODUCTION (mol/L-min)
1	0.100	0.100	0.015	1.5×10^{-3}
2	0.200	0.100	0.030	3.0×10^{-3}
3	0.300	0.100	0.045	4.5×10^{-3}
4	0.100	0.200	0.030	3.0×10^{-3}
5	0.100	0.300	0.045	4.5×10^{-3}
6	0.200	0.200	0.060	6.0×10^{-3}

TABLE 12.3 Reaction Rate Data for the Hypothetical Reaction X + Y → Z + W

EXPERIMENT NUMBER	INITIAL CONCENTRATIONS (mol/L) X	Y	RATE OF PRODUCTION OF Z (mol/L-min)
1	0.100	0.100	1.5×10^{-3}
2	0.200	0.100	3.0×10^{-3}
3	0.300	0.100	4.5×10^{-3}
4	0.100	0.200	6.0×10^{-3}
5	0.100	0.300	1.35×10^{-2}
6	0.200	0.200	1.2×10^{-2}

In both of the preceding illustrations, the numbers used for concentrations were chosen to make the relationship between concentration and rate as obvious as possible. In actual practice, however, any convenient concentrations can be used. If the rate law is not obvious from inspection of the tabulated data, it can be derived by calculations based on the generalized rate law:

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \cdots$$

These calculations are illustrated in Methodology 12.1 and Problem 12.3.

Methodology 12.1

At elevated temperatures, acetaldehyde decomposes as follows:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g)$$

The following initial reaction rates were determined for various initial concentrations of CH_3CHO at a specific temperature:

CONCENTRATION OF CH_3CHO (mol/L)	RATE OF DECOMPOSITION OF CH_3CHO (mol/L-s)
1.67×10^{-2}	5.20×10^{-4}
3.57×10^{-2}	2.37×10^{-3}
4.46×10^{-2}	3.70×10^{-3}
6.69×10^{-2}	8.32×10^{-3}

(a) What is the rate law for this reaction?
(b) Evaluate the specific rate constant at the temperature in question.

(a) First, by examining the reaction an appropriate rate law must be proposed.

There is only one reactant in this reaction; therefore, the rate law must be

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^m$$

where m is the order of the reaction.

After defining the form of the rate law, the order of the reaction must be determined. That is, the exponent m must be evaluated.

Because k is a constant, the following relationship holds for any two of the experiments:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\text{CH}_3\text{CHO}]^m}{[\text{CH}_3\text{CHO}]_2^m}$$

Continued on next page

Methodology 12.1 Continued

This equation is employed by inserting experimental values for the two rates and the concentrations.

Using the data from the first two experiments in the table,

$$\frac{5.20 \times 10^{-4}\ \text{mol/L-s}}{2.37 \times 10^{-3}\ \text{mol/L-s}} = \frac{(1.67 \times 10^{-2}\ \text{mol/L})^m}{(3.57 \times 10^{-2}\ \text{mol/L})^m}$$

In order to isolate the exponent, m, one uses the relationship that $x^m/y^m = (x/y)^m$:

$$0.219 = \left(\frac{1.67 \times 10^{-2}}{3.57 \times 10^{-2}}\right)^m$$

$$0.219 = 0.468^m$$

The value of m is obtained using logarithms. Recall that $\ln x^m = m \ln x$:

$$\ln 0.219 = m \ln 0.468$$

or

$$-1.52 = m(-0.759)$$

and

$$m = 2$$

Thus, the rate law may now be written as

$$\text{Rate} = k[CH_3CHO]^2$$

(b) In order to evaluate the rate constant for this reaction, we must use the rate law just established,

$$\text{Rate} = k[CH_3CHO]^2$$

The value of k is obtained by substituting into the rate law the concentration of CH_3CHO and the rate for any one of the experiments.

From the fourth experiment, for example

$$8.32 \times 10^{-3}\ \text{mol/L-s} = k(6.69 \times 10^{-2}\ \text{mol/L})^2$$

Next we can rearrange this equation to more clearly give k,

$$k = \frac{\text{Rate}}{[CH_3CHO]^2} = \frac{8.32 \times 10^{-3}\ \text{mol/L-s}}{(6.69 \times 10^{-2}\ \text{mol/L})^2}$$

$$k = 1.86\ \text{L/mol-s}$$

Problem 12.3

Initial reaction rates for the following reaction were measured for several different initial concentrations of reactants:

$$2\ ICl(g)\ 1\ H_2(g) \rightarrow I_2(g) + 2\ HCl(g)$$

The results obtained were

INITIAL CONCENTRATIONS (mol/L)

ICl	H_2	RATE (mol/L-sec)
5.0×10^{-2}	2.0×10^{-2}	2.46×10^{-4}
5.0×10^{-2}	5.0×10^{-2}	6.15×10^{-4}
8.2×10^{-2}	2.0×10^{-2}	4.03×10^{-4}
8.2×10^{-2}	5.0×10^{-2}	1.01×10^{-3}

What is the rate law for the reaction?

Continued on next page

Problem 12.3 *Continued*

Solution:

The generalized rate law is

$$\text{Rate} = k[\text{ICl}]^m[\text{H}_2]^n$$

Our problem is to evaluate m and n. If we choose two experiments in which $[H_2]$ was kept constant, then

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\text{ICl}]_1{}^m}{[\text{ICl}]_2{}^m}$$

Similarly, for two experiments in which [ICl] was constant, we have

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\text{H}_2]_1{}^n}{[\text{H}_2]_2{}^n}$$

Using the first and third experiments to solve for m, we have

$$\frac{2.46 \times 10^{-4}\ \text{mol/L-s}}{4.03 \times 10^{-4}\ \text{mol/L-s}} = \left(\frac{5.0 \times 10^{-2}\ \text{mol/L}}{8.2 \times 10^{-2}\ \text{mol/L}}\right)^m$$

$$0.610 = 0.61^m$$

$$m = 1$$

The data for the first and second experiments permit calculation of n:

$$\frac{2.46 \times 10^{-4}\ \text{mol/L-s}}{6.15 \times 10^{-4}\ \text{mol/L-s}} = \left(\frac{2.0 \times 10^{-2}\ \text{mol/L}}{5.0 \times 10^{-2}\ \text{mol/L}}\right)^n$$

$$0.400 = 0.40^n$$

$$n = 1$$

Thus, the reaction is first order with respect to both ICl and H_2, and the rate law is

$$\text{Rate} = k[\text{ICl}][\text{H}_2].$$

12.5 VARIATION OF REACTION RATE WITH TIME

The procedure just discussed for the determination of rate laws presents one major disadvantage. It does not permit the prediction of the concentrations of products or reactants at any specific time during the course of the reaction. Because reaction rate is dependent upon the concentrations of reactants, as a reaction proceeds, the reactants are consumed and their concentrations therefore decrease. It follows, then, that the rate is also decreasing with time. For example, consider Experiment 1 in Table 12.2 for the hypothetical reaction A + B → C. In this case, 0.015 mol/L of C was formed during the first 10 minutes of reaction, and therefore the initial rate was 1.5×10^{-3} mol/L-min. One may *not* assume from this analysis that the reaction proceeded at that rate throughout the 10-minute period. Nor may one conclude that the concentration of C was 0.0075 mol/L after 5 minutes or that it will be 0.030 mol/L after 20 minutes. The rate of the reaction was at its maximum at the instant of mixing A and B; it gradually decreased as the reaction proceeded. A plot of the concentration of the product (or reactants) would have the general shape of the curve in Figure 12.12.

With few exceptions, the rates of chemical reactions decrease with time. The precise relationship between concentrations and time depends on the order of the reaction in question. As the order of the reaction increases, the relationship becomes increasingly complex.

Zero-Order Reactions

There are a few reactions for which the reaction rate is independent of the concentration of all reactants. These are primarily gaseous decompositions on solid surfaces, in which the rate is determined not by the concentration of the gas, but rather by the surface area of the solid. One example is the decomposition of ammonia on tungsten:

$$2\,NH_3 \xrightarrow{W} N_2 + 3\,H_2$$

The general rate law for this reaction is

$$\text{Rate} = k[NH_3]^m$$

However, because the reaction proceeds at a constant rate, independent of the NH_3 concentration, the value of m must be zero, and the reaction is said to be zero-order:

$$\text{Rate} = k[NH_3]^0$$

$$\text{Rate} = k$$

If this reaction (or any zero-order reaction) is performed, analyzed for the concentration of NH_3 (or other reactants) at various measured time intervals, and the data are plotted in terms of $[NH_3]$ (or [reactant]) versus time, the graph will be a straight line with slope $= -k$. The plot for the decomposition of NH_3 at an initial concentration of 1 mol/L, with the reaction occurring at the rate of 0.010 mol/L-s, is shown in Figure 12.13. After 100 seconds, the reaction is complete and no NH_3 remains.

The linear relationship makes it relatively simple to derive an expression whereby we can calculate the concentration of reactant present at any time during the reaction. Using the generalized equation $A \rightarrow B + C + \cdots$ to represent a zero-order reaction, the rate law is

$$\text{(1)} \qquad \text{Rate} = k$$

Because the reaction rate is a measure of the change in concentration of A, $\Delta[A]$, per time interval, Δt,

$$\text{(2)} \qquad \text{Rate} = \frac{-\Delta[A]}{\Delta t}$$

where the negative sign* indicates a decrease in [A].

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* Rates must have positive values. Therefore, to accommodate the negative values of $\Delta[A]$, a negative sign is incorporated into the expression.

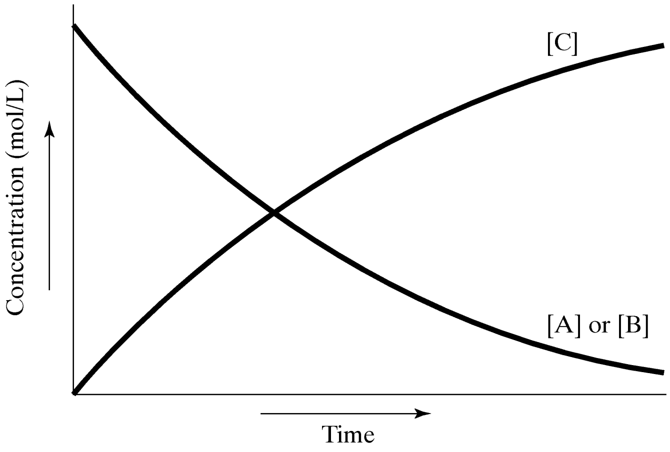

Figure 12.12 The variation of concentrations with time for the reaction $A + B \rightarrow C$.

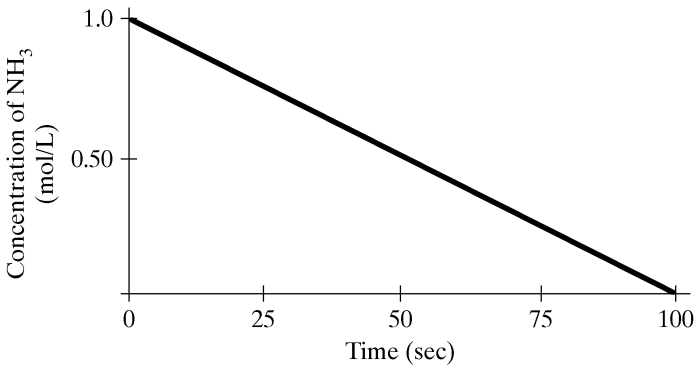

Figure 12.13 A plot of concentration vs time for a zero-order reaction.

Combining equations (1) and (2) gives

$$\frac{-\Delta[A]}{\Delta t} = k$$

and

(3) $$\Delta[A] = -k\,\Delta t$$

The change in the concentration of A is the difference between its concentration at time t, $[A]_t$, and its initial concentration at $t = 0$, $[A]_o$:

(4) $$\Delta[A] = [A]_t - [A]_o$$

Furthermore,

(5) $$\Delta t = t - 0 = t$$

Substituting equations (4) and (5) into equation (3) gives

$$[A]_t - [A]_o = -kt$$

and

(6) $$[A]_t = [A]_o - kt$$

(Calculus students will recognize that this equation is identical to one derived by integration of the equation $d[A]/dt = -k$.)

For zero-order reactions, equation (6) allows the determination of the reactant concentration at any time from a knowledge of the initial concentration of reactant and the rate constant. Also, the equation allows the determination of the time required for the reaction to reach a certain level of completion. For example, the time required for a reaction to be exactly 50% completed is called the half-life, $t_{1/2}$. At $t_{1/2}$ the concentration of reactant A is $[A]_o/2$; therefore:

$$[A]_o/2 = [A]_o - kt_{1/2}$$

Rearranging this equation gives the expression for the half-life of a zero-order reaction:

(7) $$t_{1/2} = [A]_o/2k$$

Methodology 12.2

The decomposition of HI on finely divided gold at 150 °C is a zero-order reaction:

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

At this temperature, HI decomposes at the rate of 7.20×10^{-3} mol/L-min. If the reaction is run with an initial HI concentration of 0.500 mol/L, what will the concentration of HI be after 45.0 minutes? What is the half-life for this reaction?

Continued on next page

Methodology 12.2 Continued

The first step requires us to recognize that the reaction is zero-order and to define the rate law.

For this zero-order reaction,

$$\text{Rate} = k = 7.20 \times 10^{-3}\ \text{mol/L-min}$$

In order to determine the concentration of HI after 45.0 minutes, we must examine the available data to decide which kinetic relationship to employ in this case.

The concentration of HI at time *t* is related to the rate constant and the initial concentration of HI by the expression

$$[\text{HI}]t = [\text{HI}]_o - kt$$

In the next step of the analysis, the actual values for $[\text{HI}]_o$, k and t are substituted into the equation.

$$[\text{HI}]t = 0.500\ \text{mol/L} - (7.20 \times 10^{-3}\ \text{mol/L-min} \times 45.0\ \text{min})$$

$$[\text{HI}]t = 0.500\ \text{mol/L} - 0.324\ \text{mol/L}$$

$$[\text{HI}]t = 0.176\ \text{mol/L} = 0.176\ \text{M}$$

The half-life for the reaction is determined by using k and $[\text{HI}]_o$.

$$t_{1/2} = [\text{HI}]_o/2k$$

$$t_{1/2} = 0.500\ \text{M}/(2 \times 7.20 \times 10^{-3}\ \text{mol/L-min}) = 34.7\ \text{min}$$

First-Order Reactions

As an example of a first-order reaction, consider the decomposition of hydrogen peroxide:

$$2\ H_2O_2(l) \longrightarrow 2\ H_2O(l) + O_2(g)$$

The experimental rate law for this reaction is

$$\text{Rate} = k[H_2O_2]$$

At a given temperature, the rate constant has a value of 0.050 min^{-1}. If the reaction at this temperature is started with 1.00 mol/L of H_2O_2, then measurement of the H_2O_2 concentration at various time intervals will yield the data in Table 12.4.

If these data are plotted, the curve illustrated in Figure 12.14 (a) is obtained. Unlike the plot for a zero-order reaction, the plot for a first-order reaction is not linear. However, if a plot of $\ln[H_2O_2]$ versus time is constructed (part (b)), then a straight line is obtained. This latter plot is characteristic of first-order reactions.

The linear relationship between the logarithm of the concentration and time can be derived by use of the calculus. Using $A \rightarrow B + C + \cdots$ as a general equation for a first-order reaction, the rate law is

$$\text{Rate} = k[A]$$

TABLE 12.4 The Concentration of H_2O_2 Versus Time for the First-Order Reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ ($k = 0.050\ \text{min}^{-1}$)

t(min)	0	2	5	10	20	30	40	50	60
$[H_2O_2]$	1.0	0.91	0.78	0.59	0.37	0.22	0.13	0.082	0.050

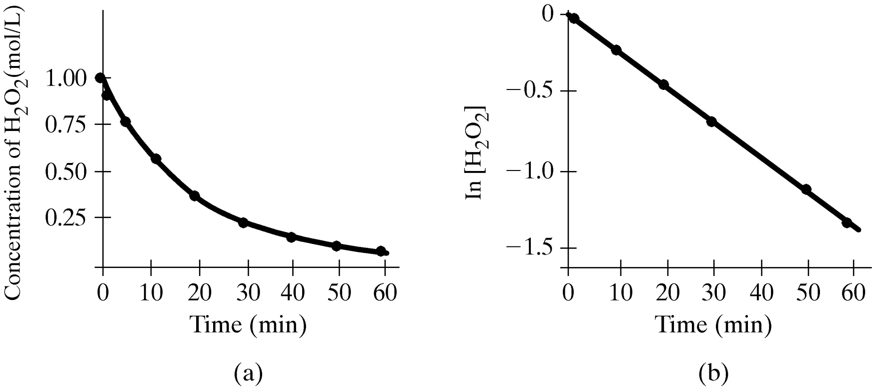

Figure 12.14 Plots of concentration vs. time for a first-order reaction.

and the rate may be defined as

$$-\frac{\Delta[A]}{\Delta t}$$

It follows that

$$-\frac{\Delta[A]}{\Delta t} = k[A]$$

Integrating the equation

$$-\frac{d[A]}{dt} = k[A]$$

between the initial concentration of A, $[A]_o$, and the concentration at time t, $[A]_t$, gives

$$\ln[A]_t - \ln[A]_o = -kt$$

or

$$\ln[A]_t = \ln[A]_o - kt$$

From this second form of the equation, a plot of $\ln[A]_t$ versus t will give a straight line with slope = $-k$ and an intercept of $[A]_o$. A third form of the equation,

$$\ln([A]_o/[A]_t) = kt$$

may be used to prepare graphs of $\ln([A]_o/[A]_t)$ versus t, which will yield a straight line with slope = k. For a first-order reaction, these equations allow us to determine the concentration of reactant remaining at any time and the time required for the reaction to reach a specific extent of completion. The half-life for a first-order reaction is

$$t_{1/2} = \ln([A]_o/[A]_o/2)/k = \ln 2/k$$

Problem 12.4

Consider the reaction

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

At a particular temperature, the rate law is

$$\text{Rate} = k[SO_2Cl_2]$$

and the rate constant has a value of 0.320 min^{-1}. What is the concentration of SO_2Cl_2 after 3.0 min if the initial concentration was 0.50 mol/L? What is the half-life for this reaction?

Continued on next page

Problem 12.4 *Continued*

Solution:

Using the equation for first-order reactions,

$$\ln[SO_2Cl_2]_t = \ln\,[SO_2Cl_2]_o - kt$$

$$\ln[SO_2Cl_2]_t = \ln(0.50\ \text{mol/L}) - (0.320\ \text{min}^{-1})(3.0\ \text{min})$$

$$[SO_2Cl_2]_t = 0.19\ \text{mol/L}$$

The reaction half-life is

$$t_{1/2} = \ln 2/0.320\ \text{min}^{-1} = 2.17\ \text{min}$$

Second-Order Reactions

In a previous example, the thermal decomposition of acetaldehyde was described as a second-order reaction:

$$CH_3CHO \longrightarrow CH_4 + CO$$

and the rate law for the reaction was therefore

$$\text{Rate} = k[CH_3CHO]^2$$

Suppose that a set of experiments with this reaction was completed, just as those done for the decomposition of NH_3 on W (zero-order) and the decomposition of H_2O_2 (first-order). Thus, starting with some known concentration of CH_3CHO, the reaction proceeds at some specific temperature, and at measured intervals the concentration of CH_3CHO remaining is determined.

A plot of $[CH_3CHO]$ versus time is not linear, nor is a plot of $\ln[CH_3CHO]$ versus time. However, if a plot $1/[CH_3CHO]$ versus time is prepared, a straight line is obtained. Again, the equation for this line can be obtained by use of the calculus. Consider the generalized equation

$$A \longrightarrow B + C + \cdots$$

where the rate law is

$$\text{Rate} = k[A]^2$$

In this case, integration yields the equation

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

This equation applies to all second-order reactions involving only one reactant. It applies also to a special case of second-order reactions, which are first-order with respect to each of two reactants:

$$A + B \longrightarrow C + D + \cdots$$

$$\text{Rate} = k[A][B]$$

The special case is that in which the initial concentrations of each reactant are the same: $[A]_o = [B]_o$. The half-life for a second-order reaction is

$$t_{1/2} = 1/k[A]_o$$

Problem 12.5

The decomposition of NO_2 is a second-order reaction:

$$2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$$

Starting with an NO_2 concentration of 0.400 mol/L, the reaction is run for 10.0 min, after which the NO_2 concentration is 0.220 mol/L.

(a) What is the value of the specific rate constant?

(b) What is the concentration of NO_2 after the reaction has run 20.0 minutes?

Solution:

(a) For this reaction,

$$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_o}$$

and

$$k = \left(\frac{1}{[NO_2]_t} - \frac{1}{[NO_2]_o}\right)\frac{1}{t}$$

$$k = (4.55\text{ L/mol} - 2.50\text{ L/mol})\ (1/10.0\text{ min})$$

$$k = 0.205\text{ L/mol-min} = 0.205\text{ M}^{-1}\text{min}^{-1}$$

(b) Using the calculated value of k, we can solve for $[NO_2]_t$:

$$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_o}$$

$$\frac{1}{[NO_2]_t} = \left(\frac{0.205\text{-L}}{\text{mol-min}} \times 20.0\text{ min}\right) + \frac{1}{0.400\text{ mol/L}}$$

$$\frac{1}{[NO_2]_t} = 6.60\text{ L/mol}$$

$$[NO_2]_t = \frac{1}{6.60\text{ L/mol}} = 0.152\text{ mol/L} = 0.152\text{ M}$$

The foregoing discussion indicates that the particular relationship that exists between concentration and time depends on the order of the reaction. This fact provides a graphical method of determining reaction order—and therefore rate law—for simple reactions. The concentration of reactants at various measured time intervals is experimentally determined, and then the collected data are plotted. If a plot of *concentration* against time is linear, the reaction is zero order. If a plot of *ln of concentration* versus time is linear, the reaction is first order. Finally, if a plot of the *reciprocal of concentration* against time is linear, we know that the reaction is second-order.

✓ Check Point 12.2

Graphical analysis of the concentration of reactant A as a function of time results in a straight line; i.e., a plot of [A] versus t yields a linear relationship.

What is the order of the reaction with respect to the concentration of A?

Solution:

zero

◇ ◇ ◇ ◇ ◇

12.6 THE ARRHENIUS EQUATION

In 1887 the Swedish chemist Svante Arrhenius formulated the relationship between reaction rate and temperature in terms of the activation energy:

$$k = Ae^{-E_a/RT}$$

where k is the specific rate constant, A is a constant that is characteristic of the reaction in question, E_a is the activation energy expressed in joules per mole, R is the molar gas constant (8.314 J/mol-K) and T is the temperature in K. The symbol e stands for the base of natural logarithms. The constant A, which may be called the **frequency factor** or ***A*-factor**, is a function of the frequency of molecular collisions and the orientation requirements for effective collisions. In other words, the A-factor corresponds to the product "pZ" given in the expression for the rate constant based on collision theory. (see Section 12.2). The term $e^{-E_a/RT}$, which is derivable from the Maxwell-Boltzmann distribution law, represents the fraction of collisions with energies equal to or greater than the activation energy.

Although the Arrhenius equation is only approximate, it is useful in the investigation of chemical reaction rates. The equation can be changed to a somewhat more usable form by taking the natural logarithm* of each side.

For any reaction, if the values of the activation energy and the constant A are known, the reaction rate constant can be evaluated for any temperature.

For a specific example, consider the following reaction in aqueous solution:

$$CO(CH_2COOH)_2 \longrightarrow CO(CH_3)_2 + 2\ CO_2$$

Because the activation energy for this reaction is 91.0 kJ/mol and A is $7.41 \times 10^{17}\ s^{-1}$, the value for the specific rate constant at any temperature may be determined. If the reaction is performed at 30 °C, then the values for T (in K) and E_a (in J/mol) are substituted into the Arrhenius equation to give k:

$$k = Ae^{-E_a/RT}$$

$$k = (7.41 \times 10^{17}\ s^{-1})e^{-[(91{,}000\ J/mol)/(8.314\ J/mol\text{-}K)(303\ K)}$$

$$k = 152\ s^{-1}$$

Using the same procedure for a temperature of 40 °C,

$$k = 482\ s^{-1}$$

Once the rate constant has been evaluated for a given temperature, the reaction rate can be predicted from the rate law. The preceding decomposition reaction is known to be first-order.[†] The rate law is therefore

$$\text{Rate} = k[CO(CH_2COOH)_2]$$

Thus, for a $CO(CH_2COOH)_2$ concentration of 0.100 mol/L, the rate at 30 °C is

$$\text{Rate} = 152\ s^{-1}\ (0.100\ mol/L) = 15.2\ mol/L\text{-}s = 15.2\ M/s$$

and the rate at 40 °C is

$$\text{Rate} = 482\ s^{-1}\ (0.100\ mol/L) = 48.2\ mol/L\text{-}s = 48.2\ M/s$$

In order to use the Arrhenius equation to calculate k for any reaction, E_a and A for that reaction must be known. These values must be determined by experiment. One method consists of measuring k at each of several different temperatures, and then plotting ln k against $1/T$. Note that the Arrhenius equation

$$\ln k = \ln A - (E_a/RT)$$

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[*] Recall that $\ln e^x = x$, and that $\ln xy = \ln x + \ln y$.

$$\ln k = \ln A - (E_a/RT)$$

[†] The units for k of s^{-1} provide an important clue.

follows the form

$$y = b + mx$$

which is the general form of a linear equation. A plot of y values against corresponding x values results in a straight line with a slope equal to m and a y-intercept equal to b. Therefore, a plot of $\ln k$ versus $1/T$ will be linear, with a slope equal to $-E_a/R$ and an intercept equal to $\ln A$.

A somewhat more convenient method requires the measurement of k at only two different temperatures. If the two rate constants are designated as k_1 and k_2, and the corresponding temperatures at which they were measured are T_1 and T_2, respectively, then

$$\ln k_1 = \ln A - (E_a/RT_1) \tag{1}$$

$$\ln k_2 = \ln A - (E_a/RT_2) \tag{2}$$

Subtracting equation (1) from equation (2) gives

$$\ln k_2 - \ln k_1 = (E_a/RT_1) - (E_a/RT_2) \tag{3}$$

Rearranging equation (3) gives

$$\ln (k_2/k_1) = (E_a/R)\left(\frac{T_2 - T_1}{T_1T_2}\right) \tag{4}$$

Finally, solving for E_a, we obtain

$$E_a = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{k_2}{k_1}\right) \tag{5}$$

The activation energy can be calculated from the two measured values of k and the two temperatures at which they were measured by using equation (5). The value of A can then be calculated from the Arrhenius equation.

Problem 12.6

The gas-phase decomposition of acetaldehyde is described by

$$CH_3CHO \longrightarrow CH_4 + CO$$

The rate constant is determined at two different temperatures as follows:

At 538 °C, $k = 0.79$ L/mol-s

At 592 °C, $k = 4.95$ L/mol-s

Calculate the activation energy for the reaction and evaluate the frequency factor (A).

Solution:

$$E_a = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{k_2}{k_1}\right)$$

$T_1 = 538\ °C = 538 + 273 = 811$ K

$T_2 = 592\ °C = 592 + 273 = 865$ K

$k_1 = 0.79$ L/mol-s

$k_2 = 4.95$ L/mol-s

$$E_a = (8.314\ \text{J/mol-K})\left(\frac{811\ \text{K} \times 865\ \text{K}}{865\ \text{K} - 811\ \text{K}}\right)\ln\left(\frac{4.95}{0.79}\right)$$

$$E_a = 2.0 \times 10^5\ \text{J/mol}$$

Continued on the next page

Problem 12.6 *Continued*

Solution: *Continued*

Using this value for E_a and either k_1 and T_1 or k_2 and T_2, one can solve for A using the Arrhenius equation.

$$\ln k = \ln A - (E_a/RT)$$

$$\ln A = \ln k_1 + (E_a/RT_1)$$

$$\ln A = \ln 0.79 + (2.0 \times 10^5 \text{ J/mol})/[(8.314 \text{ J/mol-K})\ (811 \text{ K})]$$

$$A = 6.0 \times 10^{12} \text{ L/mol-s}$$

The units of A are always the same as the units of k

12.7 REACTION MECHANISMS

Few chemical reactions occur in a single step. Most reactions involve a series of stepwise processes, sometimes called **elementary processes** to distinguish them from the overall reaction. Each of these elementary processes produces a reactive intermediate that then takes part in a subsequent step. This sequence of stepwise processes, which describes the pathway of the reaction, is called the **reaction mechanism**. Just as the equation of a reaction relates what happens, the reaction mechanism relates how it happens.

The theoretical model used for the discussion of reactions in general can be applied to each elementary process in a reaction mechanism. In each separate step, the reactants may be visualized as forming an activated complex with a specific activation energy. Moreover, for each step, we can write a rate expression that shows the relationship of the concentration of reactants to the rate of that specific step. These expressions may be derived directly from the coefficients of the reactants of the individual, or elementary, steps.

As an illustration, consider the reaction between carbon monoxide and chlorine to produce phosgene ($COCl_2$), a toxic, lung-searing gas that was used as a weapon in World War I. The equation for the reaction is

$$CO + Cl_2 \longrightarrow COCl_2$$

A mechanism that has been proposed for the reaction, along with the rate equation for each elementary step, is as follows:

(1) $Cl_2 \longrightarrow 2\,Cl$ $\quad \text{Rate}_1 = k_1[Cl_2]$

(2) $Cl + CO \longrightarrow COCl$ $\quad \text{Rate}_2 = k_2[Cl][CO]$

(3) $COCl + Cl_2 \longrightarrow COCl_2 + Cl$ $\quad \text{Rate}_3 = k_3[COCl][Cl_2]$

However, the experimentally determined rate law, which is

$$\text{Rate} = k[Cl_2]^{3/2}[CO]$$

does not correspond to any of these single-step rate equations.

Each elementary step of a mechanism requires an activated complex, or transition state. Some of these activated complexes are generated by structural changes in a single reacting species while others may be considered to be the direct result of an effective collision between two or more reacting species. The number of reacting species that take part in the elementary process—that is, those that form the activated complex—is referred to as the **molecularity** of the reaction. If only one molecule takes part, the process is said to be **unimolecular; bimolecular** denotes two reacting species; and **termolecular** denotes three. Thus, step (1) in the mechanism for $COCl_2$ production is a unimolecular process, while steps (2) and (3) are each bimolecular. (Note that molecularity is a theoretical concept based on the proposed mechanism, whereas the order of the reaction is an experimentally determined quantity.) Most elementary processes are believed to be unimolecular or bimolecular. Termolecular processes are rare because the probability of three species colliding simultaneously is extremely small.

If one of the steps of a multistep reaction has a rate that is quite low compared with the rates of all the other steps, then that slow step will determine the rate of the overall reaction. As a simple illustration of a **rate-determining step**, consider the reaction between iodine monochloride and hydrogen:

$$2\ \text{ICl} + \text{H}_2 \longrightarrow \text{I}_2 + 2\ \text{HCl}$$

Assume that this reaction proceeds by a two-step mechanism, as follows:

$$(1) \qquad \text{ICl} + \text{H}_2 \longrightarrow \text{HI} + \text{HCl} \qquad \text{Rate} = k_1[\text{ICl}][\text{H}_2]$$

$$(2) \qquad \text{HI} + \text{ICl} \longrightarrow \text{I}_2 + \text{HCl} \qquad \text{Rate} = k_2[\text{HI}][\text{ICl}]$$

The sum of the equations for the two elementary processes is the equation for the overall reaction. If one assumes that step (1), the first elementary process, is very slow compared with step (2), then as fast as HI is formed in step (1) it will be consumed in step (2). In this case, the rate of production of HI in step (1) would determine the rate of the overall reaction; i.e., step (1) would be the rate-determining step. The derived rate expression for step (1) is

$$\text{Rate} = k[\text{ICl}][\text{H}_2]$$

The reaction is bimolecular, which means that ICl and H_2 collide to form the transition state (or activated complex) for the rate-determining step. This complex has the general structure of a ring composed of four atoms, in which the H—H and I—Cl bonds are partially broken* and the H—Cl and H—I bonds are partially formed.*

Indeed, this rate expression, which was derived from the proposed mechanism, is the same as the experimentally determined rate law for the reaction. The fact that these two rate laws agree with each other is evidence of the mechanism's validity. However, this agreement between hypothesis and experiment does not prove that the mechanism is correct. Numerous other mechanisms might be postulated that would also be consistent with the experimental rate law.

An intriguing example of the way a mechanism is postulated and tested involves the reaction of iodomethane, CH_3I, with hydroxide ion in solution to yield methanol, CH_3OH, and iodide ion. When the concentration of iodomethane is doubled, the rate of the reaction also doubles. Similarly, if the concentration of hydroxide ion is doubled, the rate of reaction doubles. Therefore, this reaction is first-order with respect to both reactants and the experimental rate law is

$$\text{Rate} = k[\text{CH}_3\text{I}][^-\text{OH}]$$

The accepted mechanism for this reaction is a single-step mechanism in which the hydroxide ion forms a new bond with the carbon atom by sharing its electrons with the carbon atom. Simultaneously, the bond between carbon and iodine is broken, and the iodide ion is formed. The elementary step may be written

$$\text{CH}_3\text{I} + {}^-\text{OH} \longrightarrow \text{CH}_3\text{OH} + \text{I}^-$$

The rate law from the mechanism is the same as the experimental rate law; that is

$$\text{Rate} = k[\text{CH}_3\text{I}][^-\text{OH}]$$

The bimolecular step has a transition state that results from the collision of the two reactants. In this transition state there is a partial bond between the oxygen of the attacking hydroxide ion and the carbon atom and another partial bond between the carbon atom and the iodine atom (Figure 12.15). Additionally, the charge brought to the complex by

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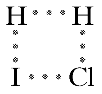
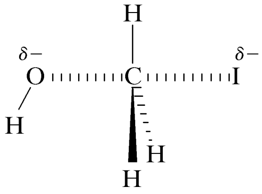
* Partial bonds in activated complexes are often indicated with broken lines.





Proposed structure of the activated complex for the reaction of hydroxide ion with iodomethane. Note that the carbon atom and hydrogen atoms are all in the same plane.

Figure 12.15 The activated complex in the reaction of hydroxide ion with methyl iodide.

the hydroxide ion is shared with the iodine atom, which will eventually leave the carbon and take a full unit negative charge with it.

The course of the reaction based upon the proposed mechanism and the associated activated complex (or transition state) suggests that the carbon atom undergoes inversion. That is, the H-atoms bonded to the carbon atom change their positions in a manner similar to the inversion that happens to an umbrella on a windy day, as shown in Figure 12.16. The reaction reaches the highest energy at the transition state. A plot of energy as a function of the progress of the reaction is called a **reaction profile**.

Additionally, if the proposed mechanism is valid, then the reaction of hydroxide ion with one enantiomer* of 2-iodobutane should give optically active 2-butanol with the inverted stereochemistry.

Indeed, when this experiment is performed, the alcohol isolated from the reaction mixture is optically active and has a configuration that is the mirror image of the starting 2-iodobutane (Figure 12.17). Thus, stereochemical information about reactants and products can play an important role in testing proposed mechanisms.

In a similar reaction, 2-iodo-2-methylbutane (or *t*-butyl iodide) is apparently attacked by hydroxide ion to produce 2-methyl-2-propanol (or *t*-butyl alcohol) and iodide ion:

$$(CH_3)_3C{-}I + {}^{-}OH \longrightarrow (CH_3)_3C{-}OH + I^-$$

However, unlike the preceding example with iodomethane, this reaction is *not* a second-order reaction. Rather, it is a first-order reaction and its rate law is

$$\text{Rate} = k[(CH_3)_3C{-}I]$$

Clearly, the rate-determining elementary step cannot involve the hydroxide ion. Only the *t*-butyl iodide is involved in this step that generates the activated complex.

The proposed mechanism for this reaction is

(1) $(CH_3)_3C{-}I \longrightarrow (CH_3)_3C^+ + I^-$ Rate $= k_1[(CH_3)_3C{-}I]$

(2) $(CH_3)_3C^+ + {}^{-}OH \longrightarrow (CH_3)_3C{-}OH$ Rate $= k_2[(CH_3)_3C^+][{}^{-}OH]$

As with all mechanisms, the sum of the elementary steps yields the overall reaction. The first step, in which the carbon-iodine bond is broken, is the rate-determining step, and therefore, the rate law based on the mechanism is the same as the experimental rate law. In this first step, the loss of the iodide anion leaves a carbocation[†] as a reactive intermediate in the reaction.

Step (2) is generally accepted as the fast step because bond formation is a favorable process and electrostatic attractive forces between the intermediate carbocation and the negatively charged hydroxide ion are strong.

---

[*] Recall that an enantiomer is one of a pair of compounds that are non-superimposable mirror images of each other. Also, each enantiomer rotates plane-polarized light to the same extent but in opposite directions. For more information review Section 8.3.

[†] Carbocations are reactive species in which a carbon atom possesses three covalent bonds and only six electrons. As predicted by the VSEPR model, carbocations have a trigonal planar geometry at the carbon that bears the positive charge.

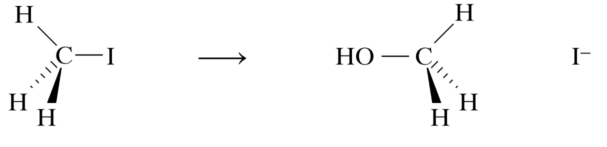


Figure 12.16 Inversion during back-side attack of hydroxide on methyl iodide.

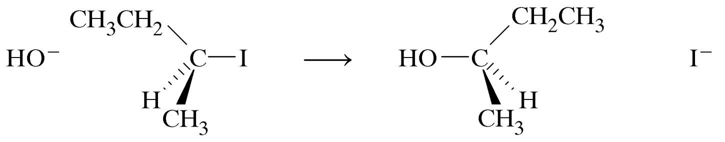


Figure 12.17 The stereochemical result of the reaction of hydroxide with 2-iodobutane.

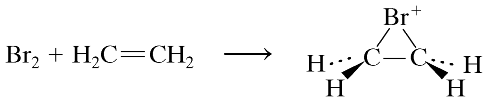
Because the carbocation is planar, attack of the hydroxide ion could occur from either face of the ion. Therefore, if the alkyl iodide was optically active at the start of the reaction, the alcohol should be an optically inactive mixture of two enantiomers (Figure 12.18). Indeed, this is the observed result for such experiments, and it supports the unimolecular nature of the mechanism associated with a carbocation intermediate.

Visualization 12.3

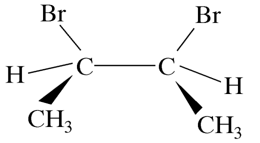
Suppose that the mechanism for the bromination of ethene

$$Br_2 + H_2C{=}CH_2 \rightarrow BrCH_2CH_2Br$$

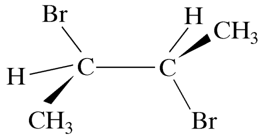
involves the following mechanism, in which Br_2 attacks the double bond from one side forming a bromonium ion that is symmetrically attached to the two carbons:



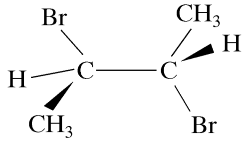
In the next step a bromide ion attacks this intermediate on the side opposite the Br_1. Which of the following would represent the product if the reaction were started with *cis*-2-butene ($CH_3CH{=}CHCH_3$) (Recall that the *cis*- prefix indicates the presence of both methyl groups on the same side of the double bond):



(a)



(b)



(c)

Solution:

Because the bromide ion attacks from the opposite side, the bromines must be across from each other. Since the starting material is *cis*-2-butene, in which the methyl groups are on the same side of the double bond, they, too, should be on the same side of the molecule. Thus (b) should be the product. Of course, there is free rotation around the central C—C single bond and thus a variety of conformations can be adopted by the molecules represented by (b). None of these conformations is the same as the conformations shown as (a) and (c).

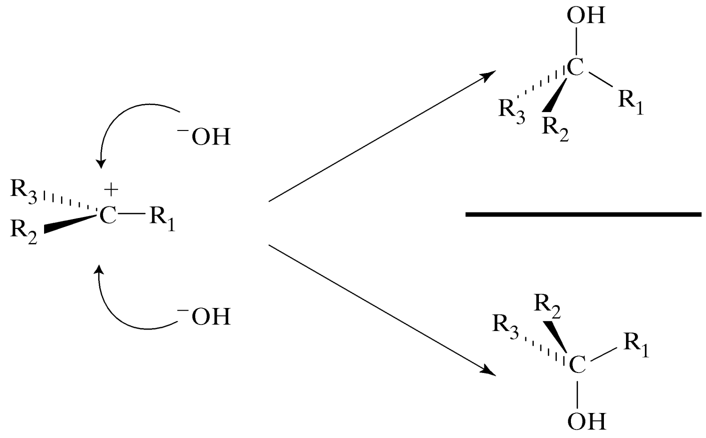


Figure 12.18 Stereochemical result of attack of hydroxide on *t*-butyl chloride.

The mechanism for a given reaction may be a function of the temperature at which the reaction is performed. For example, at higher temperatures analysis of the reaction between nitrogen dioxide and carbon monoxide

$$NO_2 + CO \longrightarrow NO + CO_2$$

produces the rate law

$$\text{Rate} = k[NO_2][CO]$$

The proposed mechanism is a single-step process in which an oxygen atom is directly transferred from the nitrogen dioxide to the carbon monoxide (Figure 12.19).

However, at lower temperatures the experimental rate law is

$$\text{Rate} = k[NO_2]^2$$

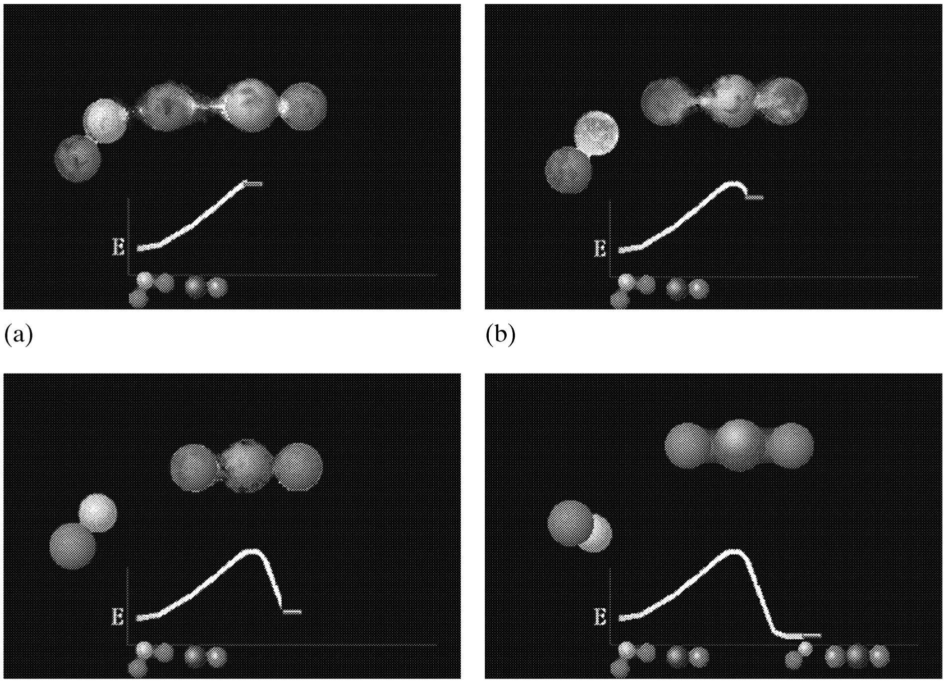
The reaction is still second-order overall, but under these conditions it is zero-order with respect to carbon monoxide and second-order with respect to nitrogen dioxide. The proposed mechanism for this lower-temperature process is

(1) $NO_2 + NO_2 \longrightarrow NO + NO_3$ $\quad$ $\text{Rate} = k_1[NO_2]^2$

(2) $NO_3 + CO \longrightarrow NO_2 + CO_2$ $\quad$ $\text{Rate} = k_2[NO_3][CO]$

The first elementary step is rate-determining in this mechanism.

It should not be assumed on the basis of the preceding examples that the reaction rate law is always the same as the rate expression for the slow step. Rate laws must be expressed in terms of the reactants of the overall reaction, and in some mechanisms the rate expression for the slow step involves intermediates. To illustrate, consider again the mechanism for phosgene production proposed earlier in this section, in which step (3) is believed to be the slow step. The rate expression for this step is $\text{Rate} = k[COCl][Cl_2]$. Yet this cannot be the rate law for the overall reaction, because COCl is an intermediate formed in the preceding step; it is not one of the original reactants. The fast steps prior to the rate determining-step also must be taken into account in this case, and correlation of the rate law with the mechanism is more complex than in the previous examples.



(a) (b)

(c) (d)

Figure 12.19 Transfer of an oxygen atom from nitrogen dioxide to carbon monoxide.

For another example of a mechanism in which the first step is not the rate-determining step, consider the conversion of 1-butanol into 1-bromobutane:

$$CH_3CH_2CH_2CH_2OH + H^+ + Br^- \longrightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

The experimental rate law for this reaction, which is third-order overall, is

$$\text{Rate} = k[CH_3CH_2CH_2CH_2OH][H^+][Br^-]$$

Although a termolecular elementary step would be consistent with this experimental rate law, such a collision is very unlikely. A more reasonable mechanism is

(1) $CH_3CH_2CH_2CH_2OH + H^+ \longrightarrow CH_3CH_2CH_2CH_2OH_2{}^+$

(2) $CH_3CH_2CH_2CH_2OH_2{}^+ \longrightarrow CH_3CH_2CH_2CH_2OH + H^+$

(3) $CH_3CH_2CH_2CH_2OH_2{}^+ + Br^- \longrightarrow CH_3CH_2CH_2CH_2Br + H_2O$

In this proposed mechanism, the third elementary step is rate-determining, and appropriate analysis of this mechanism gives a rate law that is the same as the experimentally determined one.

It is not a simple matter to establish a mechanism for most reactions. Some reactions that appear to be very simple have held the attention of research chemists for many years without any satisfactory mechanism being proposed. In fact, detailed mechanisms have been firmly established for relatively few types of reactions. As indicated earlier, the rate law for the reaction must be established and must be in agreement with any proposed mechanism, but this information alone is usually not sufficient. Other experimental evidence (for example, stereochemical relationships of products and reactants, or identification of intermediates) and often considerable chemical intuition are also required. To be acceptable, a mechanism must be consistent with all the known facts about a reaction. But even this is not proof that a proposed mechanism is correct; it only indicates that it is a likely possibility.

CHAPTER SUMMARY

In your study of reaction rates, you should:

1. Acquire an understanding of the way in which reaction rates are influenced by various conditions: the nature of the reactants, the concentration of the reactants, temperature, and catalysis.
2. Learn the postulates of the **molecular collision theory** and the **transition state theory**, and be able to use these to account for the various rate-determining factors.
3. Given a rate law, be able to perform calculations involving the rate, rate constant, and concentrations of reactants.
4. Be able to determine rate laws and orders of reaction from data on initial concentrations and rates.
5. Be able to complete calculations relating concentration to time using the following equations:

$$\begin{array}{ll} \text{zero-order:} & [A]_t = [A]_o - kt \\ \text{first} - \text{order:} & \ln[A]_t = \ln\,[A]_o - kt \\ \text{second} - \text{order:} & \dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_o} \end{array}$$

6. Be able to determine if a reaction is zero-, first-, or second-order by graphical analysis of concentration versus time data.
7. Perform calculations using the Arrhenius equation with appropriate data.
8. Acquire an understanding of the significance of reaction mechanisms and their relationship to reaction rates.

TERMS

Some of the important terms in this chapter are as follows:

Homogeneous reaction A reaction that takes place in a single phase. If a reaction mixture consists of more than one phase, the reaction is said to be **heterogeneous**.

Rate law (rate equation) A mathematical statement that expresses the relationship between reaction rate and concentration of reactants under a given set of conditions. For the generalized reaction

$$aA + bB + \cdots \longrightarrow$$

the rate law is

$$\text{Rate} = k[A]^m[B]^n \cdots$$

The constant k is the **specific rate constant**; it has a specific value for a particular reaction under a specific set of conditions. The exponents m and n denote the **order** of the reaction; m is the order with respect to reactant A, n is the order with respect to reactant B, and $m + n$ is the overall order of the reaction.

Catalyst A substance that increases the rate of a chemical reaction without being consumed in the reaction. A catalyst provides a different and "easier" pathway for the reaction to take. This phenomenon is known as **catalysis**. Substances that decrease the reaction rate are called *negative catalysts*, or *inhibitors*.

Molecular collision theory A theory of reaction rates whose basic assumption is that reacting particles must collide for a reaction to occur. Only a small fraction of molecular collisions lead to reactions. For a collision to be effective, the colliding molecules must be properly oriented toward each other and have a sufficiently high kinetic energy to overcome the repulsion of the electron clouds.

Transition state theory An extension of the collision theory based on the postulate that an effective collision between reactant molecules results in the formation of an unstable, transitory, intermediate species called the **transition state**, or **activated complex**.

Activation energy The potential energy barrier that must be overcome by reactants to form the activated complex; the difference between the potential energy of the reactants and the potential energy of the activated complex.

Arrhenius equation An equation for the relationship between the reaction rate constant, temperature, and activation energy:

$$k = Ae^{-E_a/RT}$$

Reaction mechanism The sequence of stepwise processes describing the path or course of a reaction. Each of the steps in a reaction mechanism is called an **elementary process**.

Molecularity The number of species that take part in a molecular collision to form an activated complex. Thus, elementary processes are described as **unimolecular**, **bimolecular**, and so on. *Molecularity* should not be confused with the *order* of a reaction. Molecularity is a theoretical concept based on the proposed reaction mechanism; order is an experimentally determined quantity based on the overall reaction.

PROBLEMS

1. Indicate clearly the difference in the meaning of the terms in each of the following pairs:
   (a) homogeneous reaction and heterogeneous reaction
   (b) order of reaction and molecularity
   (c) reaction rate and reaction mechanism
   (d) activated complex and activation energy
   (e) total collisions and effective collisions

2. Describe the effect of temperature on reaction rate and rationalize this effect at the molecular level.

3. Define catalysis and provide a theoretical explanation for this phenomenon.

4. Assuming each of the following reactions occurs directly by a single step, what is the order of each reaction?
   (a) $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ (b) $2\ N_2O \rightarrow 2\ N_2 + O_2$
   (c) $2\ NO + O_2 \rightarrow 2\ NO_2$ (d) $2\ HI \rightarrow H_2 + I_2$

5. Give the order for each of the reactions for which the following are the experimental rate laws:

(a) Rate = $k[NO]^2[Cl_2]$
(b) Rate = $k[N_2O]$
(c) Rate = $k[N_2O_4]$
(d) Rate = $k[CO][Cl_2]^{3/2}$

6. Explain why an increase in temperature increases the rate of any reaction, independent of whether the reaction is endothermic or exothermic.

7. Explain why iron powder rusts at a much faster rate than an iron nail.

8. Assuming that gases A and B react by the simple collision of A with B, how would an increase in pressure at a constant temperature affect the rate of the reaction?

9. For the reaction $CO + Cl_2 \rightarrow COCl_2$, the rate of formation of $COCl_2$ at a given temperature T is found to be 6.7×10^{-3} mol/L-min when the concentrations of CO and Cl_2 are each 0.10 M. The rate law for this reaction is

$$\text{Rate} = k[CO][Cl_2]^{3/2}$$

(a) Calculate the numerical value of the rate constant at temperature T.
(b) What is the rate of formation of $COCl_2$ at the same temperature if the concentrations of CO and Cl_2 are each 0.02 M?
(c) If the same reaction occurs at a temperature higher than T, will the numerical value of the rate constant be larger or smaller than the answer to part (a)?
(d) If the reaction were run in the presence of a suitable catalyst at temperature T, what effect would this have on the magnitude of the reaction rate?

10. For the reaction $2\,A + B \rightarrow C$, the rate of formation of C was measured for a number of different initial concentrations of A and B, with the following results:

[A]	[B]	RATE
0.10 M	0.10 M	2.0×10^{-3} mol/L-min
0.20 M	0.10 M	8.0×10^{-3} mol/L-min
0.30 M	0.10 M	1.8×10^{-2} mol/L-min
0.20 M	0.20 M	8.0×10^{-3} mol/L-min
0.30 M	0.30 M	1.8×10^{-2} mol/L-min

(a) Write the rate equation for the reaction.
(b) What is the order of the reaction?
(c) Calculate the specific rate constant.

11. The reaction below takes place in aqueous solution:

$$2\,ClO_2 + 2\,OH^- \longrightarrow ClO_3^- + ClO_2^- + H_2O$$

The following initial rates were obtained for this reaction at various initial concentrations:

$[ClO_2]$	$[OH^-]$	RATE (mol/L-s)
0.10	0.20	0.46
0.20	0.20	1.84
0.20	0.10	0.92

(a) Write the rate law for the reaction.
(b) What is the order of the reaction?
(c) What is the value of the specific rate constant?

12. The following initial reaction rates for corresponding initial molar concentrations of N_2O_5 were measured for the reaction:

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

$[N_2O_5]$	RATE (mol/L-min)
0.15	0.107
0.38	0.271
0.55	0.391
0.82	0.582

(a) What is the order of the reaction?
(b) Calculate the specific rate constant.

13. Consider the reaction

$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$$

At a certain temperature, the initial reaction rates were measured for a number of different initial concentrations of reactants, with the following results:

$[H_2]$	$[Br_2]$	RATE (mol/L-min)
0.40	0.40	6.05×10^{-2}
0.40	0.30	5.28×10^{-2}
0.40	0.20	4.32×10^{-2}
0.60	0.40	9.07×10^{-2}

Write the rate law and calculate the specific rate constant.

14. Compound A is mixed with B, and after 200 seconds half of A has reacted. If the reaction is first-order with respect to A, how much A is left unreacted at the end of 400 seconds? How much is left at the end of 800 seconds?

15. The thermal decomposition of ethyl chloride occurs as follows:

$$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$$

Assume that this reaction was carried out at 820 K and that the molar concentration of C_2H_5Cl was found to decrease with time according to the following data:

Time (sec)	0	10	20	30	40	50
$[C_2H_5Cl]$	0.100	0.0730	0.0532	0.0387	0.0282	0.0206

(a) Make plots to determine the order of the reaction.
(b) Calculate the specific rate constant.
(c) What is the concentration of C_2H_5Cl remaining after the reaction has run exactly 2 minutes?
(d) How long did it take to reduce the concentration of C_2H_5Cl to half the initial concentration?

16. For the following second-order reaction, an initial HI concentration of 0.800 mol/L is reduced to 0.400 mol/L in 7.25 minutes:

$$2\,HI \longrightarrow H_2 + I_2$$

(a) What is the value of k for the reaction?
(b) What is the initial rate of the reaction in mol/L-min of HI consumed?

17. The reaction below is known to be first-order with respect to each of the reactants:

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$$

When this reaction is run at 400 °C with initial concentrations of 0.200 mol/L of each reactant, the initial rate is found to be 0.0200 mol/L-s. What is the value of the specific rate constant under these conditions?

18. If the reaction $A \rightarrow B + C$ is zero-order with a rate constant of 3.20×10^{-2} mol/L-s, what will be the concentration of A after 30 seconds when the initial concentration of A is 1.00 mol/L?

19. Consider the generic reaction: $A + B \rightarrow C + D$. Suppose that Compound A is the only molecule in this reaction which absorbs visible light at a wavelength of 550 nm. Data for the disappearance of A are given below. Assume that Beer's Law applies (Absorbance = Beer's law constant times the concentration of A).

Abs (550 nm)	time (min)
0.374	2
0.312	7
0.259	14
0.203	22
0.155	32
0.108	43
0.078	54
0.050	67

(a) Is the reaction first-order, second-order, or zero-order?
(b) Determine the rate constant.
(c) What is the half-life of the reaction, $t_{1/2}$?

20. For the reaction $A \rightarrow B$, $k = 0.0223\ M^{-1}s^{-1}$. If the initial concentration of A is 1.00 *M*, what length of time will be required for the reaction to be 90.0% completed?

21. The rate constant for a particular first-order reaction was $3.2 \times 10^{-1}sec^{-1}$. The initial concentration of the reactant was 0.12 *M.* Determine the half-life for this reaction.

22. The reaction of fluorine and chlorine dioxide at 250 K and various concentrations gave the data in the table below. Provide the rate law and the average rate constant for this reaction.

$$F_2 + 2\ ClO_2 \longrightarrow 2\ FClO_2$$

Concentrations and Rates for the Reaction of Fluorine with Chlorine Dioxide

Experiment	$[F_2]$	$[ClO_2]$	Rate (M/s)
1	0.125	0.050	7.5×10^{-3}
2	0.125	0.038	5.7×10^{-3}
3	0.250	0.038	1.1×10^{-2}

23. Consider the reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

At temperatures below 225 °C, the rate of this reaction is found to be independent of the concentration of CO. The rate depends only on $[NO_2]$. From the following data, determine the rate law and evaluate *k*:

Time (min)	0	20	50	75	150	300
$[NO_2]$	0.500	0.444	0.381	0.340	0.258	0.174

24. The thermal decomposition of methyl ether occurs as follows:

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is found to have an activation energy of 349 kJ/mol and a frequency factor of $8.91 \times 10^{21}\ min^{-1}$. Calculate the value of the specific rate constant at 500°C.

25. Consider the decomposition of N_2O_5:

$$2\ N_2O_5(g) \longrightarrow 4\ NO_2(g) + O_2(g)$$

When this reaction was carried out at 25 °C, the specific rate constant was found to be $3.8 \times 10^{-5}\ s^{-1}$. The same reaction at 35 °C gave a rate constant of $1.5 \times 10^{-4}\ s^{-1}$. Calculate the activation energy and the frequency factor for the reaction.

$$E_a = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{k_2}{k_1}\right) = (0.00831\ \text{kJ/mol}) \times \frac{298\ \text{K} \times 308\ \text{K}}{308\ \text{K} - 298\ \text{K}}\ \ln\left(\frac{1.5 \times 10^{-4}\ \text{s}^{-1}}{3.8 \times 10^{-5}\ \text{s}^{-1}}\right) = 1.0 \times 10^2\ \text{kJ/mol}$$

$$\ln A = \ln k + \frac{E_a}{RT} = (\ln 3.8 \times 10^{-5}) + \frac{1/0 \times 10^5\ \text{J/mol}}{(8.314\ \text{J/K-mol})(298\ \text{K})} = 30.2$$

$$A = 1.3 \times 10^{13}\ \text{s}^{-1}$$

26. The rate law for the reaction below is: Rate = $k[ICl][H_2]$.

$$2\ ICl(g) + H_2(g) \longrightarrow I_2(g) + 2\ HCl(g)$$

(a) What is the overall order for the reaction?
(b) What is the value of the rate constant, *k*, if the initial rate of reaction was 0.37 M sec^{-1} at a given temperature and the concentrations for the reactants were each 0.025 *M*?
(c) What would the initial rate of the reaction be if the concentration of ICl was 0.35 *M* and the concentration of H_2 was 0.025 *M*?

27. The decomposition of Cl_2O_7 at 400 K obeys first-order kinetics.

$$2\ Cl_2O_7 \longrightarrow 2\ Cl_2 + 7\ O_2$$

(a) An experiment was performed in which the initial pressure of the reactant was 47.1 torr. After 165 seconds the pressure of the reactant had decreased to 16.9 torr. Calculate the rate constant for the reaction.
(b) Calculate the pressure of the reactant after 330 seconds.
(c) How much time is required for the pressure of the reactant to decrease to 1/100th of its original value?

28. At 750 K the rate constant for the reaction below is 0.00243 sec^{-1}.

$$1 \text{ mol cyclobutane} \longrightarrow 2 \text{ mol of ethylene}$$

(a) What percentage of the cyclobutane will remain after 375 seconds?
(b) What time is required for the reaction to consume 50% of the cyclobutane?
(c) What percentage of the cyclobutane will remain after 5 half-lives?
(d) If the reaction started with one mole of cyclobutane, how many moles of ethylene would be produced after two (2) half-lives?

29. Show that the half-life for a simple first-order reaction is given by the equation: $t_{1/2} = (\ln 2)/k$

30. The decomposition of nitric oxide, NO, to molecular nitrogen and molecular oxygen is a second-order reaction at 1400 K. During a time period of 1825 seconds the concentration of nitric oxide, NO, decreases from an initial value of 2.91×10^{-3} M to 1.95×10^{-3} M.

(a) What is the value of the specific rate constant for this reaction?
(b) What is the concentration of NO after the reaction has continued for an additional 1000 seconds?
(c) What is the half-life for this reaction of NO?
(d) What would be the half-life for the decomposition of nitric oxide at 1400 K if the initial concentration of NO were 7.2×10^{-2} M?

31. Show that the half-life for a simple second-order reaction is given by the equation: $t_{1/2} = 1/A_o k$

32. The combination reaction of two bromine atoms to yield molecular bromine is a bimolecular reaction. In a given experiment the concentration of the bromine atoms was 2.43×10^{-6} M after 1.22 milliseconds. The original concentration of the bromine atoms was 1.37×10^{-5} M.

(a) What is the rate law expression for this reaction?
(b) What is the value of the specific rate constant for this reaction?
(c) The same reaction was studied again. After 0.82 milliseconds the concentration of bromine atoms was 3.67×10^{-6} M. What was the initial concentration of bromine atoms at the onset of reaction?

33. The rate law for the reaction

$$2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g)$$

is

$$\text{Rate} = k[NO]^2[Br_2]$$

When the initial concentration of each reactant is 0.100 mol/L, the initial rate at 20 °C is 1.2 mol/L-min. Assuming that the rate will be exactly doubled if the temperature is increased by 10 °C, what is the activation energy for the reaction?

34. For the reaction P → D + Q, the following data were obtained:
At 300 K:

Time (min)	0	10	20	30	40	50
[P]	1.00	0.90	0.80	0.70	0.60	0.50

At 320 K:

Time (min)	0	10	20	30	40	50
[P]	1.00	0.84	0.68	0.52	0.36	0.20

(a) What is the rate law for the reaction?
(b) What is the activation energy for the reaction?

35. Postulate a two-step mechanism that is in agreement with the data of Question 12.10.

36. The reaction of carbon dioxide with an aqueous solution in which the hydroxide ion concentration is greater than 10^{-4} M occurs in two steps:

$$CO_2(aq) + OH^-(aq) \longrightarrow HCO_3^-(aq) \quad \text{slow}$$

$$HCO_3^-(aq) + OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l) \quad \text{fast}$$

(a) Write a rate equation for the disappearance of CO_2.
(b) The rate constant for the reaction is 8500 L/mol-s. If the OH^- concentration is 2.2×10^{-4} M and the CO_2 concentration is 0.44 g/L, calculate the rate of the reaction.

37. A kinetic study of the reaction A → B + C at 120 °C gave the data below:

[A] (mol/liter)	time (seconds)
4.48	0
3.67	10
2.72	25
2.01	41
1.49	54
0.74	91

(a) What is the reaction order with respect to A?
(b) Determine the rate constant, k, for this reaction.
(c) What is the half-life for the reaction at 120 °C?
(d) How long will the reaction take to be 95% complete?

38. The reaction $2\,NO_2(g) \rightarrow N_2O_4(g)$ occurs directly in a single step. If N_2O_4 is formed at the rate of 0.500 mol/L-min when the concentration of NO_2 is 2.00 mol/L, what is the rate of formation of N_2O_4 when the concentration of NO_2 is 1.00 mol/L? (Assume that the temperature remains constant.)

39. For the thermal decomposition of acetaldehyde,

$$CH_3CHO \longrightarrow CH_4 + CO$$

the following data were found to apply at 800 °C:

$[CH_3CHO]$	Decomposition rate
0.100 M	9.0×10^{-7} mol/L-s
0.200 M	3.6×10^{-6} mol/L-s
0.400 M	1.44×10^{-5} mol/L-s

(a) Write the rate law for the reaction.
(b) Calculate the value of the specific rate constant at 800 °C.
(c) Calculate the rate of the reaction when [acetaldehyde] = 0.25 M.

40. The following rate data were collected for the reaction

$$Cl_2 + CO \longrightarrow Cl_2CO$$

starting conc, M		Rate
$[Cl_2]$	$[CO]$	
0.1	0.1	1×10^{-4} M/min
0.2	0.1	2×10^{-4}
0.2	0.2	2×10^{-4}

(a) Write the rate law for this reaction.
(b) Calculate the rate constant.
(c) Postulate a mechanism consistent with your rate law.

41. Assume that the reaction $H_2 + I_2 \rightarrow 2\ HI$ takes place in a single step.
(a) What is the overall order of the reaction?
(b) What is the rate equation for the reaction?
(c) What is the rate constant for the reaction if the rate is 2.0×10^{-4} mol/L-min when initial concentrations of $[H_2] = 0.10$ M and $[I_2] = 0.20$ M are used?

42. If the reaction $H_2 + I_2 \rightarrow 2\ HI$ occurs by the following mechanism:

$$H_2 \longrightarrow 2\ H \quad \text{(slow)}$$

$$2\ H + I_2 \longrightarrow 2\ HI \quad \text{(fast)}$$

determine the rate equation for the reaction.

43. Consider the reaction

$$Xe(g) + 2F_2(g) \longrightarrow XeF_4(g)$$

(a) Give an electron-dot formula, the geometry, the hybridization, the bond angles, and the types of intermolecular forces for XeF_4.
(b) What type of reaction is this?
(c) The following are some data for the rate of formation of XeF_4 as a function of initial concentration of the starting materials.

[Xe]	$[F_2]$	Rate
1	1	1×10^{-2} mol/L/min
2	1	1×10^{-2} mol/L/min
1	2	2×10^{-2} mol/L/min

(1) Give the rate expression for this reaction.
(2) Give the overall order of the reaction.
(3) Determine the rate constant for the reaction.
(4) Postulate a mechanism that would be consistent with your rate expression. Clearly indicate which steps are slow or fast.

(d) Calculate ΔH^0 for this reaction.

44. For which reaction, A or B, are the following true?

$$\text{A}\ CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

$$\text{B}\ (CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$$

(a) The reaction is second-order overall
(b) The reaction has a two-step mechanism
(c) The reaction proceeds through an intermediate with a positive charge
(d) The transition state of the rate-determining step contains both OH and Cl partially bonded to carbon
(e) The reaction has two transition states

45. Give a correctly labeled reaction profile for the reaction

$$(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$$

46. Give the structure and geometry of the intermediate in the reaction

$$(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$$

47. Multiple-choice questions

1. The rate equation for the reaction $NH_3 + 3\ I_2 \rightarrow NI_3 + 3\ HI$ is
   (a) Rate = $k[NH_3]\,[I_2]$
   (b) Rate = $k[NH_3]\,[I_2]^3$
   (c) Rate = $k[NH_3]^3\,[I_2]$
   (d) impossible to determine without additional information

2. Which one of the following has *no* effect on the specific rate constant?
   (a) a change in temperature
   (b) a change in concentration of one or more reactants
   (c) the addition of a catalyst
   (d) an increase in the activation energy

3. Catalysts affect chemical reactions by
   (a) causing the reaction to become less exothermic
   (b) increasing the kinetic energy of the reactants
   (c) decreasing the activation energy
   (d) increasing the rate of molecular collisions

4. In a given reaction, tripling the concentration of reactant A increases the reaction rate by a factor of 9. The order of this reaction with respect to A is therefore
   (a) first (b) second (c) third (d) ninth

5. The rate law for a certain gaseous reaction is Rate = $k[A][B]$. If the pressure in the reaction vessel is doubled and all other conditions remain the same, the rate of the reaction is increased by a factor of
   (a) 0.5 (b) 2 (c) 3 (d) 4

6. In the reaction $A \rightarrow B + C$, a plot of the molar concentration of A versus time is a straight line. The order of the reaction is
   (a) zero (b) first (c) second (d) third

13

Equilibrium

In addition to the identity of the reactants and products, there are three things that a chemist would like to know about a chemical reaction: its rate, mechanism, and extent. These factors are particularly important to the chemist who synthesizes compounds. How much of the product will be obtained after how much time, and what reaction conditions will maximize the amount of product obtained, are vital considerations for the efficiency of many synthetic and industrial processes. The concepts of rate and mechanism have been explored in Chapter 12; in this chapter we will discuss the extent of chemical reactions.

It is essential at the outset to distinguish clearly between the rate and extent of reaction. The **rate** of a reaction is a measure of how quickly reactants are converted to products. The **extent** of a reaction is a measure of how much product is formed from a certain amount of reactant after the reaction has proceeded as far as it will under a given set of conditions.

Consider the conversion of *cis*-2-butene to its geometrical isomer *trans*-2-butene at 400 °C, shown in Figure 13.1. When 1.00 mol of the *cis* isomer is introduced into an empty flask at 400 °C and 400 torr, and the contents of the flask are monitored as a function of time, the data in Table 13.1 are obtained. At the beginning of the reaction, $t = 0$, only the *cis* isomer is present. After 420 minutes have elapsed, 0.10 mol of the *cis* isomer has been converted to *trans* isomer. After several weeks, 0.60 mol of the *trans* isomer is present and the composition of the reaction mixture has stabilized. Even after several months, or even several years, the percentage composition of the mixture will not change; the conversion of the *cis* to the *trans* isomer has proceeded as far as it will under this set of conditions.

If this reaction proceeded 100% to completion, 1.00 mol of the *trans* isomer and none of the *cis* isomer would be present. Since 0.60 mol of the *trans* isomer has actually been formed under the conditions, the reaction has gone 60% to completion:

$$(0.60/1.00) \times 100 = 60\%$$

This is the *extent* of the reaction. A considerable length of time was required to obtain the 60% conversion, however, and the *rate* of the reaction could be characterized, therefore, as moderately slow.

Examples of reactions with more extreme extents and rates are given in Table 13.2. The first reaction, the decomposition of nitrogen oxide, occurs at a very slow rate at room temperature. However, the extent of the reaction is high, and if sufficient time—perhaps several years—elapses, most of the nitrogen oxide will decompose to N_2 and O_2. The

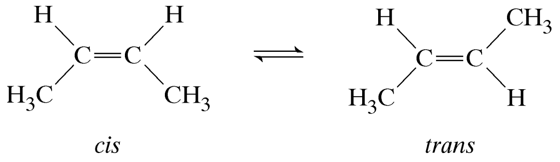


Figure 13.1 Geometrical isomers of 2-butene.

TABLE 13.1 The Extent of Isomerization of 2-Butene

MOLES OF *CIS*	MOLES OF *TRANS*	TIME
1.00	0.00	0
0.96	0.04	192 minutes
0.90	0.10	420 minutes
0.86	0.14	8 hours
0.40	0.60	several weeks
0.40	0.60	several months

TABLE 13.2 Some Reactions with Extreme Extents and Rates at Room Temperature

	RATE	EXTENT
$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$	slow	high
$SiCl_4(l) + 2\,H_2O(l) \rightleftharpoons SiO_2(s) + 4\,HCl(g)$	fast	high
$2\,H_2O(l) \rightleftharpoons 2\,H_2(g) + O_2(g)$	slow	low
$2\,NaCl(s) + H_2SO_4(l) \rightleftharpoons 2\,HCl(g) + Na_2SO_4(s)$	fast	low

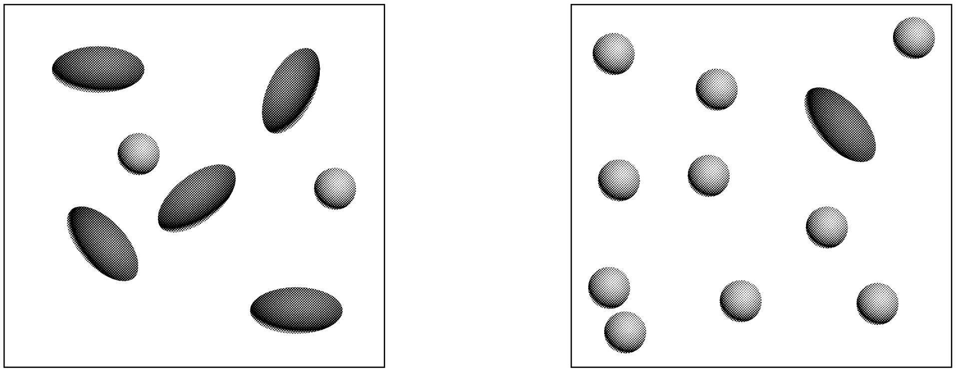
reaction of $SiCl_4$ with H_2O also has a high extent, and because its rate is quite fast, the virtually total conversion of $SiCl_4$ to SiO_2 occurs within seconds. The decomposition of water has both a low extent and a slow rate of reaction at room temperature. Thus, even if this reaction is allowed to proceed for an infinite amount of time, only a small percentage of the water will convert to H_2 and O_2. The last reaction in the table, which represents the commercial preparation of HCl, occurs at a fast rate, but only a small percentage of the reactants are converted to products at room temperature.

Visualization 13.1

A reaction

$$\text{red} \rightleftharpoons 2\ \text{blue}$$

is started with six red molecules. The following diagrams represent the reaction mixture after 10 minutes and after 10 hours.


10 min

10 hours

What can you determine about the relative rate and extent of the reaction? Has the reaction reached equilibrium after 10 hours?

Solution:

Because the composition of the mixture changes between 10 minutes and 10 hours, we can assume that the reaction has a relatively slow rate. We can certainly say that it did not reach equilibrium within the first 10 minutes. However, we can not say that it has reached equilibrium after 10 hours. If we knew the composition of the mixture after 20 hours, 10 days, etc. we could then determine whether it had reached equilibrium (if equilibrium were reached within 10 hours the composition would not change after an additional 10 hours).

The extent of the reaction is relatively high. After 10 hours, only one molecule of reactant remains. It is possible, moreover, that if the reaction has not yet reached equilibrium, the extent is actually even greater.

13.1 EQUILIBRIUM

In earlier discussions of phase transitions (Chapter 10) and the solution process (Chapter 11), we have seen that equilibrium is that stage in a physical process at which the rates of two opposing processes are equal. The same is true for a chemical reaction.

In a chemical reaction the two processes whose rates become equal at equilibrium are the forward and reverse reactions. Only a *reversible* chemical reaction, therefore, can reach a state of equilibrium. That is, equilibrium can be attained only if both the forward and reverse reactions can and do occur after the reaction is initiated. Theoretically, all reactions are reversible when carried out under the proper conditions. However, many reactions have such low rates or extents that for practical purposes they are nonreversible. The decomposition of water at room temperature is an example of such a reaction.

Let us now examine a reversible reaction—for example, the decomposition of nitrogen dioxide carried out at a temperature high enough to ensure a moderate rate of reaction. After the decomposition of NO_2 to NO and O_2 has been initiated, NO_2 molecules decompose to NO and O_2 molecules and NO and O_2 molecules recombine to form NO_2:

$$2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g) \qquad \text{forward reaction}$$

$$2\,NO_2(g) + O_2(g) \longrightarrow 2\,NO_2(g) \qquad \text{reverse reaction}$$

At the very beginning of the reaction, the concentration of NO_2 is large and the concentrations of NO and O_2 are very small. Because the rate of the forward reaction depends on the concentration of NO_2 and the rate of the reverse reaction depends on the concentrations of NO and O_2, the rate of the forward reaction will be greater than the rate of the reverse reaction at this point. As the concentrations of NO and O_2 increase and the concentration of NO_2 decreases, the rate of the reverse process will increase and the rate of the forward process will decrease. Eventually the rates will become equal, the concentrations will remain constant, and at this point the system has reached equilibrium. Indeed, equal rates and constant concentrations are the two definitive criteria of chemical equilibrium. Experimentally, however, an equilibrium can be detected only by the second criterion—the constancy of concentrations (look carefully at the diagram in Figure 13.2 to determine where equilibrium occurs).

Thus, when the decomposition of NO_2 has reached equilibrium, the amounts of NO and O_2 formed will increase no further: The reaction has proceeded as far as it will under the particular set of conditions employed. This is the definition of the extent*

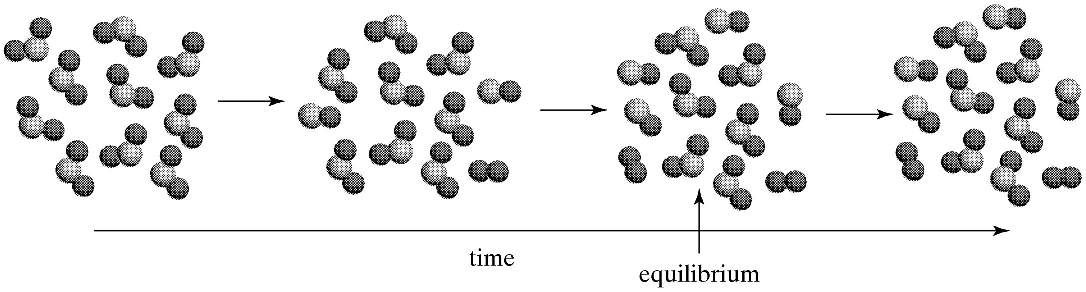


Figure 13.2 Equilibrium in the conversion of NO_2 to NO and O_2.

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* Notice that the extent of a reaction is not the same as the percent yield. It is calculated in the same way; that is, as the amount of product formed divided by the amount of product that could be formed if the reaction went to completion (theoretical yield). But the yield of a reaction is determined whenever the chemist "works up a reaction." Thus, a synthetic chemist may begin a reaction in the laboratory on Monday morning, isolate the product on Tuesday afternoon and find a yield of 45%. It is possible that this reaction may have already proceeded to equilibrium, and if the chemist has been very careful to isolate all of the product of the reaction, then this may indeed be the extent of the reaction. However, it is also possible that by Tuesday afternoon the reaction has not yet reached equilibrium. In this case the extent of the reaction, as measured at equilibrium, will be greater than the yield of 45%.

of reaction, and therefore the extent of a reversible reaction is determined after it has reached equilibrium.

Sometimes it is desirable to alter the conditions of a reaction to prevent equilibrium from occurring. In the industrial preparation of HCl (the last reaction in Table 13.2), the gaseous HCl is removed from the reaction vessel as soon as it forms. This operation prevents the HCl from combining with the Na_2SO_4 to form the reactants from the reverse reaction, and thus equilibrium cannot be attained. The NaCl and H_2SO_4 simply continue to react until one or both have been used up, and the maximum possible amount of HCl is therefore obtained. In other words, the reaction is forced to go to completion.

13.2 THE EQUILIBRIUM CONSTANT

Let us now examine the isomerization of 2-butene more carefully. Table 13.1 shows that 0.60 mol of the *trans* isomer is obtained at equilibrium when the reaction is begun with 1.00 mol of the cis isomer. In order to check the reversibility of the reaction, we can introduce 1.00 mol of the *trans* isomer into an empty 1-L flask at 400°; we will find that at equilibrium 0.60 mol of the *trans* isomer and 0.40 mol of the *cis* isomer are present. Thus, the reaction is reversible. Furthermore, we have found that the equilibrium can be approached from either side of the equation and that the relative concentrations of the isomers at equilibrium are independent of how the equilibrium is approached. Indeed, it appears that the ratio of the concentrations of the two isomers may be a constant at equilibrium.

Let us evaluate the theoretical likelihood of this suggestion. The rate of the forward reaction (the conversion of the *cis* to the *trans* isomer) depends only on the concentration of the *cis* isomer. Since this reaction is first-order with respect to the *cis* isomer, this dependence can be expressed as

$$\text{Rate}_{\text{forward}} = k_f[cis]$$

where k_f is the rate constant for the forward reaction. In the same way, the rate of the reverse reaction (the conversion of the *trans* to the *cis* isomer) can be expressed as

$$\text{Rate}_{\text{reverse}} = k_r[trans]$$

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, and therefore,

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

$$k_f[cis] = k_r[trans]$$

or, rearranging,

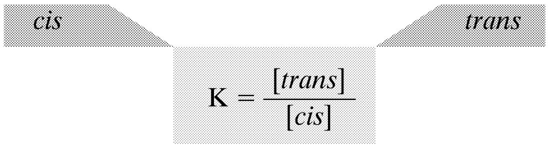
$$\frac{k_f}{k_r} = \frac{[trans]}{[cis]}$$

Theoretically, then, the ratio of the concentrations of the two isomers at equilibrium is equal to a quotient of two constants, which must, of course, be another constant:

$$\frac{k_f}{k_r} = K = \frac{[trans]}{[cis]}$$

Because the rate constants are dependent only on temperature and the presence of catalysts, and since catalysts affect the forward and reverse constants proportionately, the **equilibrium constant *K*** is dependent only on temperature.

The equilibrium constant for the 2-butene isomerization can now be calculated from the previous data on the composition of an equilibrium mixture. Regardless of from which side the equilibrium is approached, the equilibrium composition is 40% *cis* isomer and 60% *trans* isomer. The equation calls for the use of concentrations,



$$K = \frac{[\mathit{trans}]}{[\mathit{cis}]}$$

however, and since 0.60 mol of *trans* and 0.40 mol of *cis* are present in a 1-L flask (both isomers are gases at this temperature), the concentrations are 0.60 mol/L and 0.40 mol/L, respectively. Substitution of these concentrations into the equation for the equilibrium constant yields the result that for the isomerization at 400 °C, $K = 1.5$.

The considerable importance of the equilibrium expression

$$K = \frac{[\mathit{trans}]}{[\mathit{cis}]}$$

lies in its ability to describe the composition of any equilibrium mixture of two isomers at a given temperature. Suppose, for example, that 0.20 mol of the *cis* isomer is isomerized at 400 °C in a 1-L flask. At this temperature, the equilibrium mixture must consist of 40% *cis* isomer and 60% *trans* isomer. Since the total amount of the two isomers at equilibrium is 0.20 mol, the amount of *cis* present will be 0.40 × 0.20 mol = 0.08 mol, and the amount of *trans* present will be 0.60 × 0.20 mol = 0.12 mol.

The same result could have been obtained by the use of simple algebra and a knowledge of chemical stoichiometry. Since the amount of the *trans* isomer at equilibrium is unknown, we will represent it by x. Now, every mole of *cis* isomer that reacts produces a mole of *trans* isomer, and so the amount of *cis* isomer at equilibrium is the amount introduced into the flask less the amount of *trans* isomer formed. Hence, the amount of the *cis* isomer is $0.20 - x$.

The concentrations at equilibrium are

$$[\mathit{trans}] = \frac{x\ \text{mol}}{1\ \text{L}} \qquad [\mathit{cis}] = \frac{(0.20 - x)\ \text{mol}}{1\ \text{L}}$$

which can be substituted into the equilibrium expression

$$K = \frac{[\mathit{trans}]}{[\mathit{cis}]} = 1.5 \qquad K = \frac{x}{0.20 - x} = 1.5$$

Solving for x, we obtain

$$\begin{aligned} x &= 1.5(0.20 - x) = 0.30 - 1.5x \\ 2.5x &= 0.30 \\ x &= 0.12\ \text{mol/L} \end{aligned}$$

Thus, at equilibrium there is 0.12 mol/L of the *trans* isomer and 0.20 − 0.12 = 0.08 mol/L of the *cis* isomer. This procedure can be summarized in tabular form as follows:

	cis	$\rightleftharpoons$	*trans*
Start			
concentration (mol/L)	0.20		0
Change			
concentration (mol/L)	$-x$		x
Equilibrium			
concentration (mol/L)	$0.20 - x$		x
Since $x = 0.12$	0.08		0.12

Here the starting concentrations, the changes that occur in the concentrations during the reaction, and the final equilibrium concentrations are listed. Note that because x is defined as the amount of *trans* isomer produced during the reaction, x moles of the *cis* isomer are consumed, and therefore the change in the amount of the *cis* isomer is $-x$. It is also important to realize that in general, the equilibrium amount (or concentration) for a particular reactant or product will be the sum of the amount (or concentration) present at the start of the reaction and that consumed or produced during the reaction; that is, [equilibrium] = [start] + [change].

Now suppose that we come upon a mixture of *cis* and *trans* 2-butene that someone left in the laboratory (at 400 °C). Can we tell whether this mixture is at equilibrium? Assuming that we can determine the concentrations of both isomers, we can determine the ratio

$$\frac{[\textit{trans}]}{[\textit{cis}]}$$

If this ratio is equal to the equilibrium constant (1.5 at 400°C), then we can be assured that the mixture is at equilibrium.

If this ratio is less than the equilibrium constant, the concentration of the *cis* isomer is too large (and the concentration of the *trans* isomer is too small); we can conclude that the reaction was probably recently started with the *cis* isomer and that it has not yet reached equilibrium. Thus, the reaction

$$\textit{cis} \rightleftharpoons \textit{trans}$$

is proceeding from left to right and will reach equilibrium when the ratio

$$\frac{[\textit{trans}]}{[\textit{cis}]}$$

reaches 1.5.

If the ratio is greater than the equilibrium constant, then we can also conclude that the reaction is not at equilibrium and that the reaction was probably recently started by placing the *trans* isomer in solution. The reaction is therefore proceeding from right to left (from *trans* to *cis*) and when the ratio is 1.5, the reaction will be at equilibrium and the concentrations will no longer change.

This ratio, called the **reaction quotient**, $\boldsymbol{Q}$, is a convenient measure of the progress of the reaction toward equilibrium. When the reaction is at equilibrium,

$$Q = K$$

It is important to carefully work through Methodologies 13.1 and 13.2, both of which deal with the same reaction.

Methodology 13.1

Calculate the equilibrium concentrations of the two geometric isomers at a temperature at which the equilibrium constant is 4.3. The reaction is started with 0.20 mol of the trans isomer in a 3.0-L flask.

We always begin an equilibrium problem by writing down the equation and equilibrium expression for the reaction.

$$\textit{cis} \rightleftharpoons \textit{trans}$$

$$K = 4.3 = \frac{[\textit{trans}]}{[\textit{cis}]}$$

Let x be the amount of *cis* isomer at equilibrium, and set up an equilibrium table.

	cis $\rightleftharpoons$	***trans***
Start		
amount (mol)	0	0.20
concentration (mol/L)	0	$\frac{0.20}{3} = 0.067$

Continued on the next page

Methodology 13.1 Continued

Change		
amount (mol)	x	$-x$
concentration (mol/L)	$\frac{x}{3}$	$-\frac{x}{3}$
Equilibrium		
concentration (mol/L)	$\frac{x}{3}$	$\frac{0.20 - x}{3} = 0.067 - \frac{x}{3}$

Insert the equilibrium concentrations into the equilibrium expression and solve for x.

When these concentrations are inserted into the equilibrium expression, the volumes (3 L) cancel:

$$K = \frac{[trans]}{[cis]} = 4.3 = \frac{(0.20 - x \text{ mol})/3 \text{ L}}{x \text{ mol}/3 \text{ L}} = \frac{0.20 - x}{x}$$

Solving for x gives

$$x = 0.038 \text{ mol}$$

What are the amounts of each isomer at equilibrium?

At equilibrium there are 0.038 mol of *cis* isomer and 0.20 − 0.038 = 0.16 mol of *trans* isomer. The concentrations of the isomers are 0.038/3 = 0.013 mol/L of *cis* and 0.16/3 = 0.053 mol/L of *trans*.

Methodology 13.2

If 0.10 mol of the *trans* isomer is added to the equilibrium mixture in Methodology 13.1 (0.16 mol *trans*, 0.038 mol *cis*), determine the composition of the mixture after equilibrium has been reestablished.

Write the equation and equilibrium expression for the reaction.

$$cis \rightleftharpoons trans$$

$$K = 4.3 = \frac{[trans]}{[cis]}$$

What is the reaction quotient immediately after the 0.10 mol of *trans* isomer has been added?

At the very instant the 0.10 mol of *trans* isomer is added to the mixture, the concentration of *trans* isomer is 0.10 + 0.16 = 0.26 mol/3 L = 0.087 mol/L and the *cis* isomer concentration is still 0.0127 mol/L. At this instant, the reaction quotient is

$$Q = \frac{[trans]}{[cis]} = \frac{0.087 \text{ mol/L}}{0.0127 \text{ mol/L}} = 6.9$$

that is, the concentration of the *trans* isomer is more than 4.3 greater than the concentration of the *cis* isomer. The system must now adjust itself so that the ratio of concentrations is again 4.3 (so that $Q = K$).

How is equilibrium reestablished?

Equilibrium can be regained only by conversion of the *trans* isomer to the *cis* isomer, Thus, when equilibrium is reestablished, the new concentration of the *cis* isomer will be greater than 0.0127 mol/L.

Continued on the next page

Methodology 13.2 Continued

Set up the equilibrium table for the establishment of the new equilibrium.

The new equilibrium amounts can be calculated by letting x represent the amount of *trans* isomer converted to cis isomer after the 0.10 mol of *trans* isomer is added. The amount of *cis* isomer formed during the re-establishment of equilibrium is also x.

	cis	$\rightleftharpoons$	*trans*
Start (mol)	0.038		0.26
Change (mol)	x		$-x$
Equilibrium (mol)	$0.038 + x$		$0.26 - x$

Calculate the equilibrium amounts of *cis* and *trans* isomers.

At equilibrium,

$$[trans] = (0.26 - x)\ \text{mol}/3\ \text{L}$$

$$[cis] = (0.038 + x)\ \text{mol}/3\ \text{L}$$

$$\frac{[trans]}{[cis]} = 4.3$$

$$\frac{(0.26 - x\ \text{mol})/3\ \text{L}}{(0.038 + x\ \text{mol})/3\ \text{L}} = 4.3$$

$$x = 0.019\ \text{mol}$$

At the new equilibrium, then, the concentration of the *trans* isomer is (0.262 − 0.019)mol/3 L = 0.243 mol/3 L = 0.081 mol/L, and the concentration of the *cis* isomer is (0.038 + 0.019)mol/3 L = 0.057 mol/3 L = 0.019 mol/L. Thus the concentration of the *trans* isomer is once again 4.3 times as great as the concentration of the *cis* isomer.

The equilibrium expressions for more complex chemical reactions can be generalized as follows. Consider a reaction of the type

$$a\text{A} + b\text{B} + c\text{C} + \cdots \rightleftharpoons e\text{E} + f\text{F} + g\text{G} + \cdots$$

where A, B, and C represent the starting materials; E, F, and G are the products; and the letters a, b, c, and so on, are the coefficients of these materials in the balanced equation. The equilibrium expression for the reaction can be written as

$$K = \frac{[\text{E}]^e[\text{F}]^f[\text{G}]^g \cdots}{[\text{A}]^a[\text{B}]^b[\text{C}]^c \cdots}$$

For example, the equilibrium expression for the decomposition of NO is as follows:

$$2\,\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$$

$$K = \frac{[\text{N}_2]\,[\text{O}_2]}{[\text{NO}]^2}$$

Similarly, the expression for the production of NH_3 is

$$\text{N}_2(g) + 3\,\text{H}_2(g) \rightleftharpoons 2\,\text{NH}_3(g)$$

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2]\,[\text{H}_2]^3}$$

Methodology 13.3

The decomposition of N_2O_4 to NO_2 is carried out at 8°C in chloroform. When equilibrium has been established, 0.20 mol of N_2O_4 and 2.0×10^{-3} mol of NO_2 are present in 2.0 L of solution. Calculate the equilibrium constant for the reaction at 8°C.

Write the equation and the equilibrium expression for the reaction.

The balanced equation for the reaction is

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

and the corresponding equilibrium expression is

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

Convert the amounts of N_2O_4 and NO_2 present to concentrations in moles per liter of solution.

$$[NO_2] = \frac{2.0 \times 10^{-3}\ \text{mol}}{2.0\ \text{L}} = 1.0 \times 10^{-3}\ \text{mol/L}$$

$$[N_2O_4] = \frac{0.20\ \text{mol}}{2.0\ \text{L}} = 1.0 \times 10^{-1}\ \text{mol/L}$$

Because these are equilibrium concentrations, they can be directly inserted into the equilibrium expression.

$$K = \frac{[1.0 \times 10^{-3}\ \text{mol/L}]^2}{[1.0 \times 10^{-1}\ \text{mol/L}}$$

$$= \frac{1.0 \times 10^{-6}\ \text{mol}^2/\text{L}^2}{1.0 \times 10^{-1}\ \text{mol/L}}$$

$$= 1.0 \times 10^{-5}\ \text{mol/L}$$

In this case, the equilibrium constant has the units of moles per liter. Usually the units are omitted when the constant is reported.

Some Important Features of the Equilibrium Expression

There are several important features of the equilibrium expression. The first of these is that unless otherwise specified, equilibrium constants refer to the equation containing the lowest possible whole-number coefficients. For the formation of ammonia (NH_3), this equation and the corresponding equilibrium expression and constant were given above. If this equation is multiplied by 2, the equilibrium constant associated with the new equilibrium expression is the old constant raised to the second power.

$$2\ N_2 + 6\ H_2 \rightleftharpoons 4\ NH_3$$

$$K' = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} = K^2$$

where

$$K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

If the equation is multiplied by $\frac{1}{2}$, the constant K'' is $K^{1/2}$.

$$\frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{H_2} \rightleftharpoons \mathrm{NH_3}$$

$$K'' = \frac{[\mathrm{NH_3}]}{[\mathrm{N_2}]^{1/2}[\mathrm{H_2}]^{3/2}} = K^{1/2}$$

A second feature of the equilibrium expression is that it always contains the products of the equation in its numerator and the reactants in the denominator.

$$\mathrm{N_2} + 3\,\mathrm{H_2} \rightleftharpoons 2\,\mathrm{NH_3}$$

product

$$\mathrm{K} = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

If an equation is reversed, the new products are placed in the numerator.

$$2\,\mathrm{NH_3} \rightleftharpoons \mathrm{N_2} + 3\,\mathrm{H_2}$$

$$\mathrm{K}''' = \frac{[\mathrm{N_2}][\mathrm{H_2}]^3}{[\mathrm{NH_3}]^2}$$

Here the equilibrium constant K''' is $1/K$, the reciprocal of the previous constant, K.

Another feature of the equilibrium constant is that its value can often be calculated from known constants for related reactions. Suppose, for example, that the value of K_1 below has not been determined experimentally for the given reaction:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{D} \qquad K_1$$

However, suppose the constants for the following two reactions are known:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \qquad K_2$$

$$\mathrm{C} \rightleftharpoons \mathrm{D} \qquad K_3$$

Since chemical equations can be manipulated just like mathematical equations, we can add the last two equations, so that the substance C appears on opposite sides of the equality sign (arrows) and therefore cancels. The sum is the desired equation.

$$\begin{array}{r} \mathrm{A} + \mathrm{B} \rightleftharpoons \cancel{\mathrm{C}} \\ + \quad \cancel{\mathrm{C}} \rightleftharpoons \mathrm{D} \\ \hline \mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{D} \end{array}$$

However, equilibrium expressions contain the concentrations of substances as products rather than as sums. Therefore, to obtain the constant K_1, we simply multiply K_2 by K_3.

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{D} \qquad K_1 = \frac{[\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \qquad K_2 = \frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\mathrm{C} \rightleftharpoons \mathrm{D} \qquad K_3 = \frac{[\mathrm{D}]}{[\mathrm{C}]}$$

$$K_2 \times K_3 = \frac{[\cancel{C}]}{[A][B]} \times \frac{[D]}{[\cancel{C}]}$$

$$= \frac{[D]}{[A][B]} = K_1$$

A fourth feature of the equilibrium expression is that it is given in terms of concentrations. When a substance is a gas, its concentration is expressed either in moles per liter (per volume of the reaction vessel) or in terms of its partial pressure (under ideal conditions, partial pressure is proportional to concentration). When partial pressures are used, the equilibrium constant is referred to as K_p, as opposed to the designation K_c, which is used when moles per liter are the units. When the substance in question is in a liquid solution, its concentration is given in moles per liter of solution.

When the substance is a pure liquid or solid that is not in solution, its concentration is the number of moles per unit volume of the substance. For example, the concentration of 18 g of H_2O is 1 mol per 18 mL (since 1 g of H_2O occupies 1 mL at room temperature and pressure), or 55.5 mol/L. The concentration of 100 g of H_2O is exactly the same—55.5 mol/L.

The concentrations of liquids and solids that are part of a heterogeneous mixture are therefore independent of the amount present. Moreover, since the densities of liquids and solids are virtually unaffected by changes in pressure, their concentrations are also independent of pressure. At a constant temperature, then, the concentration of a liquid or solid that is not in solution is a constant. For this reason, the concentrations of such substances are generally not included in the equilibrium expression, and the equilibrium constant is adjusted to include these constant concentrations.

The decomposition of barium carbonate in a closed vessel is an example of a heterogeneous equilibrium:

$$BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$$

The equilibrium expression for this reaction could be written as

$$K' = \frac{[BaO(s)][CO_2(g)]}{[BaCO_3(s)]}$$

But since the concentrations of the two solids, BaO and $BaCO_3$, are constants, the equilibrium constant can also be written as

$$K = \underbrace{K'\frac{[BaCO_3(s)]}{[BaO(s)]}}_{\text{all constants}} = [CO_2(g)]$$

or, more simply,

$$K = [CO_2(g)]$$

This final equilibrium expression is the simple algebraic statement that at a given temperature, the concentration of CO_2 produced in this reaction is a constant.

The decomposition of water (shown earlier in Table 13.2) is an example of a heterogeneous liquid-gas reaction. Here the concentration of the liquid is constant, and the equilibrium expression is

$$2\,H_2O(l) \rightleftharpoons 2\,H_2(g) + O_2(g)$$

$$K = [H_2(g)]^2[O_2(g)]$$

A final feature of the equilibrium expression that should be considered is that, like the ideal gas law ($PV = nRT$) and Raoult's Law ($P = P°X$), the equilibrium expression describes idealized behavior. That is, the quotient below is a constant, independent of actual amounts and pressure, only at low concentrations (and constant temperature):

$$K = \frac{[\mathrm{E}]^e[\mathrm{F}]^f \cdots}{[\mathrm{A}]^a[\mathrm{B}]^b \cdots}$$

In order to illustrate several features of the equilibrium expression, let us consider the commercial preparation of gaseous carbon monoxide, which is accomplished by heating solid carbon with gaseous carbon dioxide at high temperatures. At some temperature, 0.090 mol of carbon dioxide is mixed in a 5-L flask with an excess of carbon. When equilibrium is established, 0.040 mol of carbon dioxide remains and the total pressure in the system is 1.3 atm.

First, we write the equation and equilibrium expression for the process.

$$\mathrm{C}(s) + \mathrm{CO_2}(g) \rightleftharpoons 2\,\mathrm{CO}(g)$$

$$K = \frac{[\mathrm{CO}(g)]^2}{[\mathrm{CO_2}(g)]}$$

We know that the amount of CO_2 that has been converted to CO is equal to the amount present at the start of the reaction minus the amount present at equilibrium: $0.090 - 0.040 = 0.050$ mol. According to the equation, 2 mol of CO are produced from the conversion of 1 mol of CO_2; therefore the amount of CO produced is $0.050 \times 2 = 0.10$ mol.

In order to determine the equilibrium constant, K_c, we need the equilibrium concentrations of CO and CO_2:

$$[\mathrm{CO}] = \frac{0.10\ \mathrm{mol}}{5\ \mathrm{L}} = 0.020\ \mathrm{mol/L}$$

$$[\mathrm{CO_2}] = \frac{0.040\ \mathrm{mol}}{5\ \mathrm{L}} = 0.0080\ \mathrm{mol/L}$$

We then substitute these values into the equilibrium expression:

$$K_c = \frac{(2.0 \times 10^{-2})^2}{8.0 \times 10^{-3}} = 5 \times 10^{-2}\ \mathrm{mol/L}$$

In order to determine the equilibrium constant, K_p, in terms of partial pressures, we need the partial pressure of each gaseous constituent. The partial pressure is the mole fraction of the constituent times the total pressure. Thus,

$$\begin{aligned} p_{\mathrm{CO}} &= (X_{\mathrm{CO}})(1.3\ \mathrm{atm}) = \frac{0.10\ \mathrm{mol}}{0.10\ \mathrm{mol} + 0.40\ \mathrm{mol}}(1.3\ \mathrm{atm}) \\ &= 0.93\ \mathrm{atm} \end{aligned}$$

$$\begin{aligned} p_{\mathrm{CO_2}} &= (X_{\mathrm{CO_2}})(1.3\ \mathrm{atm}) = \frac{0.040\ \mathrm{mol}}{0.10\ \mathrm{mol} + 0.040\ \mathrm{mol}}(1.3\ \mathrm{atm}) \\ &= 0.37\ \mathrm{atm} \end{aligned}$$

Finally, the partial pressures are inserted into the equilibrium expression,

$$K_p = \frac{(0.93)^2}{0.37} = 2.3\ \mathrm{atm}$$

Although we have given both K_c and K_p with their corresponding units, generally equilibrium constants are expressed without units.

Methodology 13.4 and Problems 13.1 and 13.2 illustrate the calculation of the equilibrium constant from the composition of the reaction mixture at equilibrium.

Methodology 13.4

For the reaction of nitrogen with hydrogen to form ammonia,

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

we add 0.25 mol of N_2 to 0.40 mol of H_2 in a one-liter flask. When equilibrium is established 0.20 mol of ammonia are present. Calculate the equilibrium constant.

Rewrite the equation and the equilibrium expression.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

$$K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Examine the equilibrium table below:

	$N_2(g)$	$+\ 3\,H_2(g)$	$\rightleftharpoons 2\,NH_3(g)$
Start	0.25	0.40	0
Change			
Equilibrium			0.20

Does this equilibrium table contain concentrations or amounts?

> Because the reaction occurs in a one-liter flask, the amounts given in the problem are also the concentrations; e.g. 0.20 mol/L = 0.20 M.

Why does the table contain a zero for the concentration of ammonia at the start of the reaction?

> We are told that 0.25 mol of N_2 were added to 0.40 mol of H_2 in a one-liter flask. This wording implies that the flask was empty before the N_2 and H_2 were added. Thus, at the very beginning of the reaction there was no ammonia present.

How do we determine the equilibrium concentrations of N_2 and H_2?

> We know how much ammonia was produced during the reaction. That is, 0.20 mol of ammonia was produced, and therefore this concentration goes into the change row for ammonia. We must now determine how much N_2 and H_2 were consumed during the reaction.

If 0.20 mol of ammonia was produced during the reaction, how much N_2 and H_2 were consumed during the reaction?

> These amounts are obtained from the stoichiometry of the equation. The equation tells us that every time one mole of ammonia is obtained, 0.5 mol N_2 and 1.5 mol H_2 are consumed. Thus, if 0.20 mol of ammonia are obtained
>
> $$0.20 \text{ mol} \times 0.5 = 0.10 \text{ mol of } N_2$$
> $$0.20 \text{ mol} \times 1.5 = 0.30 \text{ mol of } H_2$$
>
> were consumed.

Add these values to the equilibrium table.

	$N_2(g)$	$+\ 3\,H_2(g)$	$\rightleftharpoons 2\,NH_3(g)$
Start	0.25	0.40	0
Change	−0.10	−0.30	+0.20
Equilibrium			0.20

Continued on the next page

Methodology 13.4 Continued

Why are the concentrations of N_2 and H_2 given in the change row with a minus sign?

The minus sign indicates that during the reaction, N_2 and H_2 were consumed (used up).

Now put the concentrations of N_2 and H_2 in the equilibrium positions of the table. Remember that [equil] = [start] + [change].

	$N_2(g)$ +	$3\,H_2(g) \rightleftharpoons$	$2\,NH_3(g)$
Start	0.25	0.40	0
Change	−0.10	−0.30	+0.20
Equilibrium	0.15	0.10	0.20

Finally, place the equilibrium concentrations into the equilibrium expression and calculate *K*.

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.20)^2}{(0.15)(0.10)^3} = 2.7 \times 10^2$$

Problem 13.1

When 10 g of PCl_5 dissociates into PCl_3 and Cl_2 in a 3.0-L flask at 250 °C, 63% of the PCl_5 is converted to products. Calculate the equilibrium constant (K_c) for this reaction at 250 °C.

Solution:

The equation and corresponding equilibrium expression are

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

The number of moles of PCl_5 at the beginning of the reaction is

$$\frac{10\text{ g}}{208\text{ g/mol}} = 0.048\text{ mol}$$

At equilibrium, 63% of the PCl_5 has been converted to PCl_3 and Cl_2. Therefore, 0.63 × 0.048 mol, or 0.030 mol of PCl_3 and 0.030 mol of Cl_2, are present at equilibrium. (The stoichiometry of the equation dictates that for every molecule of PCl_5 that reacts, one molecule of PCl_3 and one molecule of Cl_2 are formed.) The amount of PCl_5 remaining at equilibrium is 0.048 − 0.030 = 0.018 mol. These results are summarized below:

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Start			
amount (mol)	0.048	0	0
Change			
amount (mol)	−0.030	0.030	0.030
Equilibrium			
amount (mol)	0.048 − 0.030	0.030	0.030
concentration (mol/L)	0.0060	0.010	0.010

The value of the equilibrium constant is therefore:

$$K_c = \frac{(1.0 \times 10^{-2})(1.0 \times 10^{-2})}{6.0 \times 10^{-3}} = 1.7 \times 10^{-2}\text{ mol/L}$$

Problem 13.2

For the gas phase reaction

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

0.40 mol of H_2 and 0.50 mol of HI are placed in an empty 1.0-L flask. When equilibrium is established 0.20 mol of I_2 are present. Calculate the equilibrium constant.

	H_2	+	I_2	$\rightleftharpoons$	2 HI
Start	0.40		0		0.50
Change	0.20		0.20		−0.40
Equilib	0.60		0.20		0.10

$$K = \frac{(HI)^2}{(H_2)(I_2)}$$

$$K = \frac{(0.10)^2}{(0.60)(0.20)} = 0.083$$

Check Point 13.1

Ethyl acetate can be prepared according to the following equation:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

At some temperature, 0.10 mol of acetic acid is mixed with 0.10 mol of ethyl alcohol in 1.0 L of solution (an unreactive solvent is used). When equilibrium has been established, 0.060 mol of ethyl acetate is present. Calculate the equilibrium constant.

Solution:

2.2

◇ ◇ ◇ ◇ ◇

13.3 THE EQUILIBRIUM CONSTANT AS A MEASURE OF EXTENT

If the equilibrium constant for a particular reaction is known, we can determine the reaction's equilibrium composition and, consequently, the amount of product formed from a given amount of reactant—that is, the extent of the reaction. Also, the relative extents of two reactions can often be ascertained by comparing their equilibrium constants.

In order to illustrate the evaluation of relative extents, let us examine two simple, generalized reactions. The first reaction can be represented as

$$A \rightleftharpoons B$$

which is a general expression for reactions such as the geometrical isomerization considered previously. Suppose that for a certain reaction of this type, the equilibrium constant is 1.0×10^{-1}. The amount of product obtained in the reaction from, say, 1.0 mol of A can be obtained by the same algebraic procedure used in the discussion of the isomerization. Accordingly, if x is used to represent the amount of B present at equilibrium, the amount of A remaining at equilibrium will be $1.0 - x$. Inserting these amounts into the equilibrium expression (note that the volume cancels in this case), we have

$$\frac{x}{10 - x} = K = 1.0 \times 10^{-1}$$

$$x = 0.091 \text{ mol}$$

Hence, from 1.0 mol of A, 0.091 mol of B has been obtained. Since total conversion of A to B would have resulted in 1.0 mol of B, the reaction has gone 9.1% to completion.

Suppose, now, that for a different reaction of the same type ($A \rightleftharpoons B$), the equilibrium constant is 1.0. In this reaction, 50% of A is converted to B. Obviously, the extent of this reaction is greater than that of the reaction for which $K = 1.0 \times 10^{-1}$.

Finally, consider a reaction of different stoichiometry,

$$A \rightleftharpoons 2\,B$$

such as the reaction $N_2O_4 \rightleftharpoons 2\,NO_2$. If we again assume an equilibrium constant of 1.0×10^{-1}, we can calculate the amount of B formed from 1.0 mol of A when the reaction is conducted in a total volume of 1 L. The stoichiometry of the equation indicates that the conversion of 1 mol of A results in the formation of 2 mol of B, and if we let x represent the amount of A converted, $2x$ is the amount of B formed at equilibrium. Since the total volume is 1.0 L, the equilibrium concentrations are

$$[A] = 1.0 - x \qquad [B] = 2x$$

and

$$K = 1.0 \times 10^{-1} = \frac{[B]^2}{[A]} = \frac{(2x)^2}{1.0 - x}$$

or

$$4x^2 = 1.0 \times 10^{-1} - 1.0 \times 10^{-1}x$$

This quadratic equation can be solved with the quadratic formula, which for the equation

$$ax^2 + bx + c = 0$$

is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Rearranging our equation to the same form results in

$$4x^2 + 1.0 \times 10^{-1}x - 1.0 \times 10^{-1} = 0$$

Thus, $a = 4$, $b = 1.0 \times 10^{-1}$, and $c = -1.0 \times 10^{-1}$. The solution to the equation is then

$$x = \frac{-1.0 \times 10^{-1} \pm \sqrt{(1.0 \times 10^{-1})^2 - 4[4(-1.0 \times 10^{-1})]}}{2(4)}$$
$$= \frac{-1.0 \times 10^{-1} \pm 1.3}{8} = \frac{1.2}{8}, -\frac{1.4}{8}$$

The negative solution cannot be the correct solution to this problem, because it would mean that at equilibrium $1.0 - (-0.175) = 1.2$ mol of A is present, which is more than was present at the beginning of the reaction. The correct solution is therefore 0.15 mol; this represents the amount of A that reacted. The amount of B present at equilibrium is twice this amount, 0.30 mol.

Total conversion of 1.0 mol of A would result in 2.0 mol of B; therefore, the extent of this reaction is

$$\frac{0.30}{2.0} \times 100 = 15\%$$

which is greater than the 9.1% extent of the $A \rightleftharpoons B$ reaction with the same equilibrium constant. Thus, comparing the equilibrium constants of two reactions will reveal their relative extents only when the reactions have the same stoichiometry; that is, when they are both $A \rightleftharpoons B$, or both $A + B \rightleftharpoons 2\,C$, and so on.

13.4 THE EFFECT OF CONCENTRATION ON EXTENT

A further complication that arises when equilibrium constants are used as an index of extent of reaction is that extent is also influenced by the concentrations of starting materials and the concentrations of any products that may be present at the beginning of the reaction. The esterification of acetic acid with ethyl alcohol provides an example of the effect of concentration on extent. Let us first calculate the amount of ethyl acetate formed when 0.10 mol of acetic acid is mixed with 0.10 mol of ethyl alcohol in a sufficient amount of nonreactive solvent to give 1 L of solution. The equation and equilibrium expression for this reaction are

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = 2.2$$

The amounts of ethyl acetate and water at equilibrium are also the concentrations in this case, because the volume of solution is 1.0 L. Because these amounts are unknown, we shall define x as the amount of ethyl acetate present at equilibrium; this is also the amount of water at equilibrium. The amounts of starting materials must be $0.10 - x$.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Start	0.10	0.10	0	0
Change	$-x$	$-x$	x	x
Equilibrium	$0.10 - x$	$0.10 - x$	x	x

Therefore:

$$K = 2.2 = \frac{(x)(x)}{(0.10 - x)(0.10 - x)} = \frac{x^2}{0.010 - 0.20x + x^2}$$

$$0.022 - 0.44x + 2.2x^2 = x^2$$

$$1.2x^2 - 0.44x + 0.022 = 0$$

$$x = 0.44 \pm \frac{\sqrt{0.194 - 0.106}}{2.4}$$

$$= 0.31, 0.060$$

The value $x = 0.31$ obtained from the quadratic equation cannot be the solution for this particular problem, because it would mean that more starting material was converted to product than was originally present (we began with only 0.10 mol of reactants). The correct solution is $x = 0.060$, which is, in moles, the amount of ethyl acetate and the amount of water present at equilibrium and also the amount of acetic acid and ethyl alcohol converted to product. The extent of the reaction is therefore

$$\frac{0.060}{0.10} \times 100 = 60\%$$

Imagine now that the reaction is run a second time at the same temperature, again using 0.10 mol of acetic acid, but with 1.0 rather than 0.10 mol of ethyl alcohol. The amounts of products at equilibrium can again be represented by x.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Start	0.10	1.0	0	0
Change	$-x$	$-x$	x	x
Equilibrium	$0.10 - x$	$1.0 - x$	x	x

Therefore:

$$K = 2.2 = \frac{(x)(x)}{(0.10 - x)(1.0 - x)}$$

$$x = 1.9, 0.096$$

The correct solution, $x = 0.096$, is the amount of acetic acid converted to products. Since the maximum amount of ethyl acetate (and H_2O) obtainable from this reaction is 0.10 mol, the percent conversion is

$$\frac{0.096}{0.10} \times 100 = 96\%$$

Increasing the concentration of one of the starting materials has therefore increased the extent of reaction. In mathematical terms, an increase in the concentration of the ethyl alcohol results in an increase in the denominator of the equilibrium expression, which must be compensated for by an increase in the numerator if a constant numerator/denominator ratio is to be maintained.

Synthetic chemists are often concerned with the reaction conditions necessary to obtain a certain amount of product. Suppose now that 0.098 mol of the ethyl acetate is desired, but that the amount of acetic acid to be used must still be 0.100 mol. How much ethyl alcohol should be mixed with the acetic acid (in 1 L of solution) in order to accomplish this goal?

In this problem the concentrations of ethyl acetate and water at equilibrium are known: both are 0.098 mol/L. The concentration of acetic acid at equilibrium is 0.100 − 0.098 = 0.002 mol/L. The only unknown, then, is the initial amount of the ethyl alcohol. Because 0.098 mol of the ethyl alcohol will be *consumed* during the reaction, the equilibrium concentration of C_2H_5OH will be $x - 0.098$.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Start	0.100	x	0	0
Change	−0.098	−0.098	0.098	0.098
Equilibrium	0.002	$x - 0.098$	0.098	0.098

Thus,

$$K = 2.2 = \frac{(0.098)(0.098)}{(0.002)(x - 0.098)}$$

$$x = 2.3 \text{ mol/L}$$

Therefore the amount of alcohol required at the beginning of the reaction is 2.3 mol, and the equilibrium concentration of alcohol is 2.3 − 0.098 = 2.2 mol/L. Methodology 13.5 and Problems 13.3 and 13.4 provide practice in somewhat more sophisticated equilibrium problems.

Methodology 13.5

At some temperature, the equilibrium constant for the reaction of N_2 with H_2 to form NH_3 in the gaseous state is 1.0. Calculate the amount of N_2 that must be added to 1.0 mol of H_2 (in a 1.0-L flask) in order to produce 0.30 mol of NH_3 at equilibrium.

Write the equation and equilibrium expression.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_2(g)$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Continued on the next page

Methodology 13.5 Continued

Now set up the equilibrium table and define x as the amount of N_2 with which we must start.

	$N_2(g)$ +	$3\ H_2(g) \rightleftharpoons$	$2\ NH_3(g)$
Start	x	1.0	0
Change	−0.15	−0.45	0.30
Equilibrium	$x - 0.15$	0.55	0.30

Simplify the math required to solve for x by substituting y as $x - 0.15$ and then solve for y.

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.30)^2}{(y)(0.55)^3} = 1.0$$

$y = 0.54$ and, therefore, $x = 0.69$ mol

Problem 13.3

At a certain temperature, the equilibrium composition of the 2-butene gas phase isomerization is 0.30 mol *trans* isomer and 0.10 mol *cis* isomer in a 3.00-L flask. How much of the *cis* isomer must be added to this mixture in order to obtain a total of 0.60 mol of the *trans* isomer when equilibrium is reestablished?

Solution:

First, write the equation for the reaction and calculate the equilibrium constant.

$$cis\text{-2-Butene} \rightleftharpoons trans\text{-2-Butene}$$

$$K = \frac{[trans]}{[cis]} = \frac{0.30\text{ mol}/3.00\text{ L}}{0.10\text{ mol}/3.00\text{ L}} = 3.0$$

Now, let x be the amount of *cis* added to the mixture and set up the equilibrium table using amounts.

	cis $\rightleftharpoons$	*trans*
Start	$0.10 + x$	0.30
Change	−0.30	0.30
Equilibrium	$0.10 + x - 0.30$	0.60

Finally, solve for x

$$K = 0.30 = \frac{(0.60\text{ mol}/3.00\text{ L})}{[(0.10 + x - 0.30)\text{ mol}/3.00\text{L}]}$$

$$= \frac{0.60}{x - 0.20}$$

$$x = 0.40\text{ mol}$$

Hence, 0.40 mol of *cis* isomer must be added to obtain a total of 0.60 mol of *trans* isomer. The equilibrium amount of *cis* isomer is 0.20 mol.

Problem 13.4

At some temperature, the equilibrium mixture of N_2, H_2, and NH_3 consists of 1.0 mol N_2, 1.0 mol of H_2, and 1.2 mol NH_3 in a 1.0-L flask. How much N_2 must be added to the mixture in order to increase the amount of NH_3 to 1.5 mol?

Continued on next page

Problem 13.4 *Continued*

Solution:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Start	1.0	1.0	1.2
Change	$x - 0.15$	-0.45	0.3
Equilibrium	$0.85 + x$	0.55	1.5

$x = 8.5$ mol

Concentrations can also be altered by a change in volume. This change will affect the extent of reaction whenever volumes do not cancel in the equilibrium expression (thereby making concentration changes equal for both reactants and products). The formation of hydrogen iodide from hydrogen and iodine in the gaseous state is an example of a reaction whose extent is not influenced by a change of volume. In the equilibrium expression for this reaction, the volume cancels.

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{moles/liter})^2}{(\text{moles/liter})(\text{moles/liter})}$$

In other words, a change in volume will change all the concentrations, but these changes are proportionately the same in both numerator and denominator.

The decomposition of PCl_5 is a reaction whose extent is influenced by a change in volume. Let us assume that at equilibrium at 250 °C there are 0.018 mol of PCl_5, 0.030 mol of PCl_3, and 0.030 mol of Cl_2 in a 3.00-L flask. The equilibrium constant for the reaction at 250 °C is 1.7×10^{-2} mol/L. If the volume of the vessel is now decreased to 1.0 L, the instantaneous new concentrations are $[PCl_5] = 0.018$ mol/L, $[PCl_3] = 0.030$ mol/L, $[Cl_2] = 0.030$ mol/L, and

$$\frac{(0.030\text{ mol/L})(0.030\text{ mol/L})}{(0.018\text{ mol/L})} = 5.0 \times 10^{-2}\text{ mol/L}$$

which is greater than the equilibrium constant. The system must now change in order to decrease the value of this quotient to its equilibrium value of 1.7×10^{-2} mol/L. This can be accomplished only if some of the products react to form the reactant. The volume change therefore brings about an increase in the amount of reactant and a decrease in the amount of products.

Since a change in volume for a reaction containing one or more gases is also accompanied by a change in pressure, the arguments above also apply to pressure changes brought about by changes in volume.

13.5 THE EFFECT OF TEMPERATURE ON EXTENT

It is an experimentally observed fact that an increase in temperature increases the extent of some reactions but decreases the extent of others. Furthermore, a comparison of the properties of both types of reactions reveals that those reactions whose extents are increased by an increase in temperature are endothermic reactions, while those whose extents are decreased are exothermic reactions. The change in extent produced by a change in temperature is a result of a change in the equilibrium constant.

The reaction of H_2 with I_2 to form HI is an example of an endothermic reaction.

$$\text{heat} + H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

The equilibrium constant for this reaction therefore increases with an increase in temperature.

The formation of ammonia from N_2 and H_2 is an example of an exothermic reaction.

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) + \text{heat}$$

In this case the equilibrium constant decreases with an increase in temperature.

13.6 LE CHATELIER'S PRINCIPLE

The effect of concentration and temperature on the extent of a reaction can be summarized qualitatively by **Le Châtelier's Principle**, which was introduced in the discussion of solution equilibrium in Chapter 11:

> **If a change occurs in one of the factors, such as concentration or temperature, under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change.**

The decomposition of N_2O_4 to NO_2 provides an apt illustration of the application of Le Châtelier's Principle.

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Consider a mixture of N_2O_4 and NO_2 that has reached equilibrium at some temperature.

1. *If N_2O_4 is added,* the concentration of N_2O_4 will instantaneously increase, and the system will adjust itself to relieve this increase. The only way this can be accomplished in a constant volume is for some of the N_2O_4 to react to form more NO_2. Stated in terms of the equilibrium expression, the increase in N_2O_4 results in an instantaneous increase in the denominator. In order to maintain the $[NO_2]^2/[N_2O_4]$ ratio at the constant K, the numerator must increase. This can happen only if some N_2O_4 is converted to NO_2.
2. *If the pressure of the system is increased* by decreasing the volume of the container, the mixture will react to reduce the pressure. Since there are twice as many product molecules as reactant molecules, the number of molecules hitting the walls of the container (and therefore the pressure) is reduced if some NO_2 is consumed to produce N_2O_4. The net result of the increase in pressure, is, then, a decrease in the amount of NO_2 present and an increase in the amount of N_2O_4 present.
3. *If the temperature is increased,* the system must react to relieve the increased heat. Since the forward reaction absorbs heat, the stress is relieved by the production of more NO_2. We conclude that the increase of temperature changes (increases) the equilibrium constant.

Problem 13.5

For the reaction

$$\text{heat} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

predict the effect of the following changes made on the system at equilibrium:

(a) the addition of $CaCO_3$

(b) the removal of CO_2

(c) an increase in the volume of the reaction vessel

(d) a decrease in temperature

Continued on the next page

Problem 13.5 *Continued*

Solution:

(a) Since the concentrations of the two solids are constants, the amount and concentration of CO_2 at equilibrium is independent of the actual amounts of $CaCO_3$ and CaO, as long as some of each is present. As dictated by the equilibrium expression

$$K = [CO_2(g)]$$

the equilibrium concentration of CO_2 must be constant at a given temperature.

(b) If a portion of CO_2 is removed from the equilibrium mixture, this stress (the change in concentration of CO_2) must be relieved by the production of more CO_2. Calcium carbonate decomposes, then, to produce more CaO and CO_2 until the concentration of CO_2 has once again reached its constant equilibrium value.

(c) An increase in the volume of the reaction vessel, which is the volume occupied by the CO_2, has the same consequence: The instantaneous decrease in pressure is compensated for by reaction of $CaCO_3$ to produce enough CO_2 to bring the pressure and concentration of CO_2 back to their initial values. At the new equilibrium, then, the concentration of CO_2 is the same but the total amount has increased.

(d) A decrease in temperature will remove heat from the equilibrium system. Since "heat" occurs on the left-hand side of the equation, this stress can be alleviated by conversion of some CO_2 and CaO to $CaCO_3$ and heat. The volume has not changed; therefore the amount and concentration of CO_2 have decreased. This is consistent with the decrease in equilibrium constant that must occur when the temperature of an endothermic reaction is decreased.

CHAPTER SUMMARY

The extent of a chemical reaction is the measure of how much product is formed from a certain amount of reactants after the reaction has proceeded as far as it can under a given set of conditions. In this chapter we have examined the factors that determine the extent of a chemical reaction, and learned to make both qualitative and quantitative predictions about the effects that various conditions have on this extent.

Because chemical reactions are simply processes that involve the making and breaking of bonds, if any particular reaction can occur, the reverse reaction can also occur under the proper conditions. Thus, if a chemical reaction takes place in a closed system, eventually both the reaction and its reverse will occur at the same rate. In other words, the concept of **dynamic equilibrium**, which has been applied to physical changes in earlier chapters, is also applicable to chemical changes.

For every chemical reaction at equilibrium under a given set of conditions, there is an **equilibrium constant**, denoted by the letter ***K***, that is characteristic of the reaction. The value of this constant varies only with temperature.

Concentrations are usually expressed as molarities. However, in gaseous reactions concentrations may be expressed as partial pressures. For some reactions, the value of the equilibrium constant calculated with molarities is different from that calculated with partial pressures. In these cases, K_c and K_p are used to distinguish between the two values.

Because the equilibrium constant is defined as a ratio of products to reactants, it is a measure of the extent of reaction. This constant is one of the most important and useful concepts of chemistry; you should understand it thoroughly and be able to apply it to a variety of problems.

The value of the equilibrium constant for a given reaction at a given temperature can be determined experimentally, and once evaluated it will always apply to that reaction at that temperature. This value permits us to make a variety of quantitative predictions about the effect of concentration on the extent of reaction. You should master the calculations used in making these predictions, as well as those used in solving other types of problems. Begin each problem by writing the equation for the reaction in question, and then determine (and tabulate) the initial amounts and concentrations of each reactant and product. Next, identify what you must solve for and carefully define your unknown (x). You can then tabulate the changes that occur during the reaction and calculate the final equilibrium concentrations. (Remember that the final concentration for each species will be the sum of the initial concentration and the change in concentration.) Finally, insert the equilibrium concentrations into the equilibrium expression, solve for x, and calculate all equilibrium concentrations.

Le Châtelier's Principle, which we applied to physical equilibria in Chapter 11, also pertains to chemical equilibria. Thus, we can make qualitative predictions about the effects of various conditions on the extent of reaction. Increasing the temperature of a system in equilibrium favors the endothermic process. Increasing the concentration of one of the substances involved in the equilibrium favors the reaction in which that substance is consumed. In reactions that involve gases, the effect of pressure can also be predicted: Increasing the pressure favors the reaction that tends to produce the smaller number of gas molecules.

In applying Le Châtelier's Principle to heterogeneous equilibria, you must be careful not to confuse the amount of a substance with its concentration. For example, adding some $KClO_3$ or some KCl to the equilibrium represented by the equation

$$2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$$

will not affect the equilibrium position. We have not changed the concentration of $KClO_3$ or KCl; we have changed only the amount.

TERMS

The important terms in this chapter are as follows:

Equilibrium constant For the hypothetical reaction

$$a\text{A} + b\text{B} + \cdots \rightleftharpoons c\text{C} + d\text{D} + \cdots$$

the equilibrium constant is the value of

$$\frac{[\text{C}]^c[\text{D}]^d\cdots}{[\text{A}]^a[\text{B}]^b\cdots}$$

when that reaction *is at equilibrium.* This quotient can also be evaluated at any point during a reaction and is called the **reaction quotient**, Q. At equilibrium, $Q = K$. The equilibrium constant is characteristic of a given reaction, but the value of this constant varies with temperature.

Le Châtelier's Principle If a change occurs in one of the conditions under which a system is in equilibrium, the system will adjust itself in the direction that tends to cancel out the effect of the change.

PROBLEMS

1. Consider the following reversible exothermic reaction:

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

How will the equilibrium constant and the extent of reaction be affected by each of the following changes, assuming the system is at equilibrium initially?

(a) More $O_2(g)$ is added, with the temperature and volume remaining constant.
(b) Some $SO_3(g)$ is removed, with temperature and volume remaining constant.
(c) The volume is decreased, with the temperature remaining constant.
(d) The temperature is increased, with the volume remaining constant.
(e) The temperature is increased, with the pressure remaining constant.
(f) A catalyst is added.

2. The endothermic reaction of solid carbon (as coke or coal) with steam at high temperatures is an important route to the industrial fuel called water gas, which is a mixture of carbon monoxide and hydrogen. Assume that the reaction is reversible and at equilibrium. How will the weight of the carbon monoxide present be affected by each of the following changes?

(a) More steam is added, with volume and temperature remaining constant.
(b) Some hydrogen is removed at constant volume and temperature.

(c) More solid carbon is added at constant volume and temperature.
(d) The volume is increased at constant temperature.
(e) The temperature is decreased at constant pressure.

3. Solid CuO reacts with gaseous CO to give solid Cu_2O and gaseous CO_2,

$$2\,CuO(s) + CO(g) \rightleftharpoons Cu_2O(s) + CO_2(g)$$

(a) If the system is at equilibrium, how will the following changes affect the number of moles of CO_2?
    1. More CO is added at constant temperature and pressure.
    2. Some Cu_2O is removed at constant temperature and pressure.
    3. The volume is decreased.
    4. A catalyst is added.
(b) When the reaction has reached equilibrium in a 1-L flask, 0.3 mol of CuO, 0.1 mol of CO, 0.2 mol of Cu_2O, and 0.25 mol of CO_2 are present. Calculate the equilibrium constant.

4. The following exothermic reaction can be used to produce hydrogen gas:

$$3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$$

What conditions should be used to produce the maximum yield of H_2? Explain your answer.

5. Consider the reaction

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

The equilibrium mixture in a 3.00-L vessel at a pressure of 2.0 atm was found to contain 21.0 g of $COCl_2$, 10.2 g of CO, and 18.7 g of Cl_2. Calculate the equilibrium constant in terms of both moles per liter and atmospheres.

6. The equilibrium constants for the gas-phase reactions of xenon with F_2 at 400°C are as follows:

$$\begin{aligned} Xe + F_2 &\longrightarrow XeF_2 \qquad K = 4 \times 10^2 \\ Xe + 2\,F_2 &\longrightarrow XeF_4 \qquad K = 2 \times 10^3 \\ Xe + 3\,F_2 &\longrightarrow XeF_6 \qquad K = 4 \times 10^1 \end{aligned}$$

Using these values, calculate the equilibrium constants for each of the following reactions:
(a) $XeF_4 \rightleftharpoons Xe + 2\,F_2$
(b) $\frac{1}{2}Xe + F_2 \rightleftharpoons \frac{1}{2}XeF_4$
(c) $XeF_2 + 2\,F_2 \rightleftharpoons XeF_6$
(d) $Xe + XeF_4 \rightleftharpoons 2\,XeF_2$
(e) $3\,XeF_2 \rightleftharpoons XeF_6 + 2\,Xe$
(f) $Xe + XeF_6 \rightleftharpoons XeF_2 + XeF_4$

7. If carbon dioxide is passed through hot carbon (coke), carbon monoxide is formed. At some temperature the equilibrium mixture is found to contain 0.11 mol of carbon monoxide and 0.89 mol of carbon dioxide at a total pressure of 1 atm.
(a) Write an equation for the reaction and the expression for K_p.
(b) Calculate the numerical value of K_p.
(c) If enough carbon dioxide is passed into the equilibrium mixture to increase the equilibrium partial pressure of carbon dioxide to 2 atm, what is the equilibrium partial pressure of carbon monoxide?

8. The equilibrium constant K_c for a gas-phase reaction can be converted to K_p by using the ideal gas equation, $PV = nRT$.
(a) Use this equation to convert moles/liter to partial pressure, thereby converting K_c to K_p, for each of the following reactions:
(b) What is the general formula for the conversion of K_c to K_p?

9. Consider the following equilibrium at 298 K with K_c = 7.04.

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

What is the value of K_p for this equilibrium?

10. For a given mixture in a 250-mL flask at 298 K, the equilibrium pressures of NO_2 and N_2O_4 are 0.392 atm and 1.16 atm, respectively. If the gases were compressed to a volume of 0.125 L, what would be the pressures and molar concentrations of NO_2 and N_2O_4 after equilibrium had been reestablished?

11. At 500 °C $K_p = 1.50 \times 10^{-5}$ for the ammonia synthesis reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$$

(a) Determine K_c for this equilibrium.
(b) If 1.40 *g* of nitrogen and 1.25 *g* of hydrogen are placed into an empty 10.0-L vessel at 500 °C, what will the yield of ammonia be when the system reaches equilibrium?

12. An equilibrium mixture of N_2, H_2, and NH_3 at some high temperature in a 3-L flask consists of 0.15 mol of N_2, 0.10 mol of H_2, and 0.050 mol of NH_3. What is the equilibrium constant?

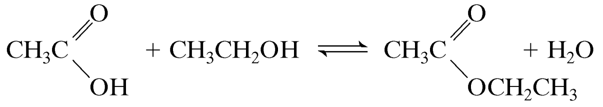
13. A mixture of nitrogen, hydrogen, and ammonia is at equilibrium and contains 0.20 mol nitrogen, 0.20 mol hydrogen, and 0.20 mol ammonia in a 1.0-L flask.
(a) Calculate the equilibrium constant.
(b) Determine how much nitrogen must be added to this mixture in order to increase the amount of ammonia to 0.30 mol.

14. The equilibrium constant for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

at 250 °C is 1.7×10^{-2} mol/L. Calculate the weight of PCl_3 formed when 1.0 mol of PCl_5 is allowed to dissociate in a 1-L vessel at this temperature.

15. Liquid acetic acid reacts with liquid ethyl alcohol to form liquid ethyl acetate and water.



$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

The reactants and products are miscible (soluble) in all proportions.
(a) When 1.00 mol of acetic acid was mixed with 0.500 mol of ethyl alcohol, the equilibrium mixture contained 0.414 mol of ethyl acetate. Calculate the equilibrium constant.

(b) If one mole of acetic acid is mixed with one mole of ethyl alcohol, what are the equilibrium amounts of all species?

16. For the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

at a given temperature, the equilibrium mixture was found to consist of 0.40 mol of CO_2, 0.40 mol of H_2, 0.20 mol of CO, and 0.20 mol of H_2O.

(a) Calculate the equilibrium constant.
(b) If 0.50 mol of CO and 0.50 mol of H_2O are mixed at this temperature, how many moles of CO_2 and H_2 will be present when equilibrium is established?
(c) If 0.50 mol of CO2 and 0.50 mol of H_2 are mixed, how many moles of CO will be present at equilibrium?
(d) If equimolar amounts of CO and H_2O are mixed, what is the extent of reaction in terms of percent conversion?
(e) If 0.40 mol of CO is mixed with 0.60 mol of H_2O, how many moles of CO_2 will be present at equilibrium?
(f) How many moles of CO must be mixed with 0.60 mol of H_2O in order to obtain 0.35 mol of CO_2 at equilibrium?

17. The following system is at equilibrium in a 1.00-L flask:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Analysis indicates that the mixture consists of 0.30 mol of CO, 0.20 mol of Cl_2, and 0.12 mol of $COCl_2$. How many moles of CO must be forced into the flask to double the amount of $COCl_2$ present?

18. The equilibrium constant for the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is 6.50 at a certain temperature. A combination of 2.24 g of CO and 2.16 g of steam was placed in a 1.00-L reaction vessel at this temperature. What weight of CO_2 was present when the system reached a state of equilibrium?

19. For the reaction

$$NH_4NO_2(s) \rightleftharpoons N_2(g) + 2\,H_2O(g)$$

the value of K_c at a certain temperature is 0.56. If 1.0 mol of NH_4NO_2 is placed in a 1.00-L vessel and the vessel is sealed and heated to that temperature, what weight of NH_4NO_2 remains at equilibrium?

20. A sample of $CaCO_3$ weighing 50.0 g is placed in a 10-L flask. The flask is sealed and heated to 500 °C. When equilibrium is reached, only 25.0 g of $CaCO_3$ remain by the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

(a) What is the value of K_c for the reaction at 500 °C?
(b) What weight of CaO is present at equilibrium?
(c) Assuming that CO_2 behaves as an ideal gas under these conditions, calculate K_p.

21. The following reversible reaction for the production of hydrogen gas is of commercial importance:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

The equilibrium constant for this reaction at 963 K is 1.87; at 1263 K, it is 0.637.

(a) Calculate the equilibrium concentrations of all the species (at both temperatures) when the reaction is begun with 1.00 mol of CO and 1.00 mol of H_2O in a 1.00-L vessel.
(b) Calculate the extent of the reaction for each temperature.
(c) Is the reaction endothermic or exothermic? Explain.
(d) How would the extent of the reaction at each temperature be affected by doubling the concentration of steam?

22. The equilibrium constant (K_c) for the reaction below is 2.0 at some temperature.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

(a) Does this constant mean that the number of moles of NO_2 is twice that of N2O4 at equilibrium?
(b) How much N_2O_4 must be introduced into a 1.0-L flask in order to obtain 0.60 mol of NO_2 at equilibrium?
(c) If 1.0 mol of NO_2 is introduced into a 1.0-L flask, how much N_2O_4 is present at equilibrium?
(d) If 1.0 mol of NO_2 is introduced into a 2.0-L flask, how much N_2O_4 is present at equilibrium?

23. The reaction

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

was carried out in a 1.0-L flask. The reaction was started by mixing 0.40 mol of H_2 with 0.50 mol of Cl_2. When equilibrium was established 0.30 mol of Cl_2 remained. Calculate the equilibrium constant.

24. The equilibrium constant for the reaction

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

is 0.10 at some temperature.

(a) Some amount of PCl_5 is added to a 1.0-L flask. When equilibrium is established 0.10 mol of PCl_3 is present. How much PCl_5 was placed in the flask at the beginning of the reaction?
(b) At some higher temperature 0.30 mol of PCl_3, 0.30 mol of Cl_2 and 0.05 mol of PCl_5 are present at equilibrium. Is the reaction exothermic or endothermic?

25. Consider the dissociation of PCl_5 into PCl_3 and Cl_2 in solution.

(a) Provide the balanced reaction equation for this decomposition.
(b) At a specific temperature 21 g of PCl_5 is dissolved in enough solvent to make 1.0 L of solution. When equilibrium has been established 15 g of PCl_5 remain in solution. Determine the equilibrium constant for this reaction.
(c) If the reaction had been started with 1.0 mol of PCl_5 in 2.0 L of solution, what amount of PCl_3 would be present at equilibrium?
(d) If the equilibrium mixture in part (b) was diluted by adding enough solvent to give a total of 10.0 L of solution, what would be the concentrations of PCl_5, PCl_3 and Cl_2 after the system re-established an equilibrium?

26. Assume that the following reaction was carried out in a 5.0-L vessel at 400 °C:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

The equilibrium mixture consisted of 0.10 mol of H_2, 0.050 mol of I_2, and 0.57 mol of HI.

(a) What is the equilibrium constant for this reaction?

(b) How much H_2 would have to be mixed with 0.50 mol of I_2 in order to get 0.80 mol of HI at equilibrium?

27. Consider the conversion of ethyne to ethane in the gas phase in a 1.0-L flask:

$$C_2H_2 + 2\,H_2 \longrightarrow C_2H_6$$

1.0 mol of C_2H_2 is mixed with 1.0 mol of H_2 and when equilibrium has been established, 0.75 mol of C_2H_2 remains.

(a) Calculate the equilibrium constant for this reaction.

(b) Some C_2H_6 is now removed from the equilibrium mixture until the amount of C_2H_2 has decreased to 0.60 mol. How much C_2H_6 was removed?

28. Consider the dissociation of N_2O_4 to NO_2 in the gas phase in a 1.0-L flask

$$N_2O_4 \longrightarrow 2\,NO_2$$

This reaction has an equilibrium constant of 1.0 at 25 °C.

(a) If the reaction is started with 1.0 mol of N_2O_4, how much NO_2 will be present at equilibrium?

(b) How much NO_2 must be placed in an empty 1.0-L flask in order to obtain 0.20 mol N_2O_4 at equilibrium?

(c) If the reaction has an equilibrium constant of 10.0 at 40 °C, is the reaction exothermic or endothermic?

(d) If the reaction is at equilibrium and the volume of the flask is expanded to 2.0 L, what will happen to the amount of N_2O_4 present?

29. Consider the reaction

$$CH_3I + OH^- \rightleftharpoons CH_3OH + I^-$$

for which the equilibrium constant at some temperature is 10.

(a) If 0.50 mol of CH_3I is mixed with 0.50 mol of OH^- (in 1 L of solution), how much CH_3OH is obtained?

(b) If 0.50 mol of CH_3I is mixed with 1.0 mol of OH^- (in 1.0 L of solution), how much CH_3OH is obtained?

(c) In order to obtain 0.60 mol of CH_3OH from 0.80 mol of CH_3I, how much OH^- must be mixed with the CH_3I?

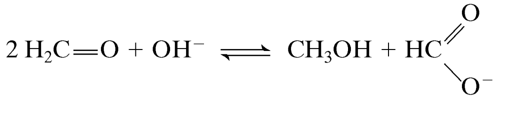
(d) Suppose that 1.0 mol of I^- is added to the equilibrium mixture of part (a). When equilibrium is reestablished, how much CH_3OH is present?

30. For the reaction

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

carried out in a 1.0-L flask, 0.30 mol of NO_2 and 0.30 mol of N_2O_4 are present at equilibrium. How much NO_2 must be removed in order to reduce the amount of N_2O_4 to 0.10 mol?

31. Formaldehyde reacts with hydroxide ion to give methanol and formate ion according to the equation



$$2\,H_2C{=}O + OH^- \rightleftharpoons CH_3OH + HCO_2^-$$

(a) In 1.0 L of solution at equilibrium, the following were present: 0.10 mol of CH_3OH, 0.60 mol of HCO_2^-, 0.10 mol of OH^-, and 0.55 mol of $H_2C{=}O$. Calculate the equilibrium constant.

(b) How many moles of OH^- must be mixed with 1.0 mol of $H_2C{=}O$ in order to obtain 0.30 mol of CH_3OH at equilibrium (in 1.0 L of solution)?

32. The equilibrium constant for the reaction below is 1.7×10^{-2} mol/L.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) If 1.0 mol of PCl_3 and 1.0 mol of Cl_2 are introduced into a 2.0-L vessel at 250 °C, what are the equilibrium concentrations?

(b) How many moles of chlorine must be removed to double the concentration of PCl_3 in (a)?

33. For the reaction

$$N_2O_4 \longrightarrow 2\,NO_2$$

performed in a 1.00-L flask, 0.30 mol of NO_2 and 0.30 mol of N_2O_4 are present at equilibrium. How much NO_2 must be removed in order to reduce the amount of N_2O_4 to 0.10 mol?

34. Consider the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At some temperature, the equilibrium mixture consists of 0.30 mol of CO_2, 0.30 mol of H_2, 0.10 mol of CO, and 0.20 mol of H_2O in a 1.00-L vessel.

(a) Calculate the equilibrium constant.

(b) How much CO must be added to this mixture at constant temperature and volume in order to increase the concentration of CO_2 to 0.40 mol/L?

(c) How much H_2 must be removed at constant temperature and volume in order to increase the concentration of CO_2 to 0.40 mol/L?

35. Assume that the reaction below was carried out in a 1-L vessel.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

At some temperature, the equilibrium mixture contained 0.10 mol of SO_3, 0.10 mol of NO, 0.10 mol of NO_2, and 0.50 mol of SO_2.

(a) What is the value of the equilibrium constant?

(b) How much NO_2 must be added to this mixture in order to double its equilibrium concentration? What will the concentrations of the other species be at this new equilibrium?

36. The reaction of sulfur dioxide gas with oxygen gas to form sulfur trioxide gas is an important step in the production of sulfuric acid.

(a) Write the expression for the equilibrium constant.

(b) If a 10.0-L vessel contains 15 mol of SO_3, 2.0 mol of O_2, and 3.0 mol of SO_2 at equilibrium at 1373 K, what is the numerical value for the equilibrium constant?

(c) How many moles of sulfur dioxide must be forced into the reaction vessel to increase the concentration of SO_3 to 1.6 mol/L?

37. At a very high temperature, chlorine gas is produced by a reaction known as Deacon's process,

$$4\,HCl(g) + O_2(g) \rightleftharpoons 2\,H_2O(g) + 2\,Cl_2(g)$$

The equilibrium mixture in a 10.0-L vessel contained the following: 7.5 mol of HCl, 0.20 mol of O_2, 8.0 mol of H_2O, and 8.0 mol of Cl_2.
(a) Calculate the equilibrium constant.
(b) How much O_2 must be added to increase the concentration of Cl_2 to 1.0 mol/L?
(c) How much water must be removed in (a) to increase the concentration of chlorine to 1.0 mol/L?

38. Consider the gas-phase reaction

$$Xe + 2\,F_2 \rightleftharpoons XeF_4$$

(a) Calculate the equilibrium constant from the observation that at some temperature, the extent of reaction is 50% when 0.20 mol of Xe and 0.40 mol of F_2 have been mixed in an empty 1.00-L bulb.
(b) How many moles of F_2 would have to be added to the equilibrium mixture of part (a) in order to increase the conversion of Xe to XeF_4 to 80%?

39. When the decomposition of $Al_2(CO_3)_3$ is performed by heating 1.00 mol in a 2.00-L flask, 1.20 mol of CO_2 is present at equilibrium.

$$Al_2(CO_3)_3(s) \rightleftharpoons Al_2O_3(s) + 3\,CO_2(g)$$

(a) Calculate the equilibrium constant.
(b) If 1.00 mol of CO_2 is added to this equilibrium mixture how many moles of $Al_2(CO_3)_3$ will be present when equilibrium is reestablished.
(c) How much CO_2 must be removed from the original equilibrium mixture in order to cause all of the $Al_2(CO_3)_3$ to disappear?

40. Choose the most correct answer.

1. The following system is at equilibrium in a closed-reaction vessel:

$$KClO_4(s) + 4\,C(s) \rightleftharpoons KCl\,(s) + 4\,CO(g)$$

If the volume of the vessel is decreased and the system is allowed to reach equilibrium at the same temperature,
(a) the concentration of CO will decrease
(b) the concentration of CO will increase
(c) the amount of KCl will decrease
(d) the amount of $KClO_4$ will decrease

2. In the given equation $2\,A + B \rightleftharpoons 2\,C$, all substances are gases. If this system is at equilibrium in a 4-L container and contains 1 mol of A, 2 mol of B, and 3 mol of C, the value of the equilibrium constant is
(a) 0.0555 (b) 0.167 (c) 6.0 (d) 18.0

3. For the reaction $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$, the units of K_p are
(a) atm (b) atm^2 (c) atm^{-1} (d) none

4. Adding a catalyst to the system $C_2H_2 + 2\,H_2 \rightleftharpoons C_2H_6$ in equilibrium will
(a) produce more C_2H_6 (b) produce more C_2H_2
(c) produce more H_2 (d) have no effect

5. If, in the hypothetical reaction $AB \rightleftharpoons A + B$, 1 mol of AB is 50% dissociated at equilibrium, then the equilibrium constant for the reaction is
(a) 0.5 (b) 1.0 (c) 2.0 (d) 0.25

6. The following system is at equilibrium at 100 °C and 1 atm pressure:

$$NH_4NO_2(s) + O_2(g) \rightleftharpoons 2\,NO(g) + 2\,H_2O(g)$$

Increasing the pressure while keeping the temperature constant will
(a) decrease the value of K
(b) decrease the amount of NO present
(c) decrease the amount of O_2 present
(d) none of the above

7. The value of the equilibrium constant for any reaction is increased by
(a) addition of a catalyst
(b) an increase in pressure
(c) an increase in temperature
(d) none of the above

14

The Extent of Reactions

The earlier discussions of phase changes and the solution process have disclosed two fundamental laws of nature. One is the tendency of physical systems to move toward the state of lowest energy; for example, the simple fact that water flows downhill. The other is the tendency toward a state of maximum disorder or randomness; for example, the diffusion of gases throughout their containers. These two laws also apply to chemical reactions.

As an example, consider the simple reaction

$$N_2(g) \rightleftharpoons 2\,N(g)$$

The lowest-energy state for this reaction is the nitrogen molecule, because energy is required to dissociate the triple-bonded diatomic nitrogen into monatomic nitrogen. If this were the only tendency of nature, all elemental nitrogen would be present as $N_2(g)$ at even moderately high temperatures. However, the state of maximum disorder for this reaction would be attained if all the nitrogen were in the form of atoms rather than molecules, because this situation would produce a greater number of particles and a correspondingly greater amount of disorder.

These two natural drives tend to force the reaction in opposite directions: the drive to low energy pushes toward the starting material (reactant), and the drive to maximum disorder pushes toward the nitrogen atoms, the product. The compromise that is attained is directly related to the establishment of equilibrium and to the magnitude of the equilibrium constant. In the sections that follow, we will examine the thermodynamic expressions of these natural laws and their relationship to the equilibrium constant will be examined.

14.1 THE LAWS OF THERMODYNAMICS

The examination of the first of the two major laws of thermodynamics begins with a simple mechanical system: the flow of water down a hillside (Figure 14.1). If this water originates from a natural spring at the top of the hill and is therefore essentially motionless at this point, then the water at the top of the hill has only potential energy; that is, it has the potential to do work because once it moves down the hill, its motion can be harnessed to do work (e.g., by a water wheel). The potential energy (PE) of a given mass of water (m) at any point on the hill is proportional to the distance of that point from the bottom of the hill (h); it is mathematically expressed by the formula $PE = mgh$, where g is the acceleration due to gravity.

As the water begins to flow down the hill, this potential energy is gradually converted to kinetic energy. For a given mass moving with a velocity v, the kinetic energy is given by the familiar expression $KE = \frac{1}{2}mv^2$. The farther the water moves down the hill, the greater the velocity it attains and therefore the greater the kinetic energy it possesses. At the same time, however, the distance from the bottom decreases, and thus the potential energy must decrease. At the bottom of the hill, the potential energy is zero and the

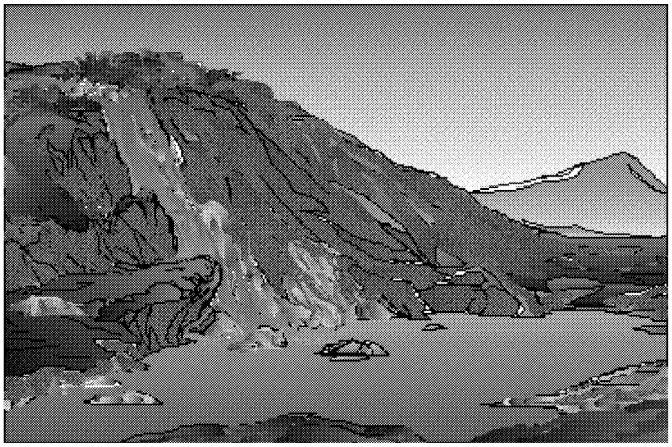


Figure 14.1 An illustration of potential vs kinetic energy.

kinetic energy has reached its maximum value. Indeed, if the hillside had an infinitely smooth surface so that there were no friction, all of the potential energy at the top of the hill would be converted to kinetic energy at the bottom. Of course, no such hillside exists; instead, there are rocks and sand and other debris. As the water travels over this surface, some of its kinetic energy is used to move these rocks and pebbles and to warm the surfaces slightly by friction. Thus, the kinetic energy of a given mass of water at the bottom is *less* than the potential energy at the top; the total energy of the water has decreased. This energy has not been lost, however. It has merely been transferred to other parts of the hillside, and the total energy of the water plus that of the hillside actually remains constant.

Because this example is concerned initially about the water, the water is the **system** under consideration and the hillside is the **surroundings**. It is difficult to measure the absolute energy of most systems, so scientists generally speak in terms of the change in energy, ΔE. This change is defined as the energy of the system at the end of a change minus the energy at the beginning. Thus, a decrease in energy always results in a negative value for ΔE. For the water system, therefore,

$$\Delta E < 0$$

but $\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$. That is, while the energy of the water decreased, the energy of the surroundings increased by the same amount. Over the centuries, this very fundamental generalization has been borne out and there are no known exceptions. As a more sweeping generalization, it can be stated as the **Law of Conservation of Energy**, or **the First Law of Thermodynamics**:

The energy of the universe remains constant.

The loss of energy of the water as it flows down the hill is due to the loss of energy to the hillside because of frictional forces and the energy imparted to boulders and other matter. The energy lost because of frictional forces is imparted to the hillside as heat, while the energy lost to boulders is mechanical work performed by the water. The change in energy of the water, or indeed of any system for which only mechanical work is possible, is given mathematically as

$$\Delta E = q - w \tag{1}$$

where q is the heat absorbed by the system and w is the work done by the system. For the water system, heat is given off, not absorbed, and so q is a negative number, while the work of moving boulders is performed by the system and thus w is a positive number. The change in energy of a mass of water from the top to the bottom of the hill must therefore be negative:

$$\Delta E = q - w < 0 \qquad \text{or} \qquad \Delta E = (-) - (+) < 0$$

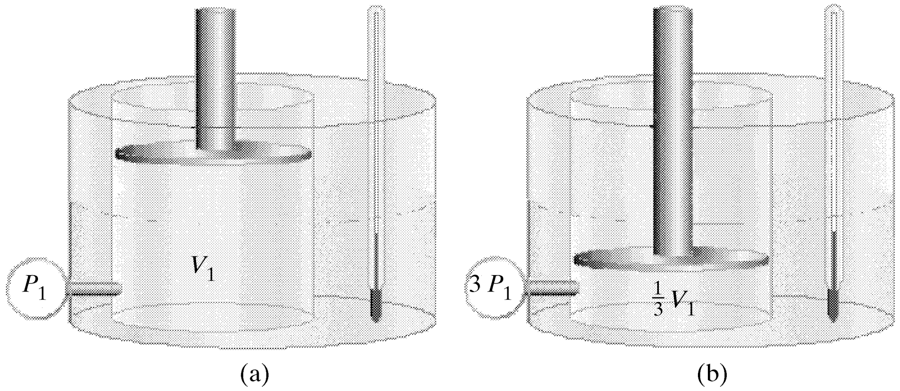


Figure 14.2 The relationship between pressure and volume for an ideal gas.

The same definition applies to other systems; e.g., the compression of an ideal gas. Imagine an ideal gas in a closed cylinder fitted with a piston and immersed in a constant-temperature bath (see Figure 14.2). Initially, the gas is at a pressure P_1 in a volume V_1 (part (a)). Next the gas is compressed to a volumethat is one-third the original volume; that is, to $\frac{1}{3}V_1$. Because the cylinder is in a constant-temperature bath, the temperature of the gas must remain constant. Therefore, according to Boyle's Law, the pressure of the gas after the compression must be $3P_1$ (part (b)). Hence, the compression can be accomplished by applying a pressure of $3P_1$ to the piston. The piston will then move to compress the gas until the internal pressure equals $3P_1$ and the piston stops. At this point the final state $\left(V_2 = \frac{1}{3}V_1, P_2 = 3P_1\right)$ has been achieved.

The values of ΔE, q, and w for this compression can be obtained. Because the gas is assumed to be an ideal gas and therefore consists of point particles with no intermolecular forces, there is no change in energy when the compression is done at a constant temperature. This condition must be true because the average kinetic energy of gas molecules is dependent only on the temperature; because the temperature remains constant, so must the kinetic energy. Moreover, because there are no intermolecular forces, the potential energy also does not change during the compression, even though the point molecules are moved closer together.

The work performed by the gas during the compression can be calculated from the pressure used to move the piston and from the resulting change in volume. The relationship required for this calculation may be derived from the definition for work in terms of a force (f) exerted over a distance (d):

$$w = fd$$

and from the fact that pressure is equal to force per unit area (A):

$$P = f/A$$

or

$$f = PA$$

Hence, by substitution, work can be expressed in terms of pressure:

$$w = (PA)d$$

Because the area of the piston multiplied by the distance that the piston moved is the change in volume (i.e., $\Delta V = A \times d$),

$$w = P\Delta V = P(V_2 - V_1) \tag{2}$$

Thus, the work done by the gas is

$$w = 3P_1\left(\frac{1}{3}V_1 - V_1\right) = 3P_1\left(-\frac{2}{3}V_1\right) = -2P_1V_1$$

Now, if ΔE for the compression is zero and w is $-2P_1V_1$, then q must be $-2P_1V_1$ in order to maintain the equality expressed by equation (1). Because q is defined as the heat absorbed by the system, the gas has released an amount of heat $2P_1V_1$ to the constant-temperature bath.

The method used above is just one of the many possible ways to accomplish the compression of a gas. For a second method, imagine that the compression is done by applying a pressure to the piston that is only a very small amount larger than the initial pressure P_1. This very small increment of pressure is called dP. The pressure $P_1 + dP$, then, will force the piston to move a very small amount, and the volume will change an infinitely small amount, dV. Now another infinitely small pressure, dP, is applied to the piston, and it produces another infinitely small compression. This procedure is repeated an infinite number of times until the final state is reached. This hypothetical procedure has two interesting features. First, at each of the infinite number of stages, the process is reversible: A small pressure change, dP, will suffice to move the piston in either direction. Second, the work necessary to accomplish the compression must be calculated by use of calculus and is $-1.1\ P_1V_1$. (The equation $w = P\Delta V$ cannot be used because the pressure is not constant; instead, it increases as the compression proceeds.) This work is the smallest amount of work required for the compression; any other procedure for the compression requires a greater amount of work.

The heat released by this hypothetical compression can be determined from equation (1):

$$q = \Delta E + w$$
$$q = 0 + (-1.1P_1V_1)$$
$$q = -1.1P_1V_1$$

From Table 14.1, which summarizes the results for the two compressions, one can see that the initial and final states of the two compressions are the same, as are the values of ΔE. However, the work and heat depend on the procedure used to accomplish the compression. In the language of thermodynamics, ΔE is said to be a **state function**; that is, it depends only on the initial and final states of a system and not on how these states are attained. Pressure and volume are also state functions. Work and heat, since they depend on how the states are attained, are not state functions.

TABLE 14.1 Compression of an Ideal Gas at Constant Temperature

	COMPRESSION PROCEDURE	
	$P_{\text{exerted}} = 3P_1$	$P_{\text{exerted}} = P + dP$
Initial state	$P = P_1, V = V_1$	$P = P_1, V = V_1$
Final state	$P = 3P_1, V = \frac{1}{3}V_1$	$P = 3P_1, V = \frac{1}{3}V_1$
Number of steps	1	∞
ΔE	0	0
w	$-2P_1V_1$	$-1.1P_1V_1$
q	$-2P_1V_1$	$-1.1P_1V_1$

Methodology 14.1

A 1.00-g sample of liquid water at 100 °C was converted to vapor at 100 °C in a closed cylinder with a frictionless piston held in place by a pressure of 1.00 atm. The heat of vaporization for water is 2.26 kJ/g. Determine ΔE, q and w.

Because heat was added to the system in order to vaporize one gram of water, q can be determined directly from the data provided. Calculate q.

$$q = 2.26 \text{ kJ/g} \times 1.00 \text{ g} = 2.26 \text{ kJ} = 2260 \text{ J}$$

Determine the amount of work done during the vaporization.

> The work is defined by $P\Delta V$.
> Thus, for this case $w = (1.00 \text{ atm})\Delta V = (1.00 \text{ atm})(V_2 - V_1)$.

Why does the volume change during the vaporization process?

> Liquid water, which occupies only a small volume, is converted into a gas, which occupies a greater volume and pushes the piston in the cylinder until the pressure within the cylinder is 1.00 atm.

Determine the initial and final volumes.

> The initial volume of one gram of liquid water at 100 °C is about 1 mL or 0.001 L.
>
> After vaporization, the water vapor may be treated as an ideal gas, which obeys $PV = nRT$ or $V = nRT/P$. Therefore,
>
> $$V_2 = [(1.00 \text{ g}/18.0 \text{ g per mole})(0.08206 \text{ L-atm/mole-K})(373 \text{ K})]/1.00 \text{ atm} = 1.70 \text{ L}$$

Now calculate the work from these values of pressure and volume.

$$w = 1.00 \text{ atm}(1.70 \text{ L} - 0.001 \text{ L}) = 1.70 \text{ L-atm}$$

In order to combine q and w in the expression for ΔE, they must have the same units. Convert L-atm into joules.

> Because 1 L-atm $= 101.3$ J,
> $w = 1.70 \text{ L-atm} \times 101.3 \text{ J/L-atm} = 172 \text{ J} = 0.172 \text{ kJ}$

Finally, evaluate ΔE.

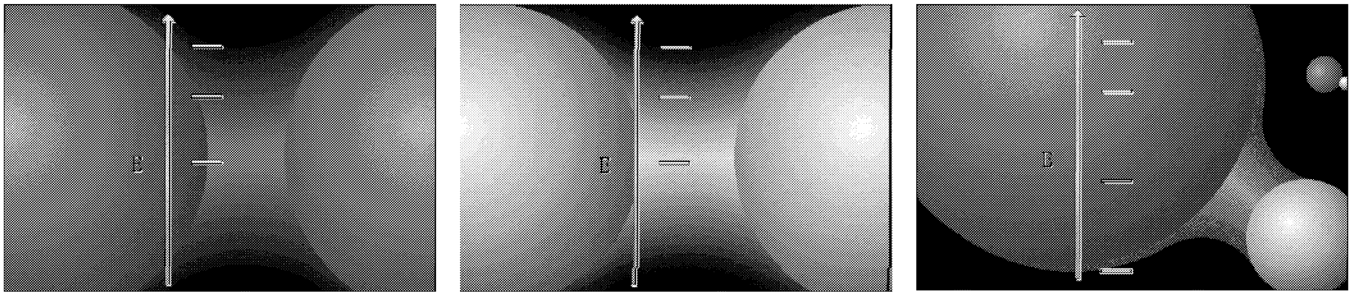
$$\Delta E = 2.26 \text{ kJ} - 0.172 \text{ kJ} = 2.09 \text{ kJ}$$

Finally, if ΔV for a process is zero, then $\Delta E = q$. In other words, for processes done at constant volume, the change in internal energy is the same as the heat change for the system; $\Delta E = q_v$, where the subscript v denotes constant volume.

The factors that affect the change in energy during a chemical reaction are more complex than those that affect the compression of an ideal gas. Mathematically, for a given reaction the difference in energy, ΔE, is equal to the sum of the energies of the products minus the sum of the energies of the reactants:

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

The energy of each species is the sum of the kinetic and potential energies associated with the electrons, the nucleus, the vibration of atoms within the molecule, the rotation and translation of the molecule, and the intermolecular forces. By far the major part of the energy of a substance (aside from the nuclear energy, which remains constant during a chemical reaction) is its electronic energy. Moreover, the spacings of the electronic energy levels are so large that at ordinary temperatures virtually all the species are in the ground electronic state. Therefore, the change in energy in a chemical reaction is primarily a reflection of the difference between the ground electronic energy levels of the reactants and products (Figure 14.3). Clearly, the energy of two molecules or moles of a sub-



(a) (b) (c)

Figure 14.3 Change in energy during the reaction of H_2 with Cl_2 (a, b) to Form HCl (c). The electronic energy levels of HCl are lower than those of H_2.

stance is twice the energy of one molecule or mole, and ΔE is therefore also dependent upon the amount of material in question.

Enthalpy

It is frequently desirable to have a measure of the heat released or absorbed in a chemical reaction. The definition of ΔE reveals that this parameter measures the heat change and the work involved. Because work is given by $P\Delta V$ for a constant-pressure process in which only mechanical work of expansion or compression occurs, the equation for ΔE can be rewritten as

$$\Delta E = q - P\Delta V$$

or, after rearrangement,

$$\Delta E + P\Delta V = q$$

This combination of variables, $\Delta E + P\Delta V$, is equal to the change in enthalpy*, ΔH, at constant pressure:

$$\Delta H = \Delta E + P\Delta V$$

Therefore, at constant pressure, because ΔH and q are both equal to $\Delta E + P\Delta V$,

$$\Delta H = q_p$$

where the subscript p denotes constant pressure. This relationship, combined with the previous one ($\Delta E = q_v$), indicates that $\Delta H = \Delta E$ if, and only if, pressure and volume are both constant.

Like energy, enthalpy is a state function and its change, ΔH, is always given by the enthalpy of the final state minus the enthalpy of the initial state. Therefore, a reaction that liberates heat has a negative ΔH and is said to be exothermic, conversely, a reaction that absorbs heat has a positive ΔH and is endothermic.

For most reactions, ΔH and ΔE are very similar in magnitude. Because $\Delta H = \Delta E + P\Delta V$, the difference between ΔH and ΔE will depend on the change in volume that occurs during a reaction conducted at constant pressure. If there is no change in volume, then

---

* In terms of the enthalpy quantity itself,

$$H = E + PV$$

This is a particularly convenient function for measuring the heat changes during chemical reactions because most reactions are done at constant-pressure (atmospheric pressure). For a constant-pressure process,

$$\Delta H = \Delta E + P\Delta V + V\Delta P$$

but $\Delta P = 0$ so,

$$\Delta H = \Delta E + P\Delta V$$

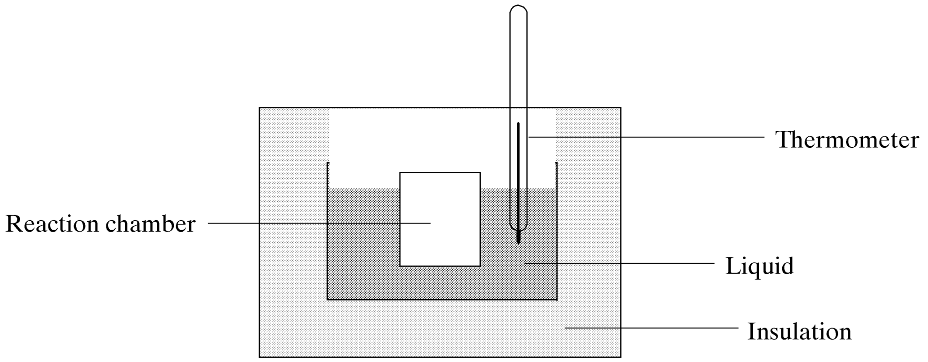


Figure 14.4 A simple calorimeter.

ΔH and ΔE will be the same. Even for gas-phase reactions, such as the following (where the volume doubles if the reaction goes to completion and if the pressure is held constant), the difference between ΔE and ΔH is only a few kilojoules:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Enthalpy changes are measured in the laboratory by using a device called a **calorimeter**. A reaction calorimeter (see Figure 14.4) generally has a container for mixing the reagents, and this container is immersed in a liquid whose temperature can be measured very accurately. When the chemical reaction proceeds in the reaction chamber, heat is transferred to or from the surrounding liquid, thereby producing a change in its temperature. Once the temperature change is known, the amount of heat transferred can be calculated if the **heat capacity** of the calorimeter (liquid + reaction chamber) is known. The heat capacity is the amount of heat required to increase the temperature by 1 °C, and it can be determined experimentally by performing a reaction with a known heat of reaction and then measuring the change in temperature of the surrounding liquid.

A typical experiment that can be used to determine the heat capacity of a given calorimeter involves the neutralization reaction

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

The heat of reaction of HCl with NaOH in dilute aqueous solution is −55.77 kJ/mol. When 0.100 mol of each is mixed in a calorimeter of the type shown in Figure 14.5, the temperature of the surrounding water (and the container) increases by 2.00 °C. This rise in temperature results because the reaction liberates heat:

$$55.77\ \text{kJ/mol} \times 0.100\ \text{mol} = 5.58\ \text{kJ}$$

Assuming that all of the heat is retained by the calorimeter; i.e., in the water and reaction chamber, the effective heat capacity of this calorimeter is

$$\frac{5.58\ \text{kJ}}{2.00\ °\text{C}} = 2.79\ \text{kJ/°C}$$

Problem 14.1

A certain reaction produces a temperature change of 1.73 °C and no change in pressure in a calorimeter with a heat capacity of 2.79 kJ/°C. Calculate $\Delta H_{\text{reaction}}$.

Solution:

The heat liberated is

$$1.73\ °\text{C} \times 2.79\ \text{kJ/°C} = 4.83\ \text{kJ}$$

Because the reaction was done at a constant pressure, this value is also the enthalpy change, ΔH, for the reaction.

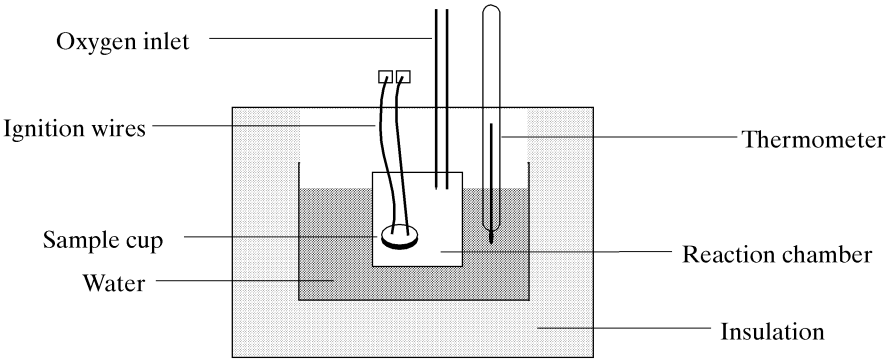


Figure 14.5 A combustion calorimeter.

Another type of device used specifically for measuring heats of combustion is called a "bomb" or combustion calorimeter. In the combustion calorimeter shown in Figure 14.5, the sample is mixed with oxygen in the reaction chamber and then ignited by an electric spark. The elements in the sample are converted to their oxides and the heat released in the process is measured as described above.

Check Point 14.1

For the reaction $Cl + Cl \rightarrow Cl_2$, $\Delta H < 0$. Which has the lower energy—two moles of chlorine atoms or one mole of chlorine molecules?

Solution:

One mole of chlorine molecules

◇ ◇ ◇ ◇ ◇

Entropy

The second fundamental drive in nature, the trend toward maximum disorder, is expressed by the thermodynamic function S, the entropy, which like energy and enthalpy, depends only on the initial and final states of a system. The change in entropy (ΔS) for a chemical reaction is defined analogously to the change in energy or enthalpy:

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

Because the magnitude of S is an indication of the amount of disorder in a system, a positive ΔS reflects an increase in disorder, while a negative ΔS denotes an increase in order. The change in entropy is an indication of the change in randomness of not only the motion of the molecules, but also in electronic, vibrational, and rotational processes. If, for example, only the ground-state vibrational level is populated in a collection of many molecules, this collection of molecules has a low-entropy (highly ordered) situation, relative to the situation where a variety of vibrational levels are populated by the same collection of molecules. The same is true for the population of the electronic and rotational levels.

At a given temperature, the more closely spaced the energy levels, the greater the number of levels that can be populated and consequently the higher the entropy. In Chapter 8 the spacings between electronic levels were shown to be greater than those between vibrational levels, which are, in turn, greater than the spacings between rotational levels. Furthermore, the translational levels are so closely spaced that they are essentially continuous. Thus, at a given temperature the number of populated translational levels is much greater than the number of rotational, vibrational, or electronic levels. Consequently, the largest part of the entropy of any collection of molecules, atoms, or ions is due to the population of many translational levels. For a solid, where the particles merely vibrate in their lattice positions, there is essentially no translational energy; in a liquid, the particles are free to move and the translational levels are closely spaced; in a gas, the

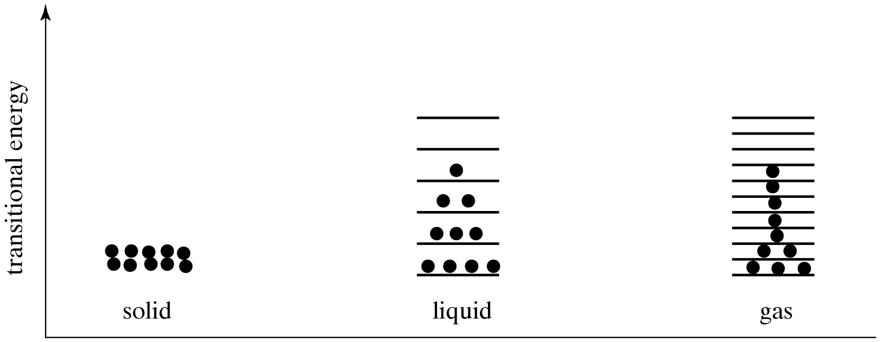


Figure 14.6 The relationship between phase and population of translational energy levels.

translational levels are even more closely spaced because of the greater freedom of movement in that state (see Figure 14.6 and the discussion in Chapter 8). At a given temperature, a greater number of translational levels are populated in the gaseous state. An increase in temperature provides energy for populating even more energy levels; therefore, the entropy of a substance increases with temperature.

The change in entropy for a particular process can be calculated if the change in heat for that process, when done in a reversible fashion at temperature T, is known. Specifically, the change in entropy is

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

If the system absorbs heat, the additional heat serves to increase the disorder of the particles that constitute the system and ΔS is therefore positive. If the system releases heat, the order increases and ΔS is negative. For example, the entropy change for the compression of an ideal gas must be calculated from the heat released when the compression is carried out by a hypothetical reversible process and is therefore

$$\Delta S = \frac{-1.1P_1V_1}{T}$$

This decrease in entropy is a reflection of the increase in order due to the decreased space available for translation of the gas molecules.

The change in entropy that accompanies a particular process is important not only because it conveys information about the change in disorder, but also because it is related to a principle known as the **Second Law of Thermodynamics**:

The total change in entropy for a process that occurs of its own accord must be positive.

This statement has two important aspects associated with it. First, the *total* entropy change, not just the entropy change for the system, must be greater than zero. That is, the sum of ΔS for the system and ΔS for the surroundings must be positive for a process that occurs of its own accord. Second, the definition of a process that occurs of its own accord must be clear. The compression of the ideal gas discussed previously is an example of a process that will proceed of its own accord *under the conditions specified*. The gas will be compressed by the application of a pressure $3P_1$, but it will not compress of its own accord if no pressure is applied to the piston. Another term used to mean "proceed of its own accord" is **spontaneous**. The cooling of a red-hot iron bar to room temperature, the expansion of a gas in a vacuum, and the melting of ice at 50 °C are all spontaneous processes; the reverses of these processes have never been observed to occur of their own accord.

The total change in entropy for the one-step compression of an ideal gas may now be determined. The heat change (q) for the system is $-1.1P_1V_1$ when the process is done reversibly (with an infinite number of steps). Because ΔS is a state function and therefore independent of how the process is performed, ΔS for the system must be $-1.1P_1V_1/T$. However, the change in entropy of the surroundings is the heat absorbed by the constant-temperature bath, $2P_1V_1$, divided by the constant temperature, T. Because the temperature is held constant, this heat is exchanged reversibly, and therefore ΔS for the surroundings is $2P_1V_1/T$. Thus, the total change in entropy is

$$\begin{aligned}\Delta S_{\mathrm{T}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}\\ &= \frac{-1.1P_1V_1}{T} + \frac{2P_1V_1}{T}\\ &= \frac{-0.9P_1V_1}{T}\end{aligned}$$

which is positive. The positive entropy change of the surroundings more than compensates for the negative entropy change due to the compression of the system.

Contrast this spontaneous compression with one that is not spontaneous. Suppose that instead of applying a pressure sufficient to move the piston to the final state, a pressure sufficient to balance the initial internal pressure (P_1) is applied (see Figure 14.7). The change in entropy for the system will again be $-1.1P_1V_1/T$, but the change in entropy of the surroundings must be calculated from the work necessary to accomplish the compression, if were it to occur: $P\Delta V$ or $P_1\left(\frac{2}{3}V_1\right) = \frac{2}{3}P_1V_1$. Thus, the heat released by the system will be and the $\frac{2}{3}P_1V_1$, heat absorbed reversibly by the surroundings will be $\frac{2}{3}P_1V_1$. The total change in entropy for the compression under these conditions is therefore

$$\begin{aligned}\Delta S_{\mathrm{T}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}\\ &= \frac{-1.1P_1V_1}{T} + \frac{0.67P_1V_1}{T}\\ &= \frac{-0.4P_1V_1}{T}\end{aligned}$$

The negative sign indicates what common sense dictates; that is, the gas cannot be compressed to a pressure of $3P_1$ by maintaining it at its initial pressure. In other words, the process under these conditions is not spontaneous.

Finally, if the gas is compressed by the hypothetical, infinitely long reversible process, then the heat released to the constant temperature bath is $1.1P_1V_1$, and the total change in entropy is therefore

$$\begin{aligned}\Delta S_{\mathrm{T}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}\\ \Delta S_{\mathrm{T}} &= \frac{-1.1P_1V_1}{T} + \frac{1.1P_1V_1}{T}\\ \Delta S_{\mathrm{T}} &= 0\end{aligned}$$

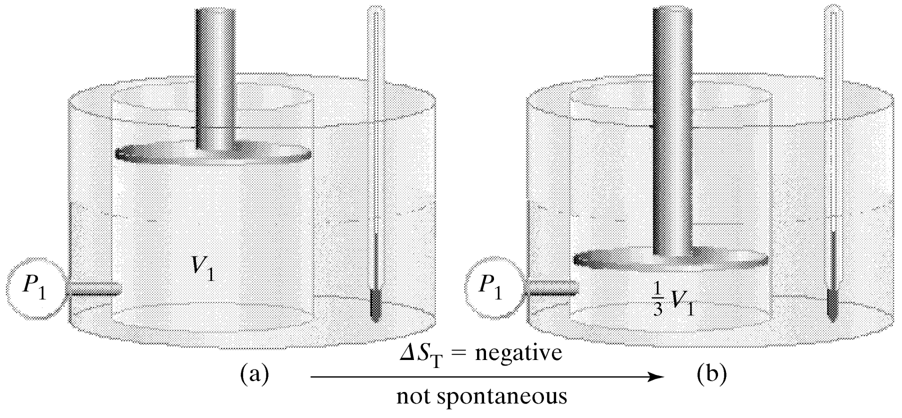


Figure 14.7 Entropy change for the non-spontaneous compression of an ideal gas.

This value of zero is an important result for thermodynamically reversible processes in general.

The total change in entropy for a spontaneous process will be positive, and the total change in entropy for a reversible equilibrium process will be zero. Although this set of generalizations can be applied directly to chemical reactions, it is more convenient to use these rules to define another thermodynamic function that can be applied with greater ease to chemical reactions.

Free Energy

Although the total entropy change for a spontaneous reaction is

$$\Delta S_{\mathrm{T}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

this inequality may be rewritten as

$$\Delta S_T = \frac{q_{\text{rev}}}{T} + \frac{q_{\text{surr}}}{T} > 0$$

The term $q_{\text{reversible}}/T$ is the entropy change for the system, ΔS_{system}. The second term contains $q_{\text{surroundings}}$, the heat lost to the surroundings, which is, by definition of the enthalpy change, the negative of ΔH for the system when the process is performed at constant pressure. Thus, for a spontaneous process at constant pressure and at temperature T,

$$\Delta S_{\mathrm{T}} = \Delta S + \left(\frac{-\Delta H}{T}\right) > 0$$

If both sides of the inequality are multiplied by T, then

$$T\Delta S - \Delta H > 0$$

If both sides are multiplied by −1, then the inequality is reversed,

$$\Delta H - T\Delta S < 0$$

The function for the free energy change, ΔG, of a system may then be defined as

$$\Delta G = \Delta H - T\Delta S$$

Therefore, the criterion for a spontaneous process is that at constant T and P, ΔG for the system must be negative. In other words, the free energy must decrease during a spontaneous process. For a process at equilibrium, the free energy change will be zero. A major advantage of using ΔG rather than ΔS as a criterion of spontaneity is that only the free energy of the system needs to be considered. Figure 14.8 shows the free energy change for the melting of ice at two different temperatures. At −20 °C the change in free energy is positive and the ice will not melt; at +20 °C the free energy change is negative and the ice will be converted to liquid water; at 0 °C the free energy change is zero and the ice and liquid water will be at equilibrium.

As an example of the application of this criterion to a phase transition, consider the evaporation of chloroethane at its boiling point, 12.3 °C.

$$CH_3CH_2Cl(l) \rightleftharpoons CH_3CH_2Cl(g)$$

At this temperature, ΔH is 24.7 kJ/mol. The value of ΔH is positive because energy is required for the process. The entropy change for the formation of 1 mol of the gas at 760 torr is also positive, 86.6 J/K-mol, because the disorder associated with the gaseous state is greater. The free energy for this change in state is therefore

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 24{,}700\ \text{J/mol} - (285\ \text{K})(86.6\ \text{J/K} - \text{mol})$$

$$\Delta G = 0$$

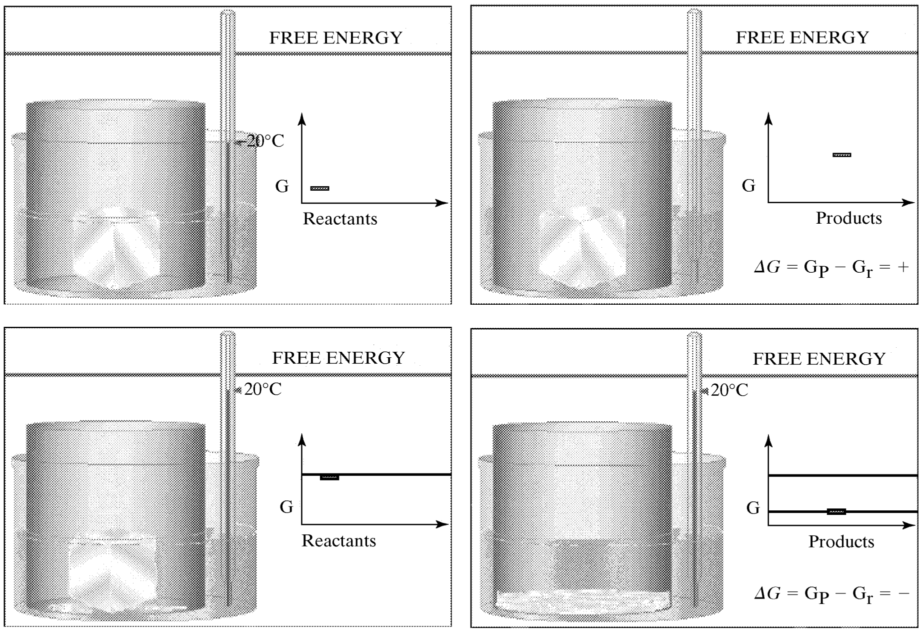


Figure 14.8 The free energy change for the melting of ice at two temperatures.

which reflects the fact that the two states are in equilibrium at this temperature and pressure.

A change in the temperature at which this process occurs will affect the free energy change. Assume, for example, that the evaporation occurs at 25 °C to form the gas at 760 torr pressure. The enthalpy change is 24.3 kJ/mol at this temperature and the entropy change is 84.9 J/K•mol, with the result that ΔG is

$$\Delta G = 24{,}300 \text{ J/mol} - (298 \text{ K})(84.9 \text{ J/K} - \text{mol})$$

$$\Delta G = -1000 \text{ J/mol}$$

This result indicates that at this temperature (25 °C) and pressure, the free energy of 1 mole of gas is lower than that of 1 mole of liquid, and the evaporation process is spontaneous. Liquid chloroethane will, indeed, vaporize to produce the gas, until the free energy of the gas produced is equal to that of the remaining liquid (assuming that the vaporization occurs in a closed system). As this point of equilibrium is approached, the free energy of the system (liquid plus gas) decreases to some minimum value at which $\Delta G = 0$.

Check Point 14.2

For a given process, $\Delta G > 0$. Is this process spontaneous or non-spontaneous?

Solution:

non-spontaneous

◇ ◇ ◇ ◇ ◇

14.2 STANDARD CONDITIONS

The four thermochemical functions, ΔE, ΔH, ΔS and ΔG, have three features in common:

1. They are state functions and consequently their values do not depend on the mechanism of the reaction; they depend *only* on the initial and final states of the system (reactants and products).

An important consequence of this feature is that energy, enthalpy, entropy, and free-energy changes are additive. Assume, for example, that you have at your disposal the enthalpy changes for the two reactions

$$\mathrm{C}(s) + \frac{1}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) \qquad \Delta H_1 = -110.5\ \mathrm{kJ} \tag{1}$$

$$\mathrm{CO}(g) + \frac{1}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_2 = -283.3\ \mathrm{kJ} \tag{2}$$

Assume further that for some reason you need the enthalpy change for the reaction

$$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_3 = ? \tag{3}$$

Both equations (1) and (2) contain some of the species of equation (3), although neither (1) nor (2) is identical to (3). The sum of equations (1) and (2) is, however, identical to (3); therefore, the sum of the enthalpy changes, ΔH_1 and ΔH_2, will yield the desired ΔH_3.

$$\begin{array}{rl}
\mathrm{C}(s) + \frac{1}{2}\,\mathrm{O_2}(\mathrm{s}) \rightleftharpoons \mathrm{CO}(g) & \quad \Delta H_1 \\
+\mathrm{CO}(g) + \frac{1}{2}\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) & \quad \Delta H_2 \\
\hline
\mathrm{C}(s) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) & \quad \Delta H_3 = \Delta H_1 + \Delta H_2
\end{array}$$

When applied to enthalpy changes, this feature is referred to as **Hess' Law**.

2. Their values depend on the amount of material in question. The energy of 10 mol of $\mathrm{CO_2}$ is 10 times that of 1 mol of $\mathrm{CO_2}$. Similarly, the free-energy change (or the energy, enthalpy, or entropy change) for the conversion of 10 mol of carbon to 10 mol of $\mathrm{CO_2}$ is 10 times that for the conversion of 1 mol.

$$\mathrm{C}(s) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) \qquad \Delta G_1$$

$$10\ \mathrm{C}(s) + 10\ \mathrm{O_2}(g) \rightleftharpoons 10\ \mathrm{CO_2}(g) \qquad \Delta G_2$$

$$\Delta G_2 = 10\ \Delta G_1$$

For this reason, the notations for ΔE, ΔH, ΔS, and ΔG for a reaction often include an indication of how many molecules are involved in the reaction. This amount, moreover, is usually one mole. For example, ΔH for equation (3) shown before is -393.8 kJ/mol of $\mathrm{CO_2}$ formed when the reaction is carried out at 25 °C and 1 atm. If the amount is not specified, it is assumed that the number of moles involved is represented by the equation written with the lowest possible integral coefficients.

3. Their values are dependent upon temperature. Over short (100 K) temperature ranges, ΔE, ΔH, and ΔS usually vary only a little, but ΔG, because of the $T\Delta S$ term in the relation $\Delta G = \Delta H - T\Delta S$, is more temperature dependent.

Because of the dependence of ΔE, ΔH, ΔS, and ΔG on conditions, it is conventional practice to define **standard conditions** for the measurement of these parameters as *one atmosphere partial pressure for all gases and one molar concentration for all substances in solution. The standard temperature is usually, but not always, 25 °C.* A value measured under these conditions is designated by a superscript zero: for instance, ΔH°, ΔS°, or ΔG°. A standard enthalpy change of 58.2 kJ for the reaction

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\ \mathrm{NO_2}(g)$$

at 25 °C indicates that when 2 mol of $\mathrm{NO_2}$ are formed at a pressure of 1 atm from 1 mol of $\mathrm{N_2O_4}$ also at 1 atm, 58.2 kJ of heat are absorbed.

14.3 THE RELATIONSHIP BETWEEN ΔG° AND K

Consideration of the laws of thermodynamics has disclosed two criteria for spontaneity: an increase in the total entropy of the universe (system plus surroundings) and, at constant temperature and pressure, a decrease in the free energy of the system. Since the free-energy criterion is easier to apply to chemical reactions, it is the one most commonly used. The decrease in free energy that can occur in a reaction is generally expressed as ΔG; therefore it seems reasonable to suppose that the more negative ΔG is, the more the reaction will proceed until the free energy of the system is minimized. Such a relationship between the free-energy change and the extent of a reaction does indeed exist; it is expressed in terms of the standard free-energy change ΔG° and the equilibrium constant K for the reaction:

$$\Delta G^\circ = -RT \ln K$$

In this expression, the ideal gas constant (R) is expressed as 8.314 J/mol-K, T is the absolute temperature, and $\ln K$ is the natural logarithm of the equilibrium constant. The relationship also may be written in terms of base 10 logarithms by using the factor 2.303 for conversion of ln to log (i.e., $\ln x = 2.303 \log x$):

$$\Delta G^\circ = -RT(2.303 \log K)$$

When the reaction involves gases, K must be expressed in partial pressures. (When the numbers of moles of gas on both sides of the equation are equal, K_p, the equilibrium constant calculated from partial pressures, is identical to K_c, the equilibrium constant calculated in terms of moles per liter.)

The significance of this relation can be appreciated more readily if the equation is written in exponential form:

$$K = e^{-\Delta G^\circ/RT}$$

Thus, if ΔG° is zero, the entire exponent is zero, and since any number raised to zero power is 1, K has the value of 1. If ΔG° is positive, the exponent is negative, and K is therefore less than 1. As an example, suppose that $\Delta G^\circ = +4.18$ kJ/mol at 25 °C. At that temperature,

$$K = e^{-(4180\ \text{J/mol})/(8.314\ \text{J/K=mol})(298\ \text{K})}$$

$$K = 0.185$$

On the other hand, if ΔG° is negative, K is greater than 1, and as the magnitude of the negative ΔG° increases, the value of K increases. The diagram in Figure 14.9 gives values of K for a variety of standard free energy changes at 25 °C.

This relationship and, for that matter, the term "spontaneous," do not take into account how much time is required for a process to reach equilibrium. They simply indicate that given sufficient time, a process will occur under the stated conditions and to an extent given by the constant K.

The major importance of ΔG° is its relationship to the equilibrium constant, and it is for this reason that it is useful to be able to determine ΔG°. This determination can be accomplished in any of several ways: (1) from a knowledge of the standard enthalpy and entropy changes for a given reaction, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, (2) from the equilibrium constant, if it is known, and (3) from the standard electromotive force of an electrochemical reaction, a concept that will be developed in Chapter 18.

K	10^{-10}	10^{-3}	0.10	1	10	10^3	10^{10}
ΔG (kJ)	+57.0	+17.1	+5.70	0	−5.70	−17.1	−57.0

Figure 14.9 The relationship between free-energy change and the equilibrium constant.

14.4 DETERMINATION OF ΔH°

Standard Heat of Formation

Many enthalpy changes are tabulated as the **standard heat of formation**, ΔH_f°, which is defined as the enthalpy change when one mole of a substance is formed from its constituent elements, each of which is in its stable form at 1 atm pressure and the temperature specified. Generally, standard heats of formation are measured at 25 °C. When 1 mol of $NO_2(g)$, for example, is formed from N_2 and O_2 at 1 atm and 25 °C, 33.9 kJ of heat are absorbed.

$$\frac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g) \quad \Delta H^\circ = \Delta H_f^\circ = 33.9\ \text{kJ/mol}$$

The enthalpy change for this reaction, which is positive because heat is absorbed, is the standard heat of formation of NO_2 (because the product is formed from the elements in their standard states).

As another example, consider the equation representing the formation of liquid methanol from its elements in their stable forms:

$$C_{\text{graphite}} + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l)$$

Graphite, an allotropic form of carbon, is used in this equation because it is the stable form of carbon at 1 atm and 25 °C. The formation of 1 mol of methanol under these conditions liberates 238.6 kJ of heat, and thus ΔH_f° for liquid methanol is −238.6 kJ/mol.

When the standard heats of formation for all substances involved in a particular reaction are known, the enthalpy change for the reaction can be calculated. The standard enthalpy change for the $N_2O_4 \rightleftharpoons 2\,NO_2$ reaction can be determined from the knowledge that $\Delta H_f^\circ(NO_2) = 33.9$ kJ/mol and $\Delta H_f^\circ\,(N_2O_4) = 9.6$ kJ/mol. First we write explicitly the equations that represent the formation of these substances from their elements.

$$\frac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g) \qquad \Delta H_f^\circ = 33.9\ \text{kJ/mol}$$

$$N_2(g) + 2\,O_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H_f^\circ = 9.6\ \text{kJ/mol}$$

If the first equation is multiplied by 2 and the second equation is reversed and added to the first, we obtain

$$\begin{array}{rcl}
N_2(g) + 2\,O_2(g) \rightleftharpoons 2\,NO_2(g) & & \Delta H^\circ = 2\Delta H_f^\circ(NO_2) = 67.8\ \text{kJ} \\
N_2O_4(g) \rightleftharpoons N_2(g) + 2\,O_2(g) & & \Delta H^\circ = -\,\Delta H_f^\circ(N_2O_4) = -9.6\ \text{kJ} \\
\hline
N_2O_4(g) \rightleftharpoons 2\,NO_2(g) & & \Delta H^\circ = 2\Delta H_f^\circ(NO_2) - \Delta H_f^\circ(N_2O_4) \\
 & & = 58.2\ \text{kJ}
\end{array}$$

The elements N_2 and O_2 cancel, and the resulting sum is the desired equation. The overall ΔH° is given by twice the ΔH_f° for NO_2 minus the ΔH_f° for N_2O_4. (Note that reversal of the second equation changes the sign of the enthalpy change.) This result suggests that ΔH° for any reaction can be obtained by simply subtracting the sum of the standard heats of formation of the reactants from that of the products after multiplying the ΔH_f° for each substance by the coefficient of that substance in the chemical equation. Hence, for the reaction

$$aA + bB \rightleftharpoons cC + dD$$

and

$$\Delta H^\circ = \Sigma\Delta H_f^\circ(\text{products}) - \Sigma\Delta H_f^\circ(\text{reactants})$$

$$\Delta H^\circ = c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D) - a\Delta H_f^\circ(A) - b\Delta H_f^\circ(B)$$

One other observation is necessary for these calculations, namely, that the standard heat of formation of any element in its standard state is zero. For the reaction

$$CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$$

the enthalpy change is

$$\Delta H^\circ = \Delta H_f^\circ(CO_2) - \Delta H_f^\circ(CO) - \frac{1}{2}\Delta H_f^\circ(O_2)$$

But since $\Delta H_f^\circ(O_2) = 0$,

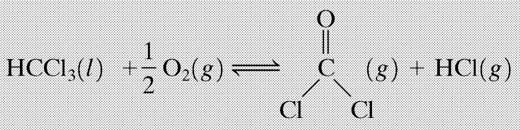
$$\Delta H^\circ = \Delta H_f^\circ(CO_2) - \Delta H_f^\circ(CO)$$

Standard heats of formation for a variety of compounds are given in Appendix 3.

Methodology 14.2

Trichloromethane decomposes in air to phosgene ($COCl_2$) and hydrogen chloride. Calculate ΔH° for this reaction at 25 °C.

First write the equation for the chemical reaction.



$$HCCl_3(l) + \frac{1}{2}O_2(g) \rightleftharpoons \overset{\overset{\large O}{\|}}{\underset{Cl\quad Cl}{C}}(g) + HCl(g)$$

Next, look up the standard heats of formation of all reactants and products, making certain that the value is for the compound in the appropriate physical state; i.e., solid, liquid or gas.

$$\Delta H_f^\circ(COCl_2) = -220.9\ \text{kJ/mol} \qquad \Delta H_f^\circ(HCl) = -95.5\ \text{kJ/mol}$$
$$\Delta H_f^\circ(HCCl_3) = -131.8\ \text{kJ/mol} \qquad \Delta H_f^\circ(O_2) = 0.0\ \text{kJ/mol}$$

Finally, use the equation

$$\Delta H_{\text{reaction}} = \Sigma\Delta H^\circ_{f\,(\text{products})} - \Sigma\Delta H^\circ_{f\,(\text{reactants})}$$

to calculate ΔH°.

$$\Delta H^\circ = \Delta H_f^\circ(COCl_2) + \Delta H_f^\circ(HCl) - \Delta H_f^\circ(HCCl_3) - (1/2)\Delta H_f^\circ(O_2)$$
$$\Delta H^\circ = -220.9 + (-92.5) - (-131.8) - (0.0)$$
$$\Delta H^\circ = -181.6\ \text{kJ}$$

Problem 14.2

Calculate ΔH° for the following reaction at 25 °C, using standard heats of formation:

$$2\ NaCl(s) + H_2SO_4(l) \rightleftharpoons Na_2SO_4(s) + 2\ HCl(g)$$

Solution:

$$\Delta H^\circ = \Delta H_f^\circ(Na_2SO_4(s)) + 2\,\Delta H_f^\circ(HCl(g)) - 2\,\Delta H_f^\circ(NaCl(s)) - \Delta H_f^\circ(H_2SO_4(l))$$
$$\Delta H^\circ = 1384.5 + 2(-92.5) - 2(-410.9) - (-811.3)$$
$$\Delta H^\circ = 63.6\ \text{kJ}$$

Heats of Combustion

Enthalpy changes can also be tabulated as standard heats of combustion, $\Delta H_c°$. Because most compounds will react with oxygen at some temperature, many enthalpy changes of this type can be obtained. In this text the use of $\Delta H_c°$ will be restricted to compounds that contain no elements other than carbon, hydrogen, and oxygen. The heat of combustion can therefore be defined as the enthalpy change accompanying the complete combustion of a substance into carbon dioxide and water. These enthalpy changes can be utilized to calculate standard enthalpy changes for reactions, as in Problem 14.3.

Problem 14.3

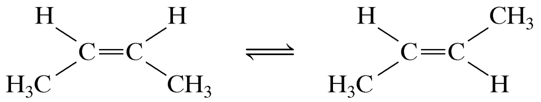
Calculate the standard enthalpy change for conversion of *cis*-2-butene to *trans*-2-butene at 25 °C from the following heats of combustion (at 25 °C):

$$\Delta H_c°(\textit{cis}\text{-2-butene}) = 2710.9 \text{ kJ/mol}$$

$$\Delta H_c°(\textit{trans}\text{-2-butene}) = 2706.9 \text{ kJ/mol}$$

Solution:

The reaction for which $\Delta H°$ is being evaluated is



and the appropriate heats of combustion can be represented by the equations

(1) $\textit{cis}\text{-}C_4H_8(g) + 6\,O_2(g) \rightleftharpoons 4\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H° = -2710.9 \text{ kJ}$

(2) $\textit{trans}\text{-}C_4H_8(g) + 6\,O_2(g) \rightleftharpoons 4\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H° = -2706.9 \text{ kJ}$

If equation (2) is reversed (and its enthalpy change altered in sign) and added to equation (1), the result is

$$\begin{array}{rl}
\textit{cis}\text{-}C_4H_8(g) + 6\,O_2(g) \rightleftharpoons 4\,CO_2(g) + 4\,H_2O(l) & \Delta H° = -2710.9 \text{ kJ} \\
\underline{4CO_2(g) + 4\,H_2O(1) \rightleftharpoons \textit{trans}\text{-}C_4H_8(g) + 6\,O_2(g)} & \underline{\Delta H° = +2706.9 \text{ kJ}} \\
\textit{cis}\text{-}C_4H_8(g) \rightleftharpoons \textit{trans}\text{-}C_4H_8(g) & \Delta H° = -4.0 \text{ kJ}
\end{array}$$

Bond Energies

The **bond energy** of a diatomic molecule is defined as the energy required to dissociate one mole of the gaseous compound into its constituent gaseous atoms. Thus, for example, the bond energy of 239.7 kJ/mol of Cl_2 is the enthalpy change at 25 °C for the process

$$Cl_2(g) \rightleftharpoons 2\,Cl(g) \qquad \Delta H° = 239.7 \text{ kJ}$$

For a polyatomic molecule, the term "bond energy" can have several different meanings. For H_2O, the energy required for the dissociation of one O—H bond is 474.5 kJ/mol.

$$H{-}O{-}H(g) \longrightarrow H(g) + O{-}H(g) \qquad \Delta H° = 474.5 \text{ kJ}$$

The dissociation of the other O—H bond, however, requires only 420.9 kJ/mol,

$$O{-}H(g) \longrightarrow O(g) + H(g) \qquad \Delta H° = 420.9 \text{ kJ}$$

The sum of these two equations represents the complete dissociation of $H_2O(g)$ into its constituent atoms, for which 895.4 kJ/mol of energy is required:

$$H{-}O{-}H(g) \longrightarrow 2\,H(g) + O(g) \qquad \Delta H° = 895.4 \text{ kJ}$$

Because two O—H bonds per molecule have been severed, the average O—H bond energy for water is 447.7 kJ/mol.

Chemists often require approximate values for ΔH if no pertinent thermochemical data are available for the reaction in question. This necessity has led to yet another definition of bond energy. If the average bond energy is obtained for a particular bond in each compound of a series, these values may be averaged to obtain a **representative bond energy** value for that bond. For example, the average O—H bond energy in water is 447.7 kJ/mol, as discovered above, and the O—H bond energy in methanol (CH_3OH) is 426.8 kJ/mol. If the O—H bond energies in these and other compounds are averaged, the value of 460.2 kJ/mol is obtained. In a similar way, average bond energies have been obtained for other single bonds, such as C—H, N—H, C—Cl, and C—Br, as well as for multiple bonds such as C═C, C═N, and C≡N. Appendix 2 contains some typical average bond energies.

Use of the exact bond energies for diatomic molecules will produce accurate $\Delta H°$ values, as illustrated by the reaction

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

The standard enthalpy change may be calculated by summing the equations (and their respective enthalpy changes).

$$\begin{array}{rl}
N_2(g) \rightleftharpoons 2\,N(g) & \Delta H° = 941.4\text{ kJ} \\
O_2(g) \rightleftharpoons 2\,O(g) & \Delta H° = 493.7\text{ kJ} \\
\underline{2\,N(g) + 2\,O(g) \rightleftharpoons 2\,NO(g)} & \underline{\Delta H° = -1255.2\text{ kJ}} \\
N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) & \Delta H° = +179.9\text{ kJ}
\end{array}$$

The first and second equations are, of course, representative of the dissociation of N_2 and O_2, and the corresponding enthalpy changes are their bond dissociation energies. The third equation is the reverse of the equation for the dissociation of NO, multiplied by 2, and the enthalpy change is the negative of twice the bond energy of NO.

In a mechanical sense, the enthalpy change was calculated by subtracting the sum of the bond energies of the products from that of the reactants, after multiplying the bond energy of each substance by the coefficient of that substance in the appropriate equation.

The procedure for obtaining approximate enthalpy changes is similar. Consider the problem of estimating $\Delta H°$ for the reaction

$$CH_3CH_3(g) + Cl_2(g) \rightleftharpoons CH_3CH_2Cl(g) + HCl(g)$$

The net result of the reaction is the breaking of one C—H bond per ethane molecule and one Cl—Cl bond per Cl_2 molecule, and the formation of one C—Cl bond per chloroethane molecule and one H—Cl bond per HCl molecule (see Figure 14.10). The energy required to break a C—H bond is estimated as the average C—H bond energy, while the energy released when a C—Cl bond is formed is estimated as the average C—Cl bond energy. For the decomposition of Cl_2 and the formation of HCl, exact diatomic bond energies can be used. Hence, addition of the following equations and enthalpy changes produces the desired estimate of $\Delta H°$.

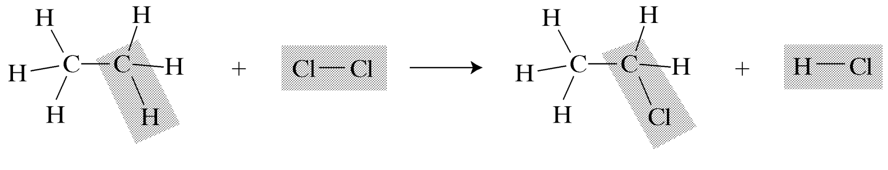


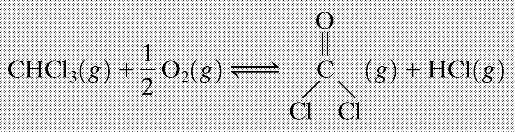
Figure 14.10 Bond breakage and bond formation in the reaction of methane with chlorine.

$$\begin{array}{rcll}
CH_3CH_3(g) & \rightleftharpoons & CH_3CH_2(g) + H(g) & \Delta H^\circ \cong 410\text{ kJ} \\
Cl_2(g) & \rightleftharpoons & 2\,Cl(g) & \Delta H^\circ = 238.5\text{ kJ} \\
Cl(g) + CH_3CH_2(g) & \rightleftharpoons & CH_3CH_2Cl(g) & \Delta H^\circ \cong -326\text{ kJ} \\
H(g) + Cl(g) & \rightleftharpoons & HCl(g) & \Delta H^\circ = -426.8\text{ kJ} \\
\hline
CH_3CH_3(g) + Cl_2(g) & \rightleftharpoons & CH_3CH_2Cl(g) + HCl(g) & \Delta H^\circ \cong -105\text{ kJ}
\end{array}$$

The value of ΔH° when obtained from standard heats of formation is -113.0 kJ, which reveals that the approximate value obtained with average bond energies is a reasonably good estimate.

Methodology 14.3

Calculate the standard enthalpy change for the following reaction from bond energy data:

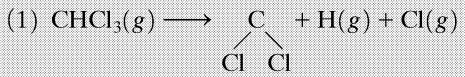


$$CHCl_3(g) + \frac{1}{2}O_2(g) \rightleftharpoons \underset{Cl\quad Cl}{\overset{\overset{O}{\|}}{C}}\ (g) + HCl(g)$$

The first steps in this type of analysis require the identification of the bonds that are broken and those that are formed in the course of the reaction.

Identify the bonds that are broken on the left-hand side of the equation.

In $CHCl_3$, 1 mole of C—Cl bonds, and 1 mole of C—H bonds are broken:



$$(1)\ CHCl_3(g) \longrightarrow \underset{Cl\quad Cl}{C} + H(g) + Cl(g)$$

In oxygen, 1/2 mole of O_2 bonds are broken:

$$(2)\ \frac{1}{2}O_2(g) \longrightarrow O(g)$$

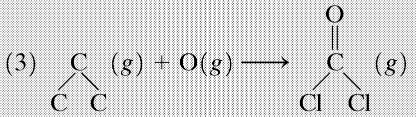
The enthalpy change associated with breaking these bonds can now be estimated:

$$\Delta H^\circ = 410.0\text{ kJ/mol (C—H)} + 326.4\text{ kJ/mol (C—C)} + (1/2)493.8\text{ kJ/mol }(O_2)$$

$$\Delta H^\circ = 983.3\text{ kJ}$$

Next, do the same type of analysis for the bonds that are formed in the reaction.

For the reaction, 1 mole of C=O bonds and 1 mole of HCl bonds are formed:



$$(3)\ \underset{C\quad C}{C}\ (g) + O(g) \longrightarrow \underset{Cl\quad Cl}{\overset{\overset{O}{\|}}{C}}\ (g) \qquad \Delta H^\circ = -799.1\text{ kJ}$$

$$(4)\ H(g) + Cl(g) \longrightarrow HCl(g) \qquad \Delta H^\circ = -426.8\text{ kJ}$$

The enthalpy change for the bond formation is now estimated:

$$\Delta H^\circ = -799.1\text{ kJ} + -426.8\text{ kJ} = -1225.9\text{ kJ}$$

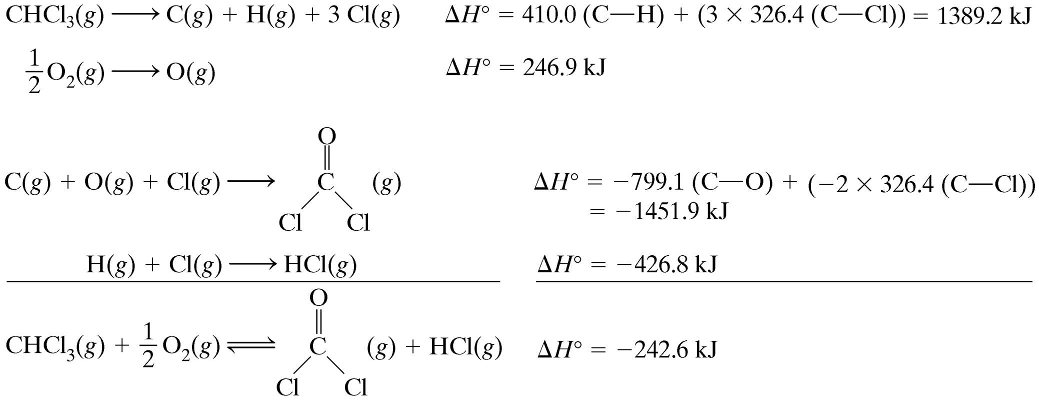
Obtain the enthalpy change for the reaction using these values.

$$\Delta H^\circ = 983.3\text{ kJ} + -1225.9\text{ kJ} = -242.6\text{ kJ}$$

The more accurate enthalpy change for this reaction, derived from the heats of formation, is -212.6 kJ.

Problem 14.4

An alternate way of estimating the $\Delta H_{\text{reaction}}$ is to allow all reactants to break down into their constituent atoms and then re-form these atoms into the products. Using this method, estimate the enthalpy change for the reaction in Methodology 14.2.



$\mathrm{CHCl_3}(g) \longrightarrow \mathrm{C}(g) + \mathrm{H}(g) + 3\ \mathrm{Cl}(g) \qquad \Delta H^\circ = 410.0\ (\mathrm{C{-}H}) + (3 \times 326.4\ (\mathrm{C{-}Cl})) = 1389.2\ \mathrm{kJ}$

$\frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{O}(g) \qquad \Delta H^\circ = 246.9\ \mathrm{kJ}$

$\mathrm{C}(g) + \mathrm{O}(g) + \mathrm{Cl}(g) \longrightarrow \mathrm{Cl_2C{=}O}\ (g) \qquad \Delta H^\circ = -799.1\ (\mathrm{C{-}O}) + (-2 \times 326.4\ (\mathrm{C{-}Cl})) = -1451.9\ \mathrm{kJ}$

$\mathrm{H}(g) + \mathrm{Cl}(g) \longrightarrow \mathrm{HCl}(g) \qquad \Delta H^\circ = -426.8\ \mathrm{kJ}$

$\mathrm{CHCl_3}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightleftharpoons \mathrm{Cl_2C{=}O}\ (g) + \mathrm{HCl}(g) \qquad \Delta H^\circ = -242.6\ \mathrm{kJ}$

$\Delta H^\circ = -242.6\ \mathrm{kJ}$

Check Point 14.3

Calculate the standard enthalpy change (using bond energies) for the reaction

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\ \mathrm{HCl}(g)$$

Solution:

−184 kJ/mol

◇ ◇ ◇ ◇ ◇

14.5 DETERMINATION OF ΔS°

The entropy of a substance is associated with its disorder, which is a result of the number of ways in which its various energy levels (translational, rotational, vibrational, and electronic) can be populated. Moreover, the accessibility of energy levels increases as the temperature increases, and therefore the entropy of a substance increases with temperature. This temperature dependence suggests that at absolute zero, any substance should be perfectly ordered; that is, all molecules or ions should occupy the lowest energy state. Numerous experiments have verified this expectation, and thus have led to the **Third Law of Thermodynamics**:

The entropy of perfect crystals of all elements and compounds is zero at absolute zero temperature.

As a result of this law, absolute entropies can be determined at any temperature. Entropies evaluated at 25 °C are listed in Appendix 3. These entropies can be used to calculate ΔS° for a given reaction by subtracting the sum of the entropies of the reactants from the sum of the entropies of the products, after multiplying the entropy value for each substance by the coefficient associated with that substance in the reaction equation.

TABLE 14.2 Standard Entropy Changes for Selected Reactions

	ΔS°(J/K) at 25 °C
(1) $PbCO_3(s) \rightarrow PbO(s) + CO_2(g)$	150.6
(2) $SiCl_4(l) + 2\,H_2O(l) \rightarrow SiO_2(s) + 4\,HCl(g)$	410.0
(3) $N_2O_4(g) \rightarrow 2\,NO_2(g)$	175.7
(4) $NH_3(g) \rightarrow \frac{1}{2}N_2\,(g) + \frac{3}{2}H_2(s)$	100.4
(5) $N_2O_4(g) \rightarrow N_2(g) + 2\,O_2(g)$	297.1
(6) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$	20.9
(7) $N_2(g) + O_2(g) \rightarrow 2\,NO(g)$	25.1

The entropy changes calculated in this way for several reactions are presented in Table 14.2. Careful analysis indicates that for those reactions in which the number of gaseous particles on both sides of the equation is the same (that is, reactions (6) and (7)), the entropy change is small. For those reactions in which the number of gaseous particles increases, the entropy changes are larger. Additionally, the data suggest that greater increases in the number of moles of gas formed correspond to increasingly larger values of ΔS. Compare, for example, the ΔS° of 410.0 J/K for reaction (2), in which 4 moles of gas are formed from liquids, with the ΔS° of 100.4 J/K for reaction (4), in which 2 moles of gaseous products are formed from 1 mole of gaseous reactant. These observations can be explained by the much greater freedom of movement (more closely spaced translational levels) of gases as compared with liquids and solids, and by the fact that an increase in the number of gaseous molecules increases the number of ways in which the translational (and other energy) levels can be populated.

Problem 14.5

Calculate ΔS° for the conversion of gaseous N_2O_4 to gaseous NO_2.

Solution:

The equation for this conversion is

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

The entropies for $N_2O_4(g)$ and $NO_2(g)$ are obtained from Appendix 3 as 304.2 J/K-mol and 240.2 J/K-mol, respectively. The standard entropy change is then

$$\Delta S^\circ = 2(240.2\ \text{J/K-mol})\ 2\ 304.2\ \text{J/K-mol} = 176.2\ \text{J/K}$$

14.6 DETERMINATION OF ΔG°

For some substances, **standard free energies of formation**, ΔG_f°, have been tabulated. The standard free energy of formation is defined as the free energy change when one mole of a substance is formed from its constituent elements, each of which is in its standard state at 1 atm pressure and the specified temperature (usually 25 °C). Standard free energies of formation are entirely analogous, therefore, to standard heats of formation and can be manipulated in exactly the same way. A listing of some ΔG_f° values is provided in Appendix 3. As Problem 14.6 indicates, ΔG_f° for any element in its standard state is zero.

Problem 14.6

Calculate ΔG° for the following reaction.

$$CH_3OH(l) + 2\,O_2(g) \rightleftharpoons CO_2(g) + 2\,H_2O(l)$$

Solution:

The free energy of formation, ΔG_f°, for each reactant and product is required. From Appendix 3 the standard free energies of formation are

$CH_3OH(l)$	−166.1 kJ/mol
$CO_2(g)$	−394.6 kJ/mol
$H_2O(l)$	−237.2 kJ/mol

Then, $\Delta G^\circ = \Sigma\Delta G_f^\circ{}_{\text{(products)}} - \Sigma\Delta G_f^\circ{}_{\text{(reactants)}}$ is used to complete the analysis. (Remember that the standard free-energy change for O_2 is zero because it is an element in its most stable form under standard conditions.)

$$\Delta G^\circ = \Delta G_f^\circ(CO_2(g) + 2\Delta G_f^\circ(H_2O(l)) - \Delta G_f^\circ(CH_3OH(l))$$

$$\Delta G^\circ = -394.6 + 2(-237.2) - (-166.1)$$

$$\Delta G^\circ = -702.9\text{ kJ}$$

In many cases, standard free energy changes must be calculated from ΔH° and ΔS° with the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Problem 14.7 is illustrative of the kinds of problems that can be solved.

Problem 14.7

Calculate ΔG° and K for the isomerization of *cis*-2-butene to *trans*-2-butene.

Solution:

In Problem 14.3, ΔH° for this process was determined as −4.0 kJ/mol (or −4000 J/mol). The standard entropy change can be obtained from the absolute entropies of 300.8 J/K-mol for the *cis*-isomer and 296.6 J/K-mol for the *trans*-isomer. Therefore:

$$\Delta S^\circ = 296.6 - 300.8 = -4.2\text{ J/K-mol}$$

Thus

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ &= -4000\text{ J} - 298\text{ K}(-4.2\text{ J/K})\\ &= -2750\text{ J}\end{aligned}$$

Now, from the relation $\Delta G^\circ = -RT(\ln K)$,

$$\ln K = \frac{-2750\text{ J/mol}}{(8.314\text{ J/K-mol})(298\text{ K})}$$

$$\ln K = +\,1.11$$

$$K = 3.0\text{ at }25\text{ °C}$$

Estimating ΔG° for a reaction is a useful tool in determining the feasibility of the process. For example, consider the preparation of chlorine monoxide (Cl_2O) by direct combination of the elements. If a chemist desired to make this compound, the value of ΔG° for the reaction could dictate the success or failure of the synthesis.

The standard free energy change for the reaction

$$Cl_2(g) + \frac{1}{2}O_2(g) \longrightarrow Cl_2O(g)$$

can be determined by simply looking up ΔG_f° (Cl_2O), because this equation represents the formation of Cl_2O from its elements in their standard states. From Appendix 3, $\Delta G_f^\circ(Cl_2O)$ is 93.7 kJ/mol. The equilibrium constant calculated from this value is 10^{-17}, which means that even under a condition of high pressure (which would favor formation of the product), virtually no product would be formed at 25 °C. Of course, because the reaction is endothermic (ΔH_f° = 76.1 kJ/mol), higher temperatures will favor the product, but even at 600 °C the extent remains small.

Moreover, the positive free energy of formation reveals that at 25 °C the compound Cl_2O is unstable relative to its constituent elements. Thus, the decomposition

$$Cl_2O(g) \longrightarrow Cl_2(g) + \frac{1}{2}O_2(g)$$

should occur. In fact, this decomposition does occur, but at a slow enough rate so that Cl_2O, once prepared, can be stored for some time.

The preparation can be accomplished by a different route, namely, by the reaction

$$HgO(s) + 2\,Cl_2(g) \longrightarrow HgCl_2(s) + Cl_2O(g)$$

The standard free energy change for this reaction, which can be obtained from standard free energies of formation, verifies the sizable equilibrium constant (10^4) for the reaction.

$$\Delta G^\circ = \Delta G_f^\circ(Cl_2O(g)) + \Delta G_f^\circ(HgCl_2(s)) - \Delta G_f^\circ(HgO(s))$$

$$\Delta G^\circ = 93.7 + (-185.8) - (-58.6)$$

$$\Delta G^\circ = -33.5 \text{ kJ}$$

Problem 14.8

Determine the feasibility of preparing chloroethene (a precursor to the important polymer polyvinyl chloride) from 1,2-dichloroethane. If this process is feasible, what conditions should be used to optimize the extent?

Solution:

The equation for the reaction is

$$ClCH_2CH_2Cl(g) \longrightarrow H_2C{=}CHCl(g) + HCl(g)$$

In order to determine the feasibility of the reaction, two things must be known: its rate and its extent. The rate is very difficult to estimate, but the extent can be determined *via* K and ΔG°.

Because standard free energies of formation for 1,2-dichloroethane and chloroethene are not given in Appendix 3, an approximate calculation of ΔH° from average bond energies is required.

$$\Delta H^\circ \cong 346\ (C{-}C) + 411\ (C{-}H) + 327\ (C{-}Cl) - 602\ (C{=}C) - 428\ (H{-}Cl) \cong 54 \text{ kJ}$$

Because there are twice as many gaseous particles on the right-hand side of the equation as on the left-hand side, the entropy change for the reaction is certainly positive. With the aid of Table 14.2, we can estimate ΔS° as approximately 140 J/K. Then

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ \cong 54{,}000 \text{ J } 2\ (298 \text{ K})(140 \text{ J/K})$$

$$\Delta G^\circ \cong 12 \text{ kJ}$$

Continued on next page

Problem 14.8 *Continued*

Solution: *Continued*

(The more accurate values obtained from heats and free energies of formation are $\Delta H^\circ = 72.4$ kJ, $\Delta S^\circ = 142.3$ J/K, and $\Delta G^\circ = 30.1$ kJ.)

At 25 °C, the reaction clearly has a low equilibrium constant. If ΔH° and ΔS° remain constant over a temperature range of a couple of hundred degrees, the temperature at which $\Delta G^\circ = 0$ (and therefore $K = 1$) may be determined.

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$
$$0 = 54{,}000\text{ J} - T(140\text{ J/K})$$
$$T = 386\text{K or } 113\ ^\circ\text{C}$$

(With more accurate values of ΔH° and ΔS° the analysis gives $T = 239$ °C.)

Therefore, optimum conditions for this reaction would be a temperature above 116 °C and relatively low pressure. (The higher temperature will also increase the rate of the reaction.)

CHAPTER SUMMARY

The first and second laws of thermodynamics provide one of the most powerful set of tools available to the scientist. They permit the synthetic and industrial chemist and the chemical engineer to determine which reactions are feasible and how to alter conditions of temperature and pressure in order to maximize yields. The thermodynamic parameter most often used for the prediction of feasibility is the free energy change, ΔG. This parameter is especially valuable because of the relationship of its value under standard conditions (ΔG°) to the equilibrium constant. You should strive, therefore, to thoroughly understand the derivation of this variable from ΔH and ΔS and its application to predictions of feasibility.

It is important to keep in mind that although ΔG° provides information about the extent of a process after equilibrium has been established, it reveals nothing about how long it takes to reach equilibrium. Since ΔG is often calculated from ΔH and ΔS, the calculation of these variables from standard heats of formation, standard heats of combustion, bond energies, and absolute entropies must be mastered.

Because the variables ΔE, ΔH, and ΔS are related by the first and second laws of thermodynamics, it is necessary to become familiar with the meaning of these laws and their mathematical expressions.

TERMS

Some important terms introduced in this chapter include:

System That portion of the universe under consideration.

Surroundings Everything in the universe outside of the system.

ΔE The change in the total energy (kinetic plus potential energy) of a system during a process. This change depends only on the initial and final states of the process, not on the path to the final state, and is therefore a state function. When the process involves only mechanical work, the change in energy can be expressed as

$$\Delta E = q - w$$

where q is the heat absorbed by the system and w is the work done by the system during the process.

First Law of Thermodynamics, or the Law of Conservation of Energy A law developed from numerous observations over several centuries: The total energy of a system and its surroundings remains constant.

q The heat absorbed by a system; it is positive if the system increases in heat energy.

w The work done by a system; it is positive if the system expends energy to produce work. The work involved in expanding or compressing a gas at a constant pressure *P* is

$$w = P\Delta V$$

If the gas is compressed, the work done by the gas is negative; if the gas expands, the work done by the gas is positive.

Reversible process A hypothetical process carried out infinitely slowly, so that the process is always in equilibrium with its surroundings.

Enthalpy, H A thermodynamic state function expressed by the equation

$$H = E + PV$$

For a process involving only expansion-compression work at constant pressure, the following relationship holds:

$$\Delta H = \Delta E + P\Delta V$$

In this case ΔH is the heat released or absorbed by a process carried out at constant pressure.

Calorimeter A device for measuring the heat changes involved in chemical reactions. The heat liberated in the reaction chamber is released to a surrounding medium, whose heat capacity is known or can be determined. From the increase in temperature of the medium and its heat capacity, the heat released by the reaction can be determined. In a "bomb" calorimeter, a sample is reacted with oxygen and the heat released can therefore be used to calculate the heat of combustion.

Heat capacity The heat required to raise the temperature of a system by 1 °C.

Entropy, S A thermodynamic state function whose change, ΔS, is given by the change in heat for a process carried out reversibly divided by the temperature at which it occurs,

$$\Delta S = \frac{q_{\text{reversible}}}{T}$$

The entropy change can be related to the change in order of a process. If ΔS is positive, the process has gone from a state of more order to one of lesser order. At the microscopic level, this increase in disorder is a result of the spreading of atoms or molecules over a greater number of energy levels.

Second Law of Thermodynamics A law based on a multitude of observations over many years: A spontaneous process is always accompanied by an increase of the entropy of the system and its surroundings (that is, an increase in the entropy of the universe).

Spontaneous process A process that under a given set of conditions will proceed without external aid.

Free energy A thermodynamic state function expressed by the equation

$$G = H - TS$$

The change in free energy at a constant temperature is given by the equation

$$\Delta G = \Delta H - T\Delta S$$

A spontaneous process occurring at a constant temperature and pressure (the conditions under which most laboratory reactions occur) is always accompanied by a decrease in free energy; that is, ΔG is negative. A process at equilibrium has a ΔG of zero. When ΔG is measured under standard conditions, it can be related to the equilibrium constant for a reaction by the expression

$$\Delta G^{\circ} = -RT \ln K$$

Standard conditions A defined set of conditions for the measurement of the thermodynamic variables (ΔH, ΔS, and ΔG): 1 atm partial pressure for gases and a concentration of 1 M for all substances in solution.

Standard heat of formation, ΔH_f° The enthalpy change for the formation of one mole of a substance from its constituent elements in their most stable elemental forms at 1 atm pressure and the temperature specified (usually 25 °C). The ΔH_f° for any element in its standard state (the most stable elemental form at 1 atm pressure and the temperature specified) is zero. The same applies to the standard free energy change, ΔG_f°.

Standard heat of combustion, ΔH_c° For compounds that contain no elements other than carbon, hydrogen, and oxygen, ΔH_c° is the enthalpy change for the complete reaction of the compound with oxygen to form $CO_2(g)$ and $H_2O(l)$ at standard conditions.

Hess' Law A law of additivity that states that the enthalpy change for a process is the sum of the enthalpy changes for any set of processes whose equations can be summed to give the equation for the overall process. The same principle applies to the other state functions (ΔE, ΔS, and ΔG).

Third Law of Thermodynamics A statement that the entropy of perfect crystals of all elements and compounds is zero at 0 *K*. As a result of this law, absolute entropies, S°, can be obtained at any other temperature.

PROBLEMS

1. In SI units, work is expressed in newton-meters. This unit is called the joule, in honor of James Joule, a British physicist. One joule is therefore the work done when a force of one newton acts through a distance of one meter. The newton is the SI unit of force and is that force which will produce an acceleration of one meter per second squared in a mass of one kilogram. Calculate the work in joules required for the compression of an ideal gas from an initial volume of 1 L and a pressure of 1 atm (1.01×10^5 N/m^2) to a final volume of $\frac{1}{3}$ L and a pressure of 3 atm. Assume that the compression is accomplished by applying a constant pressure of 3 atm to the piston.

2. Calculate q, w, ΔE, ΔH, ΔS, ΔS_{system}, $\Delta S_{\text{surroundings}}$, and ΔG for the compression described in Problem 1, carried out at 20 °C. Comment on the significance of the values obtained.

3. A substance has a heat of fusion of 7113 J/mol and an entropy of fusion of 10 J/K-mol at 25 °C. Is the substance a solid or a liquid at this temperature?

4. When 0.100 mol of methanol is burned in a combustion calorimeter, the temperature of the surrounding water increases by 0.730 °C. Calculate the heat capacity of the calorimeter. (Note: Assume that liquid water and gaseous CO_2 are the products.)

5. Indicate whether each of the following changes represents an increase or decrease in entropy:
(a) burning propene to carbon dioxide and water
(b) programming a computer
(c) converting a liquid to a solid
(d) breaking a beaker
(e) the rotting of wood
(f) assimilating chemical knowledge
(g) writing a term paper
(h) building a house

6. Carbon tetrachloride appears to be quite inert to water. Silicon tetrachloride, on the other hand, reacts vigorously with water.
(a) Using standard heats and free energies of formation, calculate the standard enthalpy, entropy, and free-energy changes for the reactions.

$$CCl_4(l) + 2\,H_2O(l) \rightleftharpoons CO_2(g) + 4\,HCl(g)$$

$$SiCl_4(l) + 2\,H_2O(l) \rightleftharpoons SiO_2(s) + 4\,HCl(g)$$

(b) Why does CCl_4 appear not to react with water?

7. Calculate ΔH° for the dissolution of magnesium fluoride

$$MgF_2(s) \longrightarrow Mg^{2+}(aq) + 2\,F^-(aq)$$

given the following enthalpy changes:

$$\begin{aligned} MgF_2(s) &\longrightarrow Mg^{2+}(g) + 2\,F^-(g) && \Delta H^\circ = 2908 \text{ kJ/mol} \\ Mg^{2+}(g) &\longrightarrow Mg^{2+}(aq) && \Delta H^\circ = -1926 \text{ kJ/mol} \\ F^-(g) &\longrightarrow F^-(aq) && \Delta H^\circ = -524 \text{ kJ/mol} \end{aligned}$$

8. Is the dissolution of CsI in distilled water at 25 °C exothermic or endothermic? Will cesium iodide spontaneously dissolve in water at 10 °C? Explain.

	ΔG_f°	ΔH_f°	S°
$CsI(s)$	−334 kJ/mol	−337 kJ/mol	123 J/mol-K
$Cs^+(aq)$	_______	−248 kJ/mol	133 J/mol-K
$I^-(aq)$	_______	−57 kJ/mol	107 J/mol-K

9. Given that the heat of formation of $LiF(s)$ is −612 kJ/mol, calculate the lattice energy of $LiF(s)$.

10. Predict the sign of ΔH° and ΔS° for the following reactions:
(a) $NaCl(s) \rightleftharpoons Na^+(g) + Cl^-(g)$
(b) $SbCl_3(s) \rightleftharpoons SbCl_3(l)$

(c) $N_2(g) \rightleftharpoons 2\,N(g)$

(d) $AgNO_3(aq) + NaCl(aq) \rightleftharpoons AgCl(s) + NaNO_3(aq)$

11. Calculate $\Delta H°$, $\Delta S°$, $\Delta G°$, and K for the gas-phase isomerization of *cis*-1,2-dichloroethene to *trans*-1,2-dichloroethene at 25 °C.

12. Calculate $\Delta H°$, $\Delta S°$, $\Delta G°$, and K for the reaction of glucose ($C_6H_{12}O_6$) with oxygen in the body to form CO_2 and liquid water (assume 25 °C). For glucose: $\Delta G_f° = -910.4$ kJ/mol, $\Delta H_f° = -1274$ kJ/mol, $S_f° = 212$ J/mol-K.

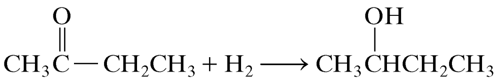
13. Which of the following reactions is most likely for the decomposition of NH_4NO_3 at room temperature? Explain your answer.

$$2\,NH_4NO_3(s) \rightleftharpoons 2\,NH_4NO_2(s) + O_2(g)$$

$$NH_4NO_3(s) \rightleftharpoons N_2(g) + 2\,H_2(g) + O_2(g)$$

$$NH_4NO_3(s) \rightleftharpoons N_2O(g) + 2\,H_2O(g)$$

14. For the gas-phase reaction



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3 + H_2 \longrightarrow CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH_3$$

(a) Calculate $\Delta H°$ using heats of formation below.
(b) Calculate $\Delta H°$ using bond energies given below.
(c) Calculate $\Delta S°$ using absolute entropies given below.
(d) Calculate $\Delta G°$.

Data:

	$\Delta H_f°$(kJ/mol)	$S°$(J/K-mol)
2-butanone(g)	−238.4	338
2-butanol(g)	−292.3	359
$H_2(g)$	0	131

Bond Energies (kJ/mol):

H—H	432
C═O	799
C—O	358
O—H	459
C—H	411
O═O	494

15. Calculate an approximate value for the standard heat of formation of the compound $H_2N-\overset{\overset{\displaystyle H}{|}}{N}-NH_2$ in the gaseous state. Is this compound likely to be thermodynamically stable at room temperature? Explain carefully.

16. The heat of formation of nitrogen trifluoride, a very stable compound, is −113 kJ/mol, while the heat of formation of nitrogen trichloride, a highly explosive compound, is about 230 kJ/mol. Can you account for this difference?

17. For the reaction

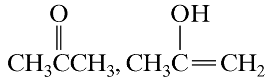
$$2\,NO_2 \rightleftharpoons N_2O_4 \qquad \Delta H°_{\text{reaction}} = -58.2\text{ kJ};\ K = 9.2$$

(a) Determine $\Delta G°_{\text{reaction}}$.
(b) Determine $\Delta S°_{\text{reaction}}$.

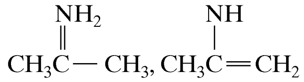
18. Estimate the enthalpy change for the gaseous reaction:

$$PH_3 + 4\,Cl_2 \longrightarrow PCl_5 + 3\,HCl$$

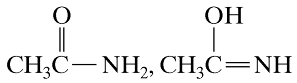
19. Structural isomers that differ only in the position of a hydrogen atom are called *tautomers*. Decide on the basis of bond energies which tautomer in each of the following pairs is thermodynamically more stable:

(a) 

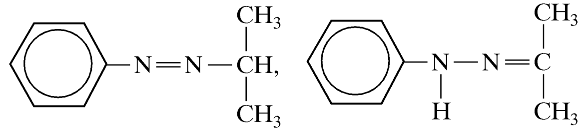
$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3,\ CH_3\overset{\overset{\displaystyle OH}{|}}{C}=CH_2$

(b) 

$CH_3\overset{\overset{\displaystyle NH_2}{\|}}{C}-CH_3,\ CH_3\overset{\overset{\displaystyle NH}{|}}{C}=CH_2$

(c) 

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-NH_2,\ CH_3\overset{\overset{\displaystyle OH}{|}}{C}=NH$

(d) 

20. Calculate $\Delta G°$ and K for the following reactions from the data given:

(a) $H_2O(s) \rightleftharpoons H_2O(l)$ $\Delta H° = 6.01$ kJ/mol $\Delta S° = 22.0$ J/K-mol
Calculate $\Delta G°$ and K at 0 °C.

(b) $1/2\,N_2(g) + 3/2\,H_2(g) \rightleftharpoons NH_3(g)$
$\Delta H° = -46$ kJ/mol $\Delta S° = -96$ J/K-mol
Calculate $\Delta G°$ and K at 25 °C and 250 °C.

21. Hydroiodic acid can be made by the direct combination of the elements.

$$H_2(g) + I_2(s) \longrightarrow 2\,HI(g)$$

(a) Calculate the standard enthalpy change for this reaction.
(b) Calculate $\Delta S°$ and $\Delta G°$ for the reaction.
(c) How will an increase in temperature affect the extent of this reaction?
(d) Assume that at some temperature the equilibrium constant for the reaction is 1.0. How much HI will be formed in a 1.0-L flask if the reaction is started with 0.010 mol of H_2 and 0.010 mol of I_2?

22. For the reaction:

$$2\,PH_3(g) + 3\,Cl_2(g) \longrightarrow 2\,PCl_3(g) + 6\,HCl(g)$$

(a) Calculate the standard enthalpy change using two methods.
(b) Why are these two values different?
(c) Calculate the standard entropy change for the reaction.
(d) Explain the sign and relative magnitude of the entropy change.
(e) Calculate the free-energy change at 25 °C.
(f) Calculate the equilibrium constant for this reaction at 25 °C.
(g) Rationalize the large negative enthalpy change for this reaction.
(h) Does the large equilibrium constant mean that this reaction can be used to prepare PCl_3 in the laboratory?

23. Consider the reaction

$$C_2H_2 + H_2 \longrightarrow C_2H_4$$

(a) Give the names of C_2H_2 and C_2H_4.
(b) Calculate the heats of combustion of C_2H_2 and C_2H_4.
(c) Calculate the $\Delta H°$ for the hydrogenation of C_2H_2.
(d) Calculate the $\Delta H°$ for the hydrogenation of C_2H_2 using bond energies.

24. Why are the $H_f°$ values for most fluorine compounds negative?

25. Consider the chlorination of methane to yield tetrachloromethane:

$$CH_4(g) + 4\ Cl_2(g) \longrightarrow CCl_4(l) + 4\ HCl(g)$$

(a) What is $\Delta H°$ in kJ/mol for this reaction if it is done at 25 °C?
(b) The value of $\Delta S°$ (in J/mol-K) for this reaction is:
(c) Is the reaction spontaneous at 25 °C?

26. The complete combustion of butane yields carbon dioxide and water:

$$C_4H_{10} + 13/2\ O_2 \longrightarrow 4\ CO_2 + 5\ H_2O$$

(a) What is the enthalpy of reaction (in kJ) for the combustion of one mole of butane?
a. −2880 b. −554 c. 2880 d. 554
(b) What is $\Delta S°$ for the reaction in J/mole-K.
a. 437 b. −232 c. 894 d. −437
(c) Is the reaction spontaneous?

27. Consider the following reaction and then answer the questions.

$$CH_4 + 2\ F_2 \longrightarrow CH_2F_2 + 2\ HF$$

(a) Estimate $\Delta H°$ reaction for this process.
(b) The actual ΔH reaction is −915 kJ/mole. Explain the difference between this value and the estimated value of ΔH.

28. What is $\Delta H°$ for the following reaction at 25 °C?

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$

29. Consider the reaction: $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

(a) What is the enthalpy change for the reaction?
a. 802 kJ/mole b. −802 kJ/mole
c. −560 kJ/mole d. 560 kJ/mole
(b) The enthalpy change for the combustion of ketene is −981 kJ/mole.

$$CH_2CO(g) + 2\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(g)$$

(c) What is $\Delta H°_{reaction}$ for the reaction below?

$$2\ CH_4(g) + 2\ O_2(g) \longrightarrow CH_2CO(g) + 3\ H_2O(g)$$

30. For the gas phase reaction

$$CH_3COCH_2CH_3 + H_2 \longrightarrow CH_3CH(OH)CH_2CH_3$$

(a) Calculate $\Delta H°$ using heats of formation
(b) Calculate $\Delta H°$ using bond energies
(c) Calculate $\Delta S°$ using absolute entropies
(d) Calculate $\Delta G°$

31. Consider the reaction of solid carbon with gaseous hydrogen to form gaseous methane at a certain temperature.

$$C(s) + 2\ H_2(g) \rightleftharpoons CH_4(g)$$

(a) If the reaction is started with 1.0 mole of CH_4 in a 1.00-L flask, when equilibrium is reached the flask contains 1.0 mole of H_2. Calculate K for the equation above.
(b) How much CH_4 must be placed in an empty 2.00-L flask in order to get 1.0 mole of H_2 at equilbrium?
(c) How much H_2 must be mixed with 1.0 mole of C(*s*) in a 1.00-L flask in order to obtain 0.70 mole of CH_4 at equilibrium?
(d) When the reaction is begun with 1.5 mole CH_4 in a 1.00-L flask, how much H_2 must be removed in order to leave 1.0 mole of H_2 at equilibrium?
(e) Calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ for the reaction at 25 °C.
(f) How would the extent of the reaction be affected by:
  1) an increase in temperature?
  2) a decrease in volume?
  3) the addition of C(s)?
(g) Calculate $\Delta H°$ for the reaction by using the appropriate bond energies and the fact that

$$C(s) \longrightarrow C(g) \qquad \Delta H° = 720\ \text{kJ/mol}$$

32. An ambitious (and interested) chemistry student decided to investigate the hydrolysis of trimethyltin chloride, $(CH_3)_3SnCl$. He set up four flasks and added to each flask 20.0 g of trimethyltin chloride, 30.0 mL of ether, and 10.0 mL of water. The student shook each flask occasionally and then after one hour separated the water layer from the other layer in the first flask, titrated the water layer with 1.0 M NaOH, and found 70% hydrolysis. After two hours the second flask was treated in the same way and 80% hydrolysis was discovered. After three hours, 85% hydrolysis was found in the third flask. The fourth flask was allowed to sit overnight, and then at the end of 24 hours the water layer was titrated and 85% hydrolysis was found. The student also isolated the tin product which was $(CH_3)_3SnOH$.

(a) Write an equation representing the hydrolysis reaction.
(b) Write an equilibrium expression for the hydrolysis reaction and determine the equilibrium constant (remember that X% hydrolysis means that if you started with one mole of compound Y, X of it has been converted to product; note also that the water must be included in the expression (assume it is soluble in ether for purposes of this calculation).
(c) Determine the free energy change for the reaction.
(d) Use the following bond energies to arrive at an approximate $\Delta H°$ for the reaction: Sn—Cl, 323 kJ/mole; O—H, 459; Sn—O, 356; and Hn—Cl, 428.

33. Which of the following possible gas-phase reactions of methane with CO_2 is thermodynamically more likely to occur at 298 K? At 1000 K?

$$CH_4 + CO_2 \rightleftharpoons 2\ CO + 2\ H2$$

$$CH_4 + CO_2 \rightleftharpoons CH_3CO_2H$$

34. The reaction of methanol with carbon monoxide in the presence of catalysts is an important commercial method of preparing acetic acid.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3CO_2H(g)$$

(a) Calculate $\Delta H°$ for the reaction from (1) bond energies (Appendix 2), (2) the following heats of combustion, and (3) standard enthalpies of formation (Appendix 3), and compare the values.

$CH_3OH(g)$ $\Delta H_c° = -764.0$ kJ/mol
$CO(g)$ $\Delta H_c° = -283.3$ kJ/mol
$CH_3CO_2H(g)$ $\Delta H_c° = -923.8$ kJ/mol

(b) Calculate $\Delta S°$ at 25 °C.
(c) Calculate $\Delta G°$ and K_p at 25 °C.
(d) Because the rate of the reaction is low at 25 °C, the reaction must be done at about 200 °C in the presence of a rhodium catalyst. Assume that $\Delta H°$ and $\Delta S°$ have the same values at 200° as at 25°, and calculate $\Delta G°$ and K_p at 200°.

35. (a) Calculate $\Delta H°$ for the dissociation of HCl(g) into gaseous ions:

$$HCl(g) \rightleftharpoons H^+ (g) + Cl^- (g)$$

(b) Would you expect the entropy change for this reaction to be favorable? Why or why not? Will the reaction occur to an appreciable extent?
(c) In water, HCl is completely dissociated into ions even though the entropy change for this reaction is negative.

$$HCl(g) \rightleftharpoons H^+ (aq) + Cl^- (aq)$$

Explain both the negative entropy change and the extent of this reaction.

36. For the reaction

$$Na(s) + H_2O(l) \rightleftharpoons Na{+}(aq) + OH^-(aq) + H_2$$

calculate the enthalpy change from the following data:

$$\Delta H_f(NaOH(s)) = -426.8 \text{ kJ/mol}$$
$$\Delta H_{soln}(NaOH(s)) = -44.8 \text{ kJ/mol}$$
$$\Delta H_f(H_2O(l)) = -241.8 \text{ kJ/mol}$$

37. Use the following heats and free energies of formation of hydrazine (at 25 °C) to answer the questions below.

$$N_2(g) + 2\,H_2(g) \longrightarrow N_2H_4(g) \qquad \Delta H_f° = 95.4 \text{ kJ/mol}$$
$$\Delta G_f° = 159.4 \text{ kJ/mol}$$
$$N_2(g) + 2\,H_2(g) \longrightarrow N_2H_4(l) \qquad \Delta H_f° = 50.6 \text{ kJ/mol}$$
$$\Delta G_f° = 149.4 \text{ kJ/mol}$$

(a) Calculate the heat and entropy of vaporization of hydrazine at 25 °C.
(b) Why is the formation of liquid hydrazine more favorable than the formation of gaseous hydrazine?
(c) Explain the fact that the formation of hydrazine is endothermic whereas the formation of hydrogen peroxide (H_2O_2) is exothermic.

38. Use the heat of vaporization of hydrazine from Question 37 and data from the appendix to calculate the heat of combustion of liquid hydrazine.

39. The heat of atomization of gaseous hydrazine is 1723.8 kJ/mol.

$$N_2H_4(g) \longrightarrow 2\,N(g) + 4\,H(g)$$

Calculate the N—N bond energy. Compare this bond energy with the N—N bond energy in O_2N—NO_2 (54.4 kJ/mol) and explain the difference.

40. The production of a combustible fuel from the gasification of coal is an old and relatively inefficient process. Current emphasis in coal gasification is on the production of methane gas, in which the last step in the process is

$$3\,H_2(g) + CO(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

(a) Using heats of formation, calculate the standard enthalpy change for the reaction.
(b) Calculate the enthalpy change from bond energies.
(c) Estimate the entropy change for the reaction. How does this agree with a calculated value?
(d) Calculate the standard free energy change for the reaction.
(e) Calculate the equilibrium constant for the reaction.

41. Consider the following gas-phase reaction:

$$N_2(g) + 2\,O_2(g) \rightleftharpoons 2\,NO_2(g)$$

Using the following bond energy data, calculate the standard enthalpy change for this reaction:

$$\text{bond energy } N_2 = 941 \text{ kJ/mol}$$
$$\text{bond energy } O_2 = 494 \text{ kJ/mol}$$
$$N{-}O \text{ bond energy in } NO_2 = 464 \text{ kJ/mol}$$

42. The standard free energies of formation of liquid water and liquid hydrogen peroxide are −237 kJ/mol and −114 kJ/mol, respectively. Calculate the standard free-energy change for the reaction

43. The standard enthalpy of formation for ammonia is −45.6 kJ/mol, and the standard entropy of formation for ammonia is −99.2 J/mol-K. Calculate the equilibrium constant at 25 °C for the reaction

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

44. A chemist is interested in the feasibility of preparing benzene (C_6H_6) directly from acetylene (C_2H_2) according to the following reaction:

$$3\,C_2H_2(g) \longrightarrow C_6H_6(l)$$

A search of the literature turns up the following information:

Upon combustion into $CO_2(g)$ and $H_2O(l)$ at 25 °C, one mole of $C_2H_2(g)$ gives off 1305 kJ and one mole of $C_6H_6(l)$ gives off 3273 kJ.

The absolute entropies at 25 °C for $C_2H_2(g)$ and $C_6H_6(l)$ are 201 J/mol-K and 173 J/mol-K, respectively.
(a) Calculate $\Delta H°$ for the reaction.
(b) Calculate $\Delta S°$ for the reaction.
(c) Calculate $\Delta G°$ for the reaction.
(d) What advice would you give to the chemist about the feasibility of this reaction?

45. Consider the following reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

(a) Use bond energies to calculate $\Delta H°$ for the reaction.
(b) Use absolute entropies to calculate $\Delta S°$ for the reaction.
(c) Calculate $\Delta G°$ and K for the reaction at 298 K.
(d) How would an increase in temperature affect K?
(e) How would an increase in the volume of the container affect the extent of the reaction?

(f) The heat of sublimation of $I_2(s)$ is 63 kJ/mol:

$$I_2(s) \rightleftharpoons I_2(g) \qquad \Delta H^\circ = 63 \text{ kJ/mol}$$

Calculate ΔH° for the following reaction

$$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$$

(g) Calculate ΔG° for the following reaction

$$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$$

46. Consider the following reaction

$$2\,PH_3(g) + 3\,Cl_2(g) \longrightarrow 2\,PCl_3(g) + 6\,HCl(g)$$

(a) Calculate the standard enthalpy change using two methods.
(b) Calculate the standard entropy change.
(c) Explain the sign and relative magnitude of the entropy change.
(d) Calculate the free energy change and the equilibrium constant at 25 °C.
(e) Rationalize the large negative enthalpy change for this reaction.

47. Explain why the heats of formation of most nitrogen compounds are positive, while the heats of formation of most fluorine compounds are negative.

48. Consider the following reaction:

$$CH_4 + 2\,F_2 \longrightarrow CH_2F_2 + 2\,HF$$

(a) Estimate ΔH° for this process.
(b) The actual ΔH° is -915 kJ/mol. Explain the difference between this value and the value for ΔH° determined in part (a).

49. Given the enthalpy changes for the following reactions:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H^\circ = -802 \text{ kJ}$$

$$CH_2CO(g) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(g) \qquad \Delta H^\circ = -981 \text{ kJ}$$

Find ΔH° for the reaction:

$$2\,CH_4(g) + 2\,O_2(g) \longrightarrow CH_2CO(g) + 3\,H_2O(g)$$

50. The equation that relates ΔG° to the equilibrium constant, K, may be used to derive an expression for K in terms of ΔH° and ΔS°:

$$-RT \ln K = \Delta G^\circ$$

Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, the equation may be written

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

or

$$\ln K = -(\Delta H^\circ/RT) + \Delta S^\circ/R$$

Therefore, a plot of ln K as a function of $1/T$ will produce a line with a slope equal to $-(\Delta H^\circ/R)$ and an intercept of $\Delta S^\circ/R$.

(a) Use the following data to determine ΔH° and ΔS° for the reaction.

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

K	T (°C)
29.0	7
9.49	25
3.92	30
1.10	50

(b) How do these values compare with ΔH° and ΔS° determined from standard values?

15

Ion-Combination Reactions

Now that we have analyzed the important characteristics of chemical reactions—their rates and extents—we are ready to take a careful look at four different types of reactions. For each type we will be particularly concerned about the extent of the reaction and will use our knowledge of equilibrium to calculate the amount of product in a given reaction. We will also develop models that allow us to explain the effect of structure (the particular atoms and groups present in a molecule) on the extent of reactions. It is important to know that most of the reactions that we will discuss take place in the solvent water. Because many of these reactions in water involve ions, the rates of the reactions are relatively fast.

There are several ways to categorize chemical reactions. For example, the term double displacement is used for reactions that have the form

$$AB + CD \longrightarrow AD + CB$$

While this is a useful formalism, we prefer to focus on the nature of the chemical process that occurs in a reaction. Consequently, we will use four different categories: ion-combination reactions, proton-transfer reactions, electron-transfer reactions, and electron-sharing reactions.

15.1 TYPES OF REACTIONS

Ion-combination reactions involve the recombination of ions or exchange of ions between ionic compounds. A simple example is the reaction of silver nitrate with sodium chloride,

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

Notice that the silver ions originally in the reactant silver nitrate are combined with the chloride ions in the product, AgCl.

Proton-transfer reactions, also called Brønsted-Lowry acid-base reactions, have a proton donor (an acid) and a proton acceptor (a base) on both sides of the equation. For example, in the reaction of acetic acid with water, the acetic acid donates a proton to water to form the hydronium ion and the acetate ion. On the product side, the hydronium ion can transfer a proton to the acetate ion to reform the reactants,

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Electron-transfer reactions, also called oxidation-reduction reactions, transfer an electron from one species to another. In the reaction of metallic zinc with copper ions, the zinc loses two electrons per atom, which are transferred to the copper ions, thereby neutralizing the positive charge and forming copper atoms. Notice that transfer of electrons can occur between the products to reform the reactants.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Electron-sharing reactions, also called Lewis acid-base reactions, involve the combination of an electron-rich species (the base) with an electron-poor species (the acid) that can share those electrons. One of the simplest examples of this type of reaction is the reaction of a proton (hydrogen ion) with a hydride ion (H^-),

$$H^+ + H^- \longrightarrow H_2$$

15.2 ION-COMBINATION REACTIONS

Perhaps the simplest type of chemical reaction is that which leads to products by recombination of the ions in two compounds. Most commonly, reactions of this type occur in aqueous solution. Recall from our earlier discussion of solutions (Chapter 10) that in aqueous solutions of ionic compounds and other strong electrolytes, the solutes are present in the form of hydrated ions—separated, charged particles that are essentially independent of one another. Thus, an aqueous solution of potassium nitrate, for example, is a solution of potassium ions and nitrate ions, and a solution of sodium chloride contains sodium ions and chloride ions. If these two solutions are mixed together, no reaction occurs, because the mixture is simply a solution of the four ions,

$$K^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq)$$

However, if instead of potassium nitrate we use a solution of silver nitrate (Ag^+, NO_3^-) and mix that solution with a solution of sodium chloride (Na^+, Cl^-), there is an immediate reaction, which results in the formation of a white precipitate of silver chloride. A reaction occurs in this case due to the low solubility of silver chloride in water. Upon mixing of the four ions, the solution becomes instantaneously supersaturated with respect to silver chloride. Silver ions and chloride ions come together to form the crystal lattice of AgCl, which precipitates as a solid until a saturated solution is obtained.

The equation for this reaction may be written in the following form:

$$AgNO_3(aq) + NaCl(aq) \rightleftharpoons AgCl(s) + NaNO_3(aq)$$

While this "molecular" equation is acceptable, it does have certain shortcomings. It does not indicate clearly the nature of the reaction; namely, that it is simply the combination of ions to form an insoluble substance. Furthermore, the equation implies that sodium nitrate has been formed as a product, when in fact the solution at the completion of the reaction merely contains sodium ions and nitrate ions in exactly the same form in which they were present at the start of the reaction. Only after sufficient water has been removed by evaporation would the compound sodium nitrate be obtained.

It is somewhat clearer, therefore, to describe the reaction by means of an **ionic equation**, which shows the nature of dissolved strong electrolytes more correctly:

$$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

Since all of the reactions dealt with in this chapter take place in aqueous solution, we can simplify the equation somewhat. Henceforth, the symbol (*aq*) will be assumed, and we will not continue to write it. We will also adopt the convention of underlining a formula to indicate a precipitate. Our ionic equation then becomes

$$Ag^+ + NO_3^- + Na^+ + Cl^- \rightleftharpoons \underline{AgCl} + Na^+ + NO_3^-$$

It is clear from this ionic equation that neither Na^+ nor NO_3^- has actually taken part in the reaction. The reaction would have been the same if any other soluble chloride salt (KCl, $CaCl_2$, and so on) or any other soluble silver salt had been used. Thus we can refine

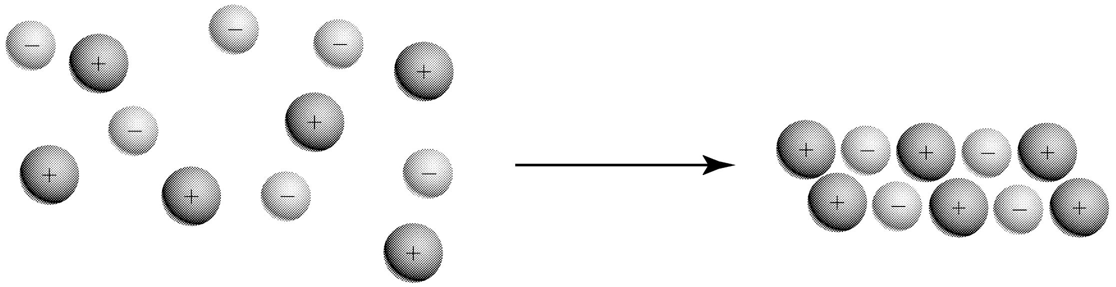


Figure 15.1 Net ionic precipitation of AgCl.

the ionic equation further by eliminating the nonparticipating ions; that is, by simply removing those substances that appear in the same form on both sides of the equation. The result is called the **net ionic equation**:

$$Ag^{+} + Cl^{-} \rightleftharpoons \underline{AgCl}$$

This equation tells us that silver ion (whatever its source) and chloride ion (whatever its source) combine to form a precipitate of silver chloride (see Figure 15.1).

Problem 15.1

Write the ionic and net ionic equations for the following "molecular" equation.

$$BaCl_2 + K_2CrO_4 \rightleftharpoons \underline{BaCrO_4} + 2\,KCl$$

Solution:

Ionic: $Ba^{2+} + 2\,Cl^{-} + 2K^{+} + CrO_4^{2-} \rightleftharpoons \underline{BaCrO_4} + 2\,K^{+} + 2\,Cl^{-}$

Net Ionic: $Ba^{2+} + CrO_4^{2-} \rightleftharpoons \underline{BaCrO_4}$

Problem 15.2

Write the ionic and net ionic equations for the following "molecular" equation.

$$MgSO_4 + 2\,NaOH \rightleftharpoons \underline{Mg(OH)_2} + Na_2SO_4$$

Solution:

Ionic: $Mg^{2+} + SO_4^{2-} + 2\,Na^{+} + 2\,OH^{-} \rightleftharpoons \underline{Mg(OH)_2} + 2\,Na^{+} + SO_4^{2-}$

Net Ionic: $Mg^{2+} + 2\,OH^{-} \rightleftharpoons \underline{Mg(OH)_2}$

15.3 THE DRIVING FORCE OF ION-COMBINATION REACTIONS

The examples of ion-combination reactions just given are reactions that take place because of the formation of a product that is only slightly soluble. The "driving force" of these reactions is the removal of ions from solution by formation of a precipitate. Not all ion-combination reactions result in precipitation, however.

In general, ion-combination reactions occur whenever a product is formed by the removal of one or more of the ions from solution. Removal, as used here, includes not only physical removal, as in precipitate formation, but any "tying up" of ions by combination with other ions or molecules. The "driving force" may be formation of a precipitate, a highly volatile insoluble substance (a gas at normal conditions), a weak electrolyte, or a complex ion.

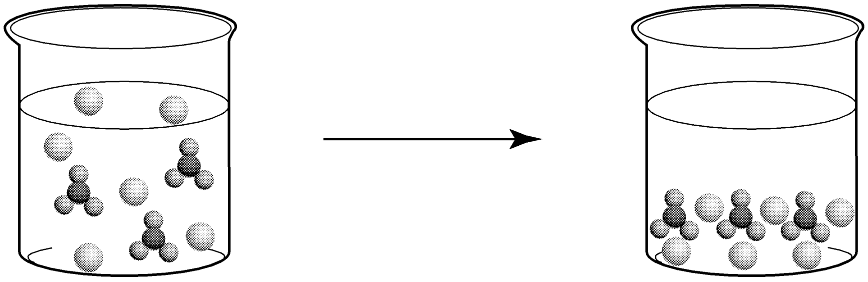
Precipitate Formation

Several examples of ion-combination reactions in which the driving force is the formation of a precipitate were given above. When the ions of a compound are mixed together in aqueous solution in such concentration that the solubility of that compound is exceeded, the compound precipitates and the solution is saturated with respect to that compound. The term "insoluble" is often used to describe the precipitate. In actual fact, however, the precipitate is not truly insoluble; it is simply a substance with low solubility. The solution above the precipitate does contain some ions of the compound, and these are in equilibrium with the precipitate: the lower the solubility of the precipitate, the greater the extent of the reaction. Precipitation reactions will be discussed in greater detail in later sections of this chapter.

Visualization 15.1

Make a sketch showing the driving force for the formation of insoluble silver carbonate. Ignore the water that surrounds the ions.

Solution:



Volatile Substance Formation

If a solution containing carbonate ion—for example, an aqueous solution of sodium carbonate—is mixed with a solution of a strong acid (such as hydrochloric acid), an effervescence is observed due to the escape of a gas, carbon dioxide. The driving force for the reaction is the formation and escape of the gas. The equations for the reaction may be written as follows:

Molecular: $Na_2CO_3 + 2\,HCl \rightleftharpoons 2\,NaCl + H_2O + CO_2(g)$

Ionic: $2\,Na^+ + CO_3^{2-} + 2\,H^+ + 2\,Cl^- \rightleftharpoons 2\,Na^+ + 2\,Cl^- + H_2O + CO_2(g)$

Net Ionic: $CO_3^{2-} + 2\,H^+ \rightleftharpoons H_2O + CO_2(g)$

(Note that we will use the abbreviated H^+ to signify the hydronium ion, H_3O^+, throughout this chapter.) This reaction occurs by a combination of ions that form the weak electrolyte carbonic acid (H_2CO_3), which then decomposes into water and CO_2, the corresponding acid anhydride,

$$CO_3^{2-} + 2\,H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2(g)$$

Sulfites and sulfides also react with acids to liberate the gases sulfur dioxide and hydrogen sulfide, respectively:

$$SO_3^{2-} + 2\,H^+ \rightleftharpoons H_2SO_3 \longrightarrow H_2O + SO_2(g)$$
$$S^{2-} + 2\,H^+ \rightleftharpoons H_2S(g)$$

In all these examples, the gases formed are weak electrolytes, and therefore the reactions would occur even if the products were not gases. Thus, for example, in the reaction of the sulfide ion with the hydronium ion, the formation of the weak electrolyte, H_2S, constitutes a removal of ions from solution, and even if H_2S were not a gas, the reaction would still take place. Because H_2S is an insoluble gas and escapes from the solution, equilibrium cannot be established and the *extent* of the reaction is increased (see Figure 15.2).

Volatile products from ion-combination reactions are not limited to weak electrolytes. For example, hydrogen chloride can be prepared by reaction of sodium chloride with concentrated sulfuric acid. Heating the reaction mixture causes HCl to be removed as a gas. This process is successful only because HCl is more volatile than H_2SO_4:

$$NaCl + H_2SO_4 \xrightarrow{\text{heat}} NaHSO_4 + HCl$$

$$Cl^- + H^+ \xrightarrow{\text{heat}} HCl(g)$$

Similarly, HNO_3 can be prepared from $NaNO_3$ and H_2SO_4, because HNO_3 is more volatile than H_2SO_4.

Weak Electrolyte Formation

Reactions that lead to the formation of a precipitate or a volatile product are usually visible reactions; we know that a reaction has occurred because we see the precipitate or the escaping gas. Not all ion-combination reactions are heterogeneous, however. Some yield products that remain in solution. Although these reactions are not “visible,” they are indicated by changes in such measurements as temperature, conductivity, or absorption spectrum. Reactions in which ions combine to form soluble, nonvolatile weak electrolytes are examples of such homogeneous reactions. The driving force is simply the “tying up” of ions through formation of undissociated molecules.

As an illustration, suppose we mix a solution of mercury(II) nitrate with a solution of sodium chloride. Both these compounds are strong electrolytes, and therefore we are really mixing together the four ions Hg^{2+}, NO_3^-, Na^+, and Cl^-. Now recall from our general rules of electrolyte strength (Chapter10) that mercury(II) chloride is a weak electrolyte; that is, a solution of $HgCl_2$ contains relatively few Hg^{2+} and Cl^- ions and a relatively large amount of $HgCl_2$ molecules. (An equilibrium exists, of course, between the ions and the molecules.) Therefore, when the two solutions are mixed, Hg^{2+} and Cl^-

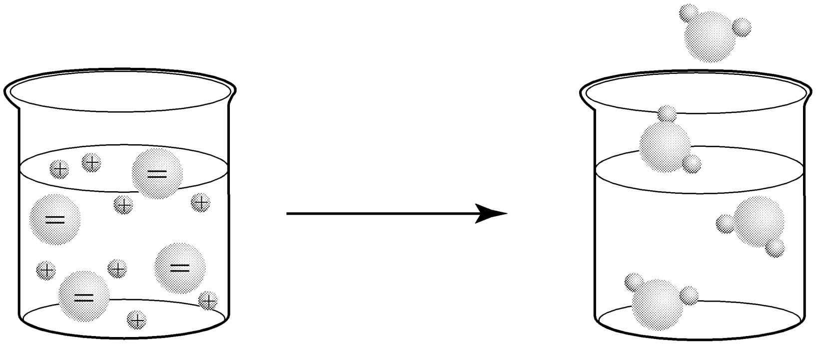


Figure 15.2 Formation of the weak electrolyte and gas, H_2S.

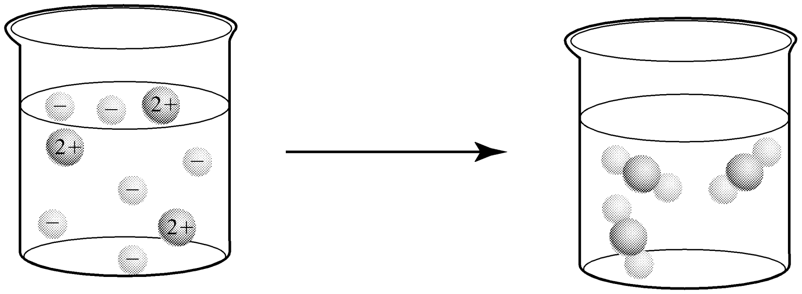


Figure 15.3 Formation of the soluble, weak electrolyte $HgCl_2$.

combine to form molecules of $HgCl_2$, which means that a reaction occurs for which the net ionic equation is

$$Hg^{2+} + 2\,Cl^- \rightleftharpoons HgCl_2$$

The product, $HgCl_2$, is too soluble to precipitate, and it is not a gas, so there is no visible evidence of reaction. Yet a reaction has occurred, for ions have combined to form a new substance that was not present in either of the reactant solutions (Figure 15.3 depicts the Hg^{2+} ions in dark grey and chloride ions in light grey; notice that the $HgCl_2$ molecules are linear).

One of the most common ion-combination reactions leading to weak electrolyte formation is aqueous acid-base neutralization. When an acid solution, such as HCl, is mixed with a solution of a base, such as NaOH, the driving force of the reaction is the combination of hydronium ions with hydroxide ions to form molecules of water.

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

$$H^+ + Cl^- + Na^+ + OH^- \rightleftharpoons Na^+ + Cl^- + H_2O$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

As another example of weak electrolyte formation, consider what happens when a strong acid is mixed with the salt of a weak acid: for example, HCl mixed with sodium acetate ($NaC_2H_3O_2$). Both reactants are strong electrolytes, but hydronium ions and acetate ions can combine to form acetic acid, which is a weak electrolyte, and this is the driving force of the reaction:

$$HCl + NaC_2H_3O_2 \rightleftharpoons HC_2H_3O_2 + NaCl$$

$$H^+ + Cl^- + Na^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2 + Na^+ + Cl^-$$

$$H^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2$$

Acetic acid, a weak electrolyte, appears in the equation as a molecule, like $HgCl_2$ and H_2O in the preceding examples.

In order to be able to predict when ion-combination reactions of this kind will occur and what the products will be, one must have some knowledge of which electrolytes are strong and which are weak. Review of the general rules of electrolyte strength in Section 10.7 is recommended at this point.

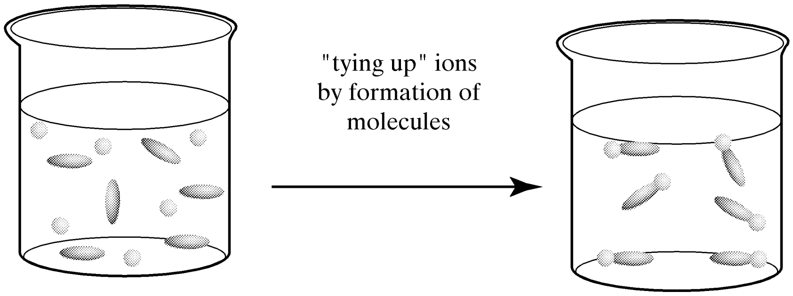
15.4 PRECIPITATION REACTIONS

The remainder of the present chapter will deal only with those ion-combination reactions that lead to formation of a precipitate.

Visualization 15.2

Make a sketch showing the driving force for the formation of acetic acid from protons and acetate ions. Use a gray circle for hydrogen ions and an ellipse for acetate ions. Ignore the water that surrounds the ions.

Solution:



General Solubility Rules

In order to be able to predict whether mixing certain ions together in aqueous solution will result in a precipitation reaction, it is necessary to have some knowledge of the solubilities of those ionic compounds that might result from the mixture. For example, suppose we are asked, "What reaction, if any, will occur upon mixing a solution of $Pb(NO_3)_2$ with a solution of KCl?" To answer this question we need to know what insoluble compound(s), if any, can be formed by combinations of any of the four ions in the mixture. More specifically, we need to know whether KNO_3 or $PbCl_2$, or both, are insoluble. If we are given the knowledge that KNO_3 is soluble but $PbCl_2$ is "insoluble," we can predict that the ionic equation for the reaction that takes place is

$$Pb^{2+} + 2\,Cl^- \rightleftharpoons \underline{PbCl_2}$$

The solubilities of the more common ionic compounds have been determined, and are recorded in the chemical literature. It is convenient, however, to have some qualitative knowledge about the solubilities of various common compounds in order to make predictions without having to consult tables of solubilities. Table 15.1 provides some useful qualitative rules about the solubilities of some common ionic compounds in water. It should be noted that the rules are general, and that there are some exceptions. Furthermore, the term "insoluble" should be understood to mean "slightly soluble." As a rough

TABLE 15.1 General Rules of Solubility in Water

1. All nitrates, chlorates, and acetates are *soluble* except the acetates of Ag and Hg(I), which are moderately soluble.
2. Practically all sodium, potassium, and ammonium salts are *soluble*.
3. All chlorides, bromides, and iodides are *soluble* except those of Ag, Hg(I), and Pb(II).
4. All fluorides are *soluble* except those of Mg, Ca, Sr, Ba, and Pb(II).
5. All sulfates are *soluble* except those of Sr, Ba, and Pb(II), which are insoluble, and those of Ca and Ag, which are moderately soluble.
6. All carbonates, sulfites, phosphates, oxalates, and chromates are *insoluble* except those of Na, K, and NH_4^+.
7. All sulfides are *insoluble* except those of the alkali and alkaline earth metals and NH_4^+.
8. All hydroxides are *insoluble* except those of the alkali metals. The hydroxides of Ca, Sr, and Ba are moderately soluble.

approximation, the term "insoluble," as used in this table, applies to compounds whose solubilities are less than 0.010 mol/L at 25 °C; "soluble" substances are those with solubilities greater than 0.10 mol/L at 25 °C; and a substance with a solubility between 0.01 *M* and 0.10 *M* is referred to as "moderately soluble."

Solubility Product

When a precipitate is formed by the combination of ions in solution, an equilibrium is established between the precipitated compound and the dissolved ions of that compound. Thus, when silver chloride is precipitated by a reaction of silver ions and chloride ions, the crystals of AgCl are in equilibrium with Ag^+ and Cl^- in solution, as represented by the equation

$$Ag^+ + Cl^- \rightleftharpoons \underline{AgCl}$$

As long as the conditions are not changed, AgCl will continue to crystallize from solution (the process to the right) and to dissolve (the process to the left); and these two processes will occur at the same rate, so that there is no net change in the amount of solid or dissolved ions. That is, the solution resulting from the reaction is saturated with silver chloride.

Recall from our discussion of the solution process (Chapter 10) that if an ionic solid, such as AgCl, is stirred with water, it will *dissolve* (ions will leave the surface of the crystal), and eventually a saturated solution will be obtained. This saturated solution is a system in equilibrium represented by the equation

$$\underline{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

In short, the same equilibrium is established in the precipitation of a solid from its ions as in the dissolution of the solid in water; it is merely being reached from different starting points. Hence, the relationship between the extent of a precipitation reaction and the solubility of the precipitate formed is clear: *the less soluble the precipitate, the greater the extent of the reaction.*

As we have seen in Chapter 13, the equilibrium constant of a reaction is a measure of the extent of that reaction. In order to make quantitative predictions about precipitation reactions, it is necessary for us to apply the concept of the equilibrium constant to the equilibrium of saturated solutions. As an example, let us return to our saturated solution of silver chloride, for which the equilibrium is represented as

$$\underline{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

Now, according to the convention for writing equilibrium constants, we may write

$$\frac{[Ag^+][Cl^-]}{[AgCl]} = K$$

But this is a heterogeneous equilibrium; the AgCl is not dissolved in the solution and its molar concentration is constant. Thus, for convenience we may simply incorporate the value of [AgCl] into the equilibrium constant, which allows us to write

$$[Ag^+][Cl^-] = K[AgCl] = \text{constant}$$

This new constant, which is simply a modified equilibrium constant for a particular kind of equilibrium, is called the **solubility product constant** and is usually symbolized as K_{sp}. Thus, we have

$$K_{sp} = [Ag^+][Cl^-]$$

This equation indicates that in any **saturated** aqueous solution of silver chloride—one in which solid AgCl is in equilibrium with its ions—the product of the molar concentration of silver ion and the molar concentration of chloride ion must be constant. If in some way $[Ag^+]$ is reduced, $[Cl^-]$ must increase proportionately, and vice versa. The actual value of the constant varies with temperature, just as the values of all equilibrium constants do.

As further illustrations, let us consider the equilibria involved and the solubility product expressions for some other "insoluble" salts: Ag_2CrO_4, CaF_2, and $Ca_3(PO_4)_2$.

$$\underline{Ag_2CrO_4} \rightleftharpoons 2\,Ag^+ + CrO_4{}^{2-} \qquad K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$$

$$\underline{CaF_2} \rightleftharpoons Ca^{2+} + 2F^- \qquad K_{sp} = [Ca^{2+}][F^-]^2$$

$$\underline{Ca_3(PO_4)_2} \rightleftharpoons 3\,Ca^{2+} + 2\,PO_4{}^{3-} \qquad K_{sp} = [Ca^{2+}]^3[PO_4{}^{3-}]^2$$

These illustrations show that for an ionic compound with the general formula A_nB_m, we may write

$$\underline{A_nB_m} \rightleftharpoons n\,A^{m+} + m\,B^{n-}$$

and

$$K_{sp} = [A^{m+}]^n[B^{n-}]^m$$

Problem 15.3

Write the solubility product expressions for Ag_2CO_3 and $Al(OH)_3$.

Solution:

$$Ag_2CO_3\ K_{sp} = [Ag^+]^2[CO_3{}^{2-}]$$

$$Al(OH)_3\ K_{sp} = [Al^{3+}][OH^-]^3$$

The actual values of solubility product constants cannot be assigned on the basis of theoretical considerations, but must be determined experimentally. A number of different methods have been used, but one of the simplest, which is applicable to many salts, involves calculation of the constant from the carefully measured solubility of the compound. In order to illustrate these calculations, let us determine the K_{sp} for BaF_2 from its solubility of 1.326 g/L at 25 °C.

First, we determine the solubility of BaF_2 in moles per liter:

$$\frac{1.326\ g/L}{175.3\ g/mol} = 7.564 \times 10^{-3}\ mol/L$$

We can now calculate the concentration of each product in a saturated solution. The equation for the equilibrium is written as

$$\underline{BaF_2} \rightleftharpoons Ba^{2+} + 2\,F^-$$

As the equation indicates, for each mole of BaF_2 dissolved, the solution contains 1 mol of Ba^{2+} and 2 mol of F^-. Therefore, in the saturated solution of BaF_2,

$$[Ba^{2+}] = 7.564 \times 10^{-3}\ mol/L$$

and

$$[F^-] = 2(7.564 \times 10^{-3}) = 1.512 \times 10^{-2}\ mol/L$$

The equilibrium table for this problem is set up in terms of the number of moles of BaF_2 (m) per liter of solution.

	$BaF_2 \rightleftharpoons$	Ba^{2+}	$+ 2\,F^-$
Start	solid	0	0
Change	$-m$	$+m$	$+2m$
Equil	solid	m	$2m$

$$m = 7.564 \times 10^{-3}$$

When we substitute the concentrations into the solubility product expression and solve for K_{sp}, we get the following:

$$\begin{aligned} K_{sp} &= [Ba^{2+}][F^-]^2 \\ &= (7.564 \times 10^{-3})(1.512 \times 10^{-2})^2 \\ &= 1.73 \times 10^{-3} \text{ or, to one significant figure,} \\ K_{sp} &= 2 \times 10^{-6} \end{aligned}$$

Methodology 15.1

The solubility of $CaSO_4$ at 10 °C is found to be 1.06 g/L of solution. What is the value of K_{sp} for $CaSO_4$ at 10 °C?

Begin by writing the equation for the dissolution of $CaSO_4$.

$$\underline{CaSO_4} \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

Since equilibrium constants are based on concentrations in terms of molarity, we must first express the solubility as moles per liter. Calculate the solubility of $CaSO_4$ in moles per liter.

This can be done by dividing the solubility in grams per liter by the molar mass of $CaSO_4$.

$$\frac{1.06\ \text{g/L}}{136.1\ \text{g/mol}} = 7.79 \times 10^{-3}\ \text{mol/L}$$

What are the concentrations of Ca^{2+} and SO_4^{2-} in solution?

The equation shows that for each mole of $CaSO_4$ dissolved, there is 1 mol of Ca^{2+} and 1 mol of SO_4^{2-} in solution. Therefore, if 7.79×10^{-3} mol/L of $CaSO_4$ has dissolved, the concentrations of ions must be

$$[Ca^{2+}] = 7.79 \times 10^{-3}\ \text{mol/L}$$
$$[SO_4^{2-}] = 7.79 \times 10^{-3}\ \text{mol/L}$$

Prepare an equilibrium table as discussed in Chapter 14.

	$\underline{CaSO_4}$ $\rightleftharpoons$	Ca^{2+} +	SO_4^{2-}
Start	solid	0	0
Change	solid	$+7.79 \times 10^{-3}$ mol/L	$+7.79 \times 10^{-3}$ mol/L
Equil	solid	7.79×10^{-3} mol/L	7.79×10^{-3} mol/L

Notice that the table emphasizes the fact that before we add solid $CaSO_4$ to water, there are no calcium or sulfate ions in the water. After the solid has been carefully mixed with the water, 7.79×10^{-3} mol/L of the solid dissolves. At equilibrium, there are 7.79×10^{-3} mol/L of calcium ions and 7.79×10^{-3} mol/L of sulfate ions in equilibrium with solid calcium sulfate.

Write the expression for the solubility product constant.

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

Finally, calculate K_{sp}

$$K_{sp} = (7.79 \times 10^{-3})(7.79 \times 10^{-3})$$
$$K_{sp} = 6.07 \times 10^{-5}$$

Although we could legitimately express the K_{sp} to three significant figures, we will use only one significant figure for the numerical value of K_{sp}. This convention is a result of the relative uncertainty in the experimental values of K_{sp} for most compounds and other factors (for example, competing equilibria), which should keep us alert to the relative precision of these values. Thus,

$$K_{sp} = 6 \times 10^{-5}$$

Problem 15.4

The following is an example of a simple way to experimentally determine the K_{sp}.

A 10.00-g sample of LiF is weighed and mixed thoroughly with 1.00 L of distilled water for an hour. During this time we hope that equilibrium will be established and, although we can not really see it happening, we assume that some LiF has gone into solution. So, after an hour of stirring, we carefully filter the mixture and collect the solid LiF in a previously weighed filter crucible. After drying the LiF in an oven for several hours, we weigh the crucible containing the LiF. The weight of the crucible containing the LiF is 31.63 g. The weight of the empty crucible was 23.45 g.

(a) How much LiF has dissolved in the 1 L of water?
(b) What is the molar solubility of LiF?
(c) Calculate the K_{sp} for LiF.
(d) If 1.00 mol of Li^+ were added to 1.00 mol of F^- in 1.0 L of solution, what is the extent of the reaction

$$Li^+ + F^- \rightleftharpoons \underline{LiF}$$

(e) What is the equilibrium constant for the reaction

$$Li^+ + F^- \rightleftharpoons \underline{LiF}$$

Solution:

The weight of the LiF in the crucible is 31.63 − 23.45 = 8.18 g. Thus, 10.00 − 8.18 = 1.82 g of LiF dissolved.

$$(1.82\text{ g/L})/(25.94\text{ g/mol}) = 0.0702\text{ mol per liter}$$

$$K_{sp} = [Li^+][F^-] = (0.0702)(0.0702) = 4.93 \times 10^{-3} = 5 \times 10^{-3}$$

The molar solubility of LiF is 0.070 mol/L, which means that any time you add more than 0.07 mol of LiF to 1.0 L of solution, only 0.070 mol/L of LiF will dissolve. So, in this reaction all but 0.070 mol of LiF will precipitate. In other words, 1.00 − 0.070 = 0.93 mol of solid LiF will form. If the reaction had gone 100% to completion, 1.00 mol of solid LiF would have formed. Therefore the extent of the reaction is 93% [(0.93/1.00) × 100].

Because this reaction is the reverse of the reaction used to calculate the K_{sp}, its equilibrium constant is the reciprocal of the K_{sp}: $K = \frac{1}{K_{sp}}$. Thus, $K = 200$.

✓ Check Point 15.1

Calculate the K_{sp} for $Al(OH)_3$ from the fact that 0.70 mg of $Al(OH)_3$ dissolves in 1.0 L of water.

Solution:

2×10^{-19}

◇ ◇ ◇ ◇ ◇

The solubility product constants for most of the common "insoluble" ionic compounds have been evaluated and are given in Appendix 4. The availability of K_{sp} values makes possible several kinds of calculations pertaining to solubility and precipitation phenomena. One of the obvious applications of the solubility product constant is illustrated by the calculation of the solubility of Ag_2CrO_4 at 25 °C.

As always, we first write the expression for the equilibrium process:

$$Ag_2CrO_{4(s)} \rightleftharpoons 2\,Ag^+ + CrO_4^{2-}$$

followed by the equilibrium expression:

$$[Ag^+]^2[CrO_4^{2-}] = K_{sp} = 2 \times 10^{-12}$$

For each mole of Ag_2CrO_4 dissolved, the solution contains 1 mol of CrO_4^{2-} and 2 mol of Ag^+. Therefore, letting s equal the solubility, we have

$$s = [CrO_4^{2-}] = \frac{1}{2}[Ag^+]$$

and

$$[Ag^+] = 2[CrO_4^{2-}] = 2s$$

[In this case we will not set up an equilibrium table; the solutions to many "K_{sp}-type" problems are straightforward and the table is not necessary.]

Substitution of the appropriate values into the solubility product expression and solving for s gives

$$(2s)^2(s) = K_{sp} = 2 \times 10^{-12}$$
$$4s^3 = 2 \times 10^{-12}$$
$$s = \sqrt[3]{5 \times 10^{-13}}$$
$$s = 8 \times 10^{-5}\ \text{mol/L}$$

Therefore, a saturated solution of Ag_2CrO_4 at 25 °C contains 8×10^{-5} mol of Ag_2CrO_4 per liter of solution. The concentration of chromate ion in that solution is also 8×10^{-5} mol/L, but the concentration of silver ion is $2(8 \times 10^{-5}) = 1.6 \times 10^{-4}\ M$.

Methodology 15.2

Calculate the solubility of silver chloride at 25 °C.

First write the equation for the dissolution of AgCl,

$$\underline{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

Write the K_{sp} equilibrium expression and look up the value of K_{sp} for AgCl in Appendix 4.

$$[Ag^+][Cl^-] = K_{sp} = 2 \times 10^{-10}$$

If we let s equal the solubility of AgCl at 25 °C in moles per liter, then, since for each mole of AgCl that dissolves, one mole of silver ions and one mole of chloride ions appear in solution, the concentration of these ions are also given by s. Set up the equilibrium table.

$$s = [Ag^+] = [Cl^-],$$

and

	$AgCl \rightleftharpoons$	Ag^+	$+ Cl^-$
Start	solid	0	0
Change	solid	$+s$	$+s$
Equil	solid	s	s

Insert s into the expression for K_{sp} and solve for it.

$$s^2 = [Ag^+][Cl^-] = 2 \times 10^{-10}$$
$$s = \sqrt{2 \times 10^{-10}} = 1 \times 10^{-5}\ \text{mol/L}$$

Thus, a saturated solution of AgCl at 25 °C contains 1×10^{-5} mol of AgCl per L of solution.

Express the solubility in grams per liter.

If we wish to express this solubility in terms of grams per liter, we simply multiply this answer by the weight of 1 mole.

$$1 \times 10^{-5}\ \text{mol/L} \times 143\ \text{g/mol} = 1 \times 10^{-3}\ \text{g/L}$$

One may be tempted to assume that the smaller the value of K_{sp}, the less soluble the compound. Comparison of the solubilities of AgCl and Ag_2CrO_4 in the preceding example and Methodology 15.2 reveals the fallacy of this assumption. Silver chromate has a smaller K_{sp} (2×10^{-12}) than silver chloride (2×10^{-10}); yet the molar solubility of Ag_2CrO_4 is more than five times that of AgCl. The direct comparison of relative solubilities with K_{sp} values is valid only for compounds with the same ion ratio (the ratio of the number of cations to the number of anions or vice versa). Thus, referring to Appendix 4, we may correctly predict that $BaCO_3$ is more soluble than $BaCrO_4$, which in turn is more soluble than AgBr, for these are all compounds with an ion ratio of 1:1.

Precipitation

Precipitation reactions have several practical uses in chemistry. They are employed in industrial preparations of ionic compounds such as Li_2CO_3. They have played an important role in the development of analytical chemistry, especially in gravimetric analyses and the identification of cations and anions by chemical methods. Although many of these classical analytical procedures have been supplanted by spectroscopic techniques, they are still used in many quality control procedures because of their reliability and low cost.

In developing procedures designed to precipitate a compound, it is useful to be able to calculate what concentration of reagents are necessary for precipitation to occur. For example, suppose that 10 mL of a 0.0001 *M* solution of $AgNO_3$ is added to 10 mL of a 0.0001 *M* solution of Na_2CrO_4. The precipitation reaction desired involves the formation of Ag_2CrO_4,

$$2\,Ag^+ + CrO_4^{2-} \rightleftharpoons \underline{Ag_2CrO_4}$$

The expression for the K_{sp} for Ag_2CrO_4 is

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 2 \times 10^{-12}$$

which indicates that in a saturated solution of silver chromate the product

$$[Ag^+]^2[CrO_4^{2-}]$$

will have the value of 2×10^{-12}. If, in a particular solution, the concentrations of the $[Ag^+]^2[CrO_4^{2-}]$ ions are such that their product, the reaction quotient Q,

$$Q = [Ag^+]^2[CrO_4^{2-}]$$

has a value less than the K_{sp}, the solution cannot be saturated and therefore a precipitate will not form.

In the problem at hand, the value of Q after the solutions are mixed is (note that the mixing of the solution causes the initial concentrations to change)

$$(5 \times 10^{-5})^2(5 \times 10^{-5}) = 1 \times 10^{-13}$$

Thus, Q is lower than the K_{sp} (2×10^{-12}) and Ag_2CrO_4 will not precipitate.

If the concentrations had been 0.001 *M* for both ions, the value of Q would have been $(0.001)^2(0.001) = 1 \times 10^{-9}$, which is greater than the value of K_{sp} and therefore silver chromate would have precipitated. In fact, the silver chromate would have continued to precipitate until the value of Q reached its equilibrium value of 2×10^{-12}.

Problem 15.5

Determine whether Ag_2SO_4 will precipitate when 1 mL of 0.2 *M* $AgNO_3$ is added to 4 mL of 0.1 *M* Na_2SO_4.

Solution:

The net ionic reaction is

$$2Ag + SO_4^{2-} \rightleftharpoons Ag_2SO_4$$

The concentrations of the ions immediately after the solutions are mixed are

$$[Ag^+] = 0.2/5 = 0.04\ M$$

$$[SO_4^{2-}] = 0.1 \times 4/5 = 0.08\ M$$

Notice that in calculating the concentrations of the ions, we have assumed that the volume of the two solutions are additive, an assumption that is generally true for dilute solutions. The concentrations could also have been calculated by determining the number of moles of ion and then dividing by the total volume. For Ag^+ there are

$$0.001\ L \times 0.2\ mol/L = 2 \times 10^{-4}\ mol\ Ag^+ \text{ in a total of } 5\ mL$$

The concentration of Ag^+ is therefore $\dfrac{2 \times 10^{-4}\ mol}{0.005\ L} = 4 \times 10^{-2}\ M$

The expression for K_{sp} is $[Ag^+]^2[SO_4^{2-}] = 6 \times 10^{-5}$ and we must now proceed to calculate the value of Q immediately after mixing the solutions.

$$Q = [Ag^+]^2[SO_4^{2-}] = (0.04)^2(0.08) = 1 \times 10^{-4}$$

The value of Q immediately after mixing therefore exceeds the K_{sp}, and silver sulfate will precipitate until the value of Q reaches the value of the K_{sp} (6×10^{-5}).

Problem 15.6

What concentration of Na_2CO_3 is required to precipitate $CuCO_3$ from a solution of 0.001 *M* $CuSO_4$?

Solution:

The precipitation reaction is

$$Cu^{2+} + CO_3^{2-} \rightleftharpoons CuCO_3$$

The expression for the K_{sp} of $CuCO_3$ is

$$[Cu^{2+}][CO_3^{2-}] = 1 \times 10^{-10}$$

Thus, if the concentration of Cu^{2+} is 0.001, the value of the product

$[Cu^{2+}][CO_3^{2-}]$ will equal the K_{sp} when

$$[CO_3^{2-}] = \frac{1 \times 10^{-10}}{0.001} = 1 \times 10^{-7}\ M$$

15.5 THE EFFECT OF ELECTROLYTES ON SOLUBILITY

Thus far, our discussion of solubility and its relationship to solubility product has dealt only with solubilities of ionic compounds in pure water. Let us now examine the effects on solubility of the presence of other electrolytes in the solution.

The Common Ion Effect

Imagine the following experiment: To one liter of water we add some solid $BaSO_4$ and, with stirring, we allow sufficient time for equilibrium to be established (that is, for the solution to become saturated). Then, by some convenient method, we determine how much of the $BaSO_4$ has dissolved. In other words, we measure the solubility of $BaSO_4$ in water. Suppose we then repeat the procedure, except that instead of using water we use an aqueous solution containing sulfate ion, such as a 0.01 *M* solution of Na_2SO_4. We will find that more $BaSO_4$ dissolved in pure water than in the 0.01 *M* Na_2SO_4 solution. Similarly, if we determine the solubility of $BaSO_4$ in an aqueous solution of some soluble barium salt (for example, 0.01 *M* $BaCl_2$), we will discover that $BaSO_4$ is less soluble in that solution than it is in pure water. In short, the solubility of $BaSO_4$ is decreased by the presence of either Ba^{2+} or SO_4^{2-}. This phenomenon, which is referred to as the **common ion effect**, may be generalized as follows: The solubility of an ionic compound is decreased by the presence in the solution of an ion in common with the compound.

This effect is predictable from Le Châtelier's Principle. The equilibrium in a saturated solution of $BaSO_4$ is expressed by

$$\underline{BaSO_4} \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

In pure water the concentrations of Ba^{2+} and of SO_4^{2-} must be equal. But if additional sulfate ion is present, then that constitutes an increase in the SO_4^{2-} concentration (a stress on the system), which will favor the process to the left, using up Ba^{2+} and producing more solid $BaSO_4$. Thus, less $BaSO_4$ is dissolved because of the presence of the extra sulfate ion. The same conclusion is reached by considering the effect of additional barium ions.

If we apply the concept of the solubility product, we reach the same qualitative conclusion. According to the expression

$$[Ba^{2+}][SO_4^{2-}] = K_{sp}$$

$[Ba^{2+}]$ times $[SO_4^{2-}]$ must remain constant. Therefore, an increase in $[SO_4^{2-}]$ must mean a decrease in $[Ba^{2+}]$, and vice versa. Furthermore, the solubility product constant enables us to calculate the degree to which the solubility is lowered by a given concentration of common ion.

As an example, let us calculate the solubility (in moles per liter) of $BaSO_4$ in (a) water, (b) 0.01 *M* K_2SO_4 solution, and (c) 0.02 *M* $Ba(NO_3)_2$ solution (K_{sp} for $BaSO_4 = 1.0 \times 10^{-10}$). In water, the concentrations of barium ion and sulfate ion are the same; that is,

$$[Ba^{2+}] = [SO_4^{2-}] = s.$$

Therefore:

$$\begin{aligned} [Ba^{2+}][SO_4^{2-}] &= 1 \times 10^{-10} \\ s^2 &= 1 \times 10^{-10} \\ s &= 1 \times 10^{-5}\ \text{mol/L} \end{aligned}$$

When we dissolve $BaSO_4$ in the 0.01 *M* K_2SO_4 solution, we must consider the fact that the SO_4^{2-} in the solution came from two sources: some was present in the K_2SO_4 solution, and some entered the solution as the $BaSO_4$ was dissolved. For each mole of Ba^{2+} present in this solution, one mole of $BaSO_4$ must have dissolved. Therefore:

$$s = [Ba^{2+}]$$

Thus:

$$[SO_4^{2-}] = 0.01 + s$$

	$\underline{BaSO_4} \rightleftharpoons$	Ba^{2+} +	SO_4^{2+}
Start	solid	0	0.01
Change	$-s$	$+s$	$+s$
Equil	solid	s	$0.01 + s$

Substitution of these values in the solubility product expression gives us

$$[Ba^{2+}][SO_4^{2-}] = 1 \times 10^{-10}$$
$$s(0.01 + s) = 1 \times 10^{-10}$$

This is a quadratic equation, which can be solved by application of the quadratic formula. However, the calculation can be simplified considerably, without introducing any error, by making an approximation. The value of s is quite small compared with 0.01. Even when the solvent is pure water, s has a value of only 0.00001, and it will be even smaller in this case because of the common ion effect. Hence, within the number of significant figures we have to work with, $0.01 + s$ is equal to 0.01. That is

$$[SO_4^{2-}] = 0.01 + s = 0.01$$

With this approximation, the quadratic equation is avoided, and the solution becomes much simpler:

$$s(0.01) = 1 \times 10^{-10}$$
$$s = 1 \times 10^{-8}\ \text{mol/L}$$

We can determine the solubility of $BaSO_4$ in $Ba(NO_3)_2$ solution by following the same line of reasoning and making the same approximation. Thus, we have

$$s = [SO_4^{2-}]$$
$$[Ba^{2+}] = 0.02 + s = 0.02$$

	$\underline{BaSO_4} \rightleftharpoons$	Ba^{2+} +	SO_4^{2-}
Start	solid	0.02	0
Change	$-s$	$+s$	$+s$
Equil	solid	$0.02 + s$	s

$$[Ba^{2+}][SO_4^{2-}] = 1 \times 10^{-10}$$
$$s(0.02) = 1 \times 10^{-10}$$
$$s = 5 \times 10^{-9}\ \text{mol/L}$$

Methodology 15.3

Calculate the solubility of $Mg(OH)_2$ in $1M$ Mg^{2+} solution.

What is the first thing you should do?

Write the equation for the dissolution of magnesium hydroxide and the K_{sp} expression.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2\,OH^-$$
$$[Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$$

Is the following table correct?

	$Mg(OH)_2 \rightleftharpoons$	Mg^{2+} +	$2\,OH^-$
Start	0	1	0
Change	$-x$	$1 + x$	x
Equil	satd	1	x

No. If you define x as the solubility of $Mg(OH)_2$ in moles per liter, then the concentration of OH^- must be $2x$; that is, every time one mole of $Mg(OH)_2$ dissolves, two moles of OH^- are formed.

Continued on the next page

Methodology 15.3 Continued

You could also decide to define x as the concentration of OH^-, but in this case $[Mg^{2+}] = x/2$ and the solubility of $Mg(OH)_2$ would be $x/2$.

Calculate the solubility of magnesium hydroxide.

$$[Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$$
$$(1)(2x)^2 = 1.8 \times 10^{-11}$$
$$4x^2 = 1.8 \times 10^{-11}$$
$$x = 2 \times 10^{-6}\,M$$

✓ Check Point 15.2

Calculate the solubility of $Mg(OH)_2$ in $1M$ OH^- solution.

Solution:

$2 \times 10^{-11}\,M$

◇ ◇ ◇ ◇ ◇

The Effect of Acids

The effect of acids on the solubility of ionic compounds depends on the particular composition of the compound—more specifically, on the nature of the anion. Suppose we compare the solubility of AgCl in water with its solubility in a dilute acid solution, such as 0.01 M HNO_3. (The acid chosen must be one that does not have an ion in common with the solute and that will not react with it. Thus, in this case we could not use HCl as our acid, nor HBr or HI, since Br^- and I^- will react with Ag^+.) Although the solubility will be found to be slightly higher in the acid solution than in water (this is known as the **salt effect**), there is no effect on the solubility that is specifically due to the electrolyte being an acid. The same is true for a number of other slightly soluble salts, including, for example, AgBr, PbI_2, and $BaSO_4$.

On the other hand, if we compare the solubility in water with the solubility in acid solution of any one of a large number of other ionic compounds (CaF_2, ZnS, BaC_2O_4, $Mg(OH)_2$, $CaCO_3$, to name just a few), we will find that the solubility in acid solution is considerably greater than in pure water.

What is the difference between these two categories of salts that accounts for the difference in the effect of acids on their solubilities? All the compounds of the second group—those that show a marked increase in solubility in the presence of an acid—contain anions that are the anions of weak acids (slightly dissociated electrolytes). Hydronium ions combine with these anions and "tie them up" in molecules, thereby upsetting the equilibrium between undissolved and dissolved solute.

As a specific example, consider the solubility of calcium fluoride. Let us suppose we have prepared a saturated solution of CaF_2 in water. The equilibrium in that solution is

$$\underline{CaF_2} \rightleftharpoons Ca^{2+} + 2\,F^-$$

Now, suppose we add some acid (HCl or HNO_3) to the solution. Because HF is a weak electrolyte, hydronium ions from the acid we have added will combine with fluoride ions from the solution to form molecules of HF, and another equilibrium will be set up in the mixture, namely

$$H^+ + F^- \rightleftharpoons HF$$

The more acid we add, the greater the concentration of H^+, and the more HF will be formed and F^- will be removed from solution. Removal of F^- upsets the heterogeneous equilibrium between CaF_2 and its dissolved ions, causing the process to the right to be favored. In other words, more CaF_2 must dissolve in order to reestablish equilibrium conditions, and the solubility of CaF_2 has been increased. The total effect of the acid in dissolving the CaF_2 can be represented as a single equation that is the sum of the two equilibria involved:

$$\begin{aligned} CaF_2 &\rightleftharpoons Ca^{2+} + 2\,F^- \\ 2\,H^+ + 2\,F^- &\rightleftharpoons 2\,HF \\ \underline{CaF_2} + 2\,H^+ &\rightleftharpoons Ca^{2+} + 2\,HF \end{aligned}$$

The solubilties of all salts containing anions of weak acids are increased by the presence of acid. These salts include carbonates, fluorides, oxalates, sulfides, sulfites, nitrites, phosphates, and so forth. The solubilities of hydroxides are also increased by the presence of acids, for their anions (OH^-) combine with hydronium ions to form water molecules (as depicted in Figure 15.4):

$$\begin{aligned} \underline{Mg(OH)_2} &\rightleftharpoons Mg^{2+} + 2\,OH^- \\ 2\,H^+ + 2\,OH^- &\rightleftharpoons 2\,H_2O \\ \hline Mg(OH)_2 + 2\,H^+ &\rightleftharpoons Mg^{2+} + 2\,H_2O \end{aligned}$$

It is now clear why the members of our first group of salts—the chlorides, bromides, and iodides—do not show increased solubility in the presence of acids. These contain anions of strong acids (HCl, HBr, HI, and H_2SO_4). The extent of the reaction of hydronium ions with them to form molecules is very low, and the equilibrium is not affected. In general, the solubilities of salts containing anions of strong acids are not altered appreciably by the presence of acids.

The extent to which acid increases the solubility of an ionic compound depends both on the solubility product of the compound and on the relative strength of the weak acid formed. The smaller the solubility product, the less the dissolving effect of a given concentration of acid. Thus, for example, it is possible to separate a mixture of ZnS and CuS by using the proper concentration of hydrochloric acid. The ZnS ($K_{sp} = 10^{-23}$) will dissolve, leaving behind the CuS ($K_{sp} = 10^{-45}$). The calculations involved in such a separation will be discussed in the next chapter.

The Complex Ion Effect

Our discussion of the common ion effect established the principle that the solubility of an ionic compound is decreased by the presence of an electrolyte having an ion in common with the compound. One might infer from this statement and from the illustrative calculations presented that the greater the concentration of the common ion, the lower the solubility. This is not always the case, however, for some slightly soluble salts react with an excess of their own anions to form complex ions (the nature of which will be discussed in Chapter 17), resulting in an increase in solubility.

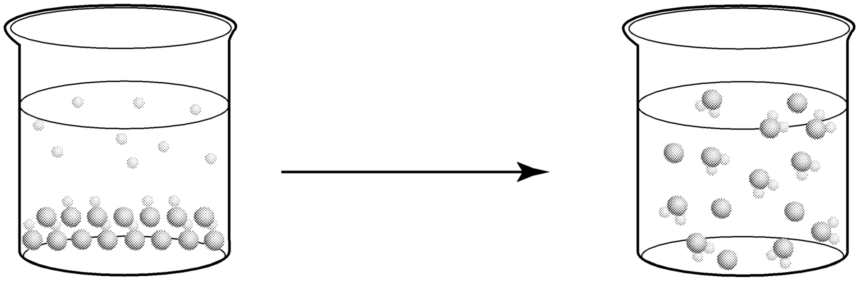


Figure 15.4 Dissolution of a hydroxide by combination of the hydroxide anion with H^+ to form the weak electrolyte water.

A striking example of this **complex ion effect** is provided by lead iodide. If a solution containing iodide ions is added slowly to a solution of lead (II) ions, a yellow precipitate of lead iodide (PbI_2) is formed. As addition of the I^- is continued, the amount of precipitate increases, but only up to a point. Addition of I^- beyond that point results in a gradual dissolving of the precipitate, and if the addition is carried far enough, the entire precipitate will redissolve. The equation for the precipitation is

$$Pb^{2+} + 2\,I^- \rightleftharpoons \underline{PbI_2}$$

The reaction responsible for the redissolving is the formation of the complex ion PbI_4^{2-}:

$$\underline{PbI_2} + 2\,I^- \rightleftharpoons PbI_4^{2-}$$

CHAPTER SUMMARY

In continuing our study of the reactions of matter we find it convenient to categorize chemical reactions into four different types—ion-combination, proton transfer, electron-sharing, and electron-transfer—with a chapter devoted to each type. In this chapter we have dealt with **ion-combination reactions**, with major emphasis on those that yield a precipitate. You should be able to write net ionic equations for these reactions.

The factors that govern the precipitation of an ionic compound in a chemical reaction are the same factors that govern the solubility of that compound in water. Therefore, you must thoroughly understand the phenomena involved in a saturated solution of an ionic solid. You may find it helpful to review Chapter 10 at this point. You should also memorize the general solubility rules in Table 15.1, and learn to use these rules to predict what reaction, if any, will occur upon mixing solutions of various ionic compounds.

The **solubility product constant** (K_{sp}) enables us to treat solubility phenomena quantitatively. This constant is simply the equilibrium constant for the equilibrium that exists in a saturated solution of an ionic compound. All the rules and conventions concerning equilibrium constants that were presented in Chapter 13 are applicable to K_{sp}. You should develop the ability to use this equilibrium constant to solve a variety of problems, including the following:

1. Given the solubility of an ionic compound in water, calculate the value of K_{sp} for that compound.
2. Calculate the solubility of an ionic compound in water.
3. Calculate the concentration of each ion in a saturated solution of an ionic compound.
4. Given K_{sp} for an ionic compound, calculate the solubility of that compound in a solution containing a known concentration of a common ion.
5. Carry out the calculations necessary to predict whether a precipitate will form when two solutions of given concentrations are mixed.
6. Calculate the concentration of an ion necessary to cause precipitation from a solution of given concentration of another ion.

The solubility of an ionic compound is influenced by several factors: the common ion effect, the salt effect, the acid effect, and the complex ion effect. You should thoroughly understand each of these effects and be able to explain how they influence solubility. In connection with the acid effect, you will find it helpful to review the section on electrolytes in Chapter 10.

TERMS

Some new terms introduced in this chapter are as follows:

Net ionic equation An equation that describes a reaction in which ions take part. Only the substances that actually react and the substances that are produced appear in this equation.

Solubility product constant, K_{sp} The equilibrium constant for the equilibrium that exists in a saturated solution of an ionic compound in water. In a saturated solution of the hypothetical compound A_nB_m, the equilibrium that exists is represented by the equation

$$A_nB_m \rightleftharpoons nA^{m+} + mB^{n-}$$

and the solubility product constant is

$$K_{sp} = [A^{m+}]n[B^{n-}]^m$$

Common ion effect The decrease in solubility of an ionic compound due to the presence in the solution of an ion that is in common with the compound.

Salt effect The increase in solubility of an ionic compound due to the presence in the solution of ions that are not in common with the compound.

Acid effect The increase in solubilities of ionic compounds containing anions of weak acids due to the presence of acids in the solution.

Complex ion effect The increase in solubility of some ionic compounds due to an excess of the anion of the particular compound, which results from the formation of complex ions.

PROBLEMS

1. Provide the net ionic equation for the reaction:

$$NaOH(aq) + MgSO_4(aq) \longrightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$$

2. Aqueous solutions of the following pairs of compounds are mixed together. For each pair, write the net ionic equation for the reaction (if any) that occurs.
(a) $NaClO + HNO_3$ (b) $KF + Pb(NO_3)_2$
(c) $KF + NaOH$ (d) $Pb(NO_3)_2 + (NH_4)_2C_2O_4$
(e) $NiSO_4 + K_2S$

3. For each of the following aqueous reactions give the products and estimate the extent of the reaction.
(a) $K_2CO_3 + Pb(NO_3)_2 \rightarrow$ (b) $Mg(OH)_2 + HCl \rightarrow$
(c) $BaS + HCl \rightarrow$ (d) $BaSO_4 + Ag_2S \rightarrow$

4. Indicate for each reaction whether $K > 1$ or $K < 1$.
(a) $Na_2SO_4 + BaCl_2 \rightarrow 2\ NaCl + BaSO_4$
(b) $FeS + 2\ KCl \rightarrow FeCl_2 + K_2S$
(c) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ H_2O$
(d) $BaCO_3 + 2\ HCl \rightarrow BaCl_2 + H_2CO_3$

5. Which of the following compounds are insoluble in water?
(a) $AgNO_3$ (b) $AlPO_4$ (c) $PbCO_3$
(d) $NaOH$ (e) $Fe(OH)_3$ (f) $NiSO_3$
(g) $NH_4C_2H_3O_2$ (h) $CuSO_4$ (i) AgI
(j) $BaSO_4$ (k) $CoCl_2$ (l) $Mn(NO_3)_2$

6. Which of the following salts would precipitate if they were formed by a reaction of appropriate compounds in aqueous solution?

KNO_3, $PbCl_2$, LiOH, $BaSO_4$, $CaCl_2$, $Cu(OH)_2$

7. When magnesium chloride is mixed with sodium phosphate, magnesium phosphate precipitates. What volume of 0.20 *M* sodium phosphate is required to react with 50 mL of 0.20 *M* magnesium chloride?

8. How much precipitate is formed when 50.0 mL of 0.50 *M* $SbCl_3$ and 40.0 mL of 0.50 *M* Na_2S are combined?

9. Give the K_{sp} expressions for the following compounds:

AgCl Ag_2CO_3 $Al(OH)_3$

10. A saturated solution of LiF contains 1.8 g of the salt per liter of solution. Determine the K_{sp} for LiF.

11. The solubility of $Cu(IO_3)_2$ in water at 25 °C is 1.35 g/L of solution. Calculate K_{sp} for the compound at 25 °C.

12. The solubility of MgC_2O_4 at 18 °C is found to be 1.04 g/L. Calculate the solubility product constant for MgC_2O_4 at 18 °C.

13. If the solubility of PbF_2 is 0.4655 g/L at 9 °C, what is the value of K_{sp} for PbF_2 at that temperature?

14. The solubility of $Pb_3(PO_4)_2$ at 25 °C is 1.29×10^{-7} mol/L. Calculate K_{sp} at 25 °C.

15. Calculate the K_{sp} for $Ca_3(PO_4)_2$ from the fact that in a saturated solution the calcium ion concentration is 1.2×10^{-5} *M*.

16. What is the molar concentration of silver ion (i.e., $[Ag^+]$) in a saturated silver sulfate solution?

17. Calculate the molar solubility of $PbCl_2$.

18. Calculate the solubility in moles per liter of each of the following compounds at 25 °C: AgBr, $Mg(OH)_2$, ZnS, and Li_2CO_3 ($K_{sp} = 2 \times 10^{-3}$).

19. The solubility product constant for $Mg_3(PO_4)_2$ has a value of 4×10^{-13} at 25 °C. What is the molar concentration of magnesium ion and of phosphate ion in a saturated solution of $Mg_3(PO_4)_2$ at 25 °C?

20. The solubility product constant for $MgNH_4PO_4$ is 3×10^{-13}. Calculate the solubility (in grams per liter) of this salt.

21. Which contains the greater weight of iron: one liter of saturated $Fe(OH)_2$ solution or one liter of saturated FeS solution?

22. Which is more soluble in water at 25 °C, aluminum hydroxide or manganese hydroxide?

23. Calculate the number of liters of water needed to dissolve one mole of mercury(II) sulfide.

24. Calculate the molar solubility of $BaCrO_4$ in each of the following:
(a) pure water
(b) 0.050 M $BaCl_2$ solution
(c) 0.050 M K_2CrO_4 solution

25. Calculate the molar solubility of $Mg(OH)_2$ in each of the following:
(a) pure water
(b) 0.020 M $Mg(NO_3)_2$ solution
(c) 0.020 M KOH solution

26. The K_{sp} of $Fe(OH)_3$ is 6×10^{-38}.
(a) Calculate the molar solubility of $Fe(OH)_3$ in pure water.
(b Calculate the solubility of $Fe(OH)_3$ in 1 M NaOH solution.

27. (a) What is the molar concentration of silver ion in a saturated silver phosphate (Ag_3PO_4) solution?
(b) Is silver phosphate more soluble or less soluble in 0.05 M Na_3PO_4 solution than in water? Explain this effect.
(c) Is silver phosphate more soluble or less soluble in 3 M HNO_3 solution than in water? Explain this effect.

28. Which is more soluble—AgCl or Ag_2S? $K_{sp}(Ag_2S) = 1 \times 10^{-50}$

29. Do the following reactions have a high or low extent of reaction?

$$\underline{CoS} + CuCl_2 \rightleftharpoons \underline{CuS} + CoCl_2$$

30. Determine if a precipitate is formed when 1 L of a 2×10^{-5} M solution of NaCl is mixed with 1 L of a 2×10^{-6} M solution of $AgNO_3$.
(a) Which of the following best represents the reaction that could take place when these solutions are mixed?
1. $Na^+ + NO_3^- \rightleftharpoons NaNO_3$
2. $NaCl + AgNO_3 \rightleftharpoons AgCl + NaNO_3$
3. $Ag^+ + Cl^- \rightleftharpoons \underline{AgCl}$
(b) What determines whether solid AgCl will be formed?
1. How insoluble AgCl is?
2. The temperature?
3. The solubility product expression and the K_{sp}?
(c) Is the solubility product exceeded by the ion concentrations in this solution?

31. Will a precipitate form in a solution 2×10^{-4} M in Mg^{2+} and 1×10^{-3} M in OH^-?
(a) Is the following the correct net ionic equation of the processes that occur in solution?

$$Mg^{2+} + OH^- \rightleftharpoons \underline{Mg(OH)_2}$$

(b) Which of the following is correct for the K_{sp} expression in this case?
1. $(2 \times 10^{-4})(2 \times 10^{-3})^2$
2. $(2 \times 10^{-4})(1 \times 10^{-3})^2$
3. $(2 \times 10^{-4})(1 \times 10^{-3})$
(c) Will $Mg(OH)_2$ precipitate?

32. Assume that 1.0×10^{-3} mol of K_2SO_4 is added to 1 L of a saturated solution of $PbSO_4$. Calculate the molar concentration of lead ion in the solution before and after the addition of the K_2SO_4.

33. If 0.100 g of NaF is added to 100 mL of a saturated solution of CaF_2, what is the final concentration of Ca^{2+} in the solution?

34. Calculate the K_{sp} for $Ca_3(PO_4)_2$ from the fact that the calcium ion concentration is 1×10^{-5} mol/L in a saturated solution. How many grams of Na_3PO_4 must be added to 1 L of a 1 M Ca^{2+} solution in order to begin to precipitate $Ca_3(PO_4)_2$?

35. Will a precipitate form when 1.0 mL of 0.010 M $AgNO_3$ is added to 15 mL of 0.010 M Na_2SO_4?

36. What is the maximum concentration of sulfide ion that can be present in a 0.0050 M solution of $Mn(NO_3)_2$ without a precipitate of MnS being formed?

37. Solid $BaSO_4$ is added to 250 mL of 0.025 M K_2SO_4 and the mixture is stirred until equilibrium is established. What weight of $BaSO_4$ dissolved?

38. A small amount of solid silver chloride is thoroughly stirred with a 0.10 M solution of sodium iodide. After some time it can be seen that the white precipitate of silver chloride is being replaced by a yellow precipitate. Explain.

39. Is silver chromate (Ag_2CrO_4) more soluble in a solution that is 0.10 M in silver ion or in a solution that is 0.10 M in chromate ion?

40. Bromide ion is determined gravimetrically by addition of excess $AgNO_3$ to precipitate AgBr. After addition of the $AgNO_3$ is complete, the solution above the precipitate has a volume of 450 mL and is 5.0×10^{-3} M in Ag^+. What weight of Br^- remains unprecipitated?

41. A solution of dilute hydrochloric acid is slowly added to a 0.10 M solution of lead nitrate until no further precipitation is observed. The precipitate is filtered off, and when dilute sulfuric acid is added to the filtrate, a white precipitate forms. Explain, and write appropriate equations.

42. Will a precipitate form when 1.0 L of a 2.0×10^{-5} M solution of NaCl is mixed with 1.0 L of a 2.0×10^{-6} M solution of $AgNO_3$?

43. Will a precipitate form in a solution 2×10^{-4} M in Mg^{2+} and 1×10^{-3} M in OH^-?

44. If hydroxide ion is added to a 0.01 M solution of Mg^{2+}, what concentration of OH^- will be necessary to first precipitate $Mg(OH)_2$?

45. What is the minimum concentration of SO_4^{2-} necessary to cause precipitation of the metal sulfate from each of the following solutions?
(a) 1.0×10^{-3} M $Ba(NO_3)_2$
(b) 1.0×10^{-3} M $Ca(NO_3)_2$
(c) 1.0×10^{-3} M $Pb(NO_3)_2$

46. If equal volumes of the two solutions in each of the following pairs are mixed together, indicate whether or not a precipitate will be formed.

(a) 1.0×10^{-3} M $MgCl_2$ and 1.0×10^{-3} M Na_2CO_3
(b) 1.0×10^{-3} M $CaCl_2$ and 1.0×10^{-4} M NaF
(c) 1.0×10^{-5} M $Pb(NO_3)_2$ and 1.0×10^{-5} M Na_2S
(d) 1.0×10^{-2} M $Ni(NO_3)_2$ and 1.0×10^{-5} M Na_2S

47. In each of the following cases show whether a precipitate will form under the given conditions.
(a) 1 ml of 0.1 M $AgNO_3$ is added to 1 liter of 0.01 M Na_2SO_4.
(b) 1 g $Pb(NO_3)_2$ is put into 100 ml of 0.01 M HCl.
(c) 1 ml of 1 M NaOH is added to 1 L of 10^{-4} M $Mg(NO_3)_2$.
(d) 1 ml of 1 M NH_3 is added to 1 L of 10^{-4} M $Mg(NO_3)_2$.
(e) 1 ml of 0.1 M $Sr(NO_3)_2$ is added to 1 L of 0.01 M HF.
(f) 1 ml of 0.01 M $Ba(NO_3)_2$ is added to 1 L of 0.1 M $Na_2C_2O_4$.
(g) 1 mg of $CaCl_2$ and 1 mg $Na_2C_2O_4$ are put in a liter of water.

48. If chloride ion is added to a 0.10 M solution of $Pb(NO_3)_2$ at 100 °C, what is the maximum concentration of Cl^- that could be present without precipitation of $PbCl_2$? If the solution is also 0.10 M in $AgNO_3$ and $Hg_2(NO_3)_2$, how much Ag^+ and Hg_2^{2+} will remain in solution when this Cl^- concentration is reached? (At 100 °C, K_{sp} for $PbCl_2$ is 6.9×10^{-3}, K_{sp} for AgCl is 5×10^{-8}, and K_{sp} for Hg_2Cl_2 is 1×10^{-14}.)

49. The solubility product constants for Ag_2CrO_4 and $Ag_2Cr_2O_7$ are 2×10^{-12} and 2×10^{-7}, respectively. What effect will the addition of silver ion have on the chromate-dichromate equilibrium?

$$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

50. An aqueous solution is 0.10 M in both sulfate ion and chromate ion. Powdered lead(II) nitrate is slowly dissolved in the well-stirred solution. (Assume no volume change.)
(a) What is the concentration of Pb^{2+} when $PbSO_4$ first starts to precipitate?
(b) What is the concentration of Pb^{2+} when $PbCrO_4$ first starts to precipitate?
(c) Which compound precipitates first?
(d) When the second anion just starts to precipitate, what is the molar concentration of the anion that precipitates first?

51. Which of the following compounds are more soluble in the presence of acid?
(a) $BaSO_4$ (b) $BaSO_3$ (c) CoS

52. Calculate the solubility of Ag_2SO_4 in g per liter of solution. In which of the following solutions is Ag_2SO_4 more soluble? If it is more soluble write an equation to show why it is more soluble.
(a) HNO_3 (b) NH_3 (c) $AgNO_3$

53. Which of the following compounds will be significantly more soluble in a HNO_3 solution than in pure H_2O?
(a) $AgC_2H_3O_2$ (b) AgBr (c) $Mg(OH)_2$
(d) ZnS (e) PbI_2

54. Silver oxalate ($Ag_2C_2O_4$) has a solubility product constant of 9×10^{-12}. Calculate the following:
(a) The molar solubility of $Ag_2C_2O_4$ in water.

$$Ag_2C_2O_4 \rightleftharpoons 2\,Ag^+ + C_2O_4^{2-}$$

(b) The concentrations of Ag^+ and $C_2O_4^{2-}$ in a saturated solution of $Ag_2C_2O_4$.
(c) The molar solubility of $Ag_2C_2O_4$ in 0.010 M $AgNO_3$ solution.

55. Calculate the solubility of $Ni(OH)_2$ in 1 M Ni^{2+} solution.

56. Calculate the solubility of $Ca_3(PO_4)_2$ in 1 M Ca^{2+} solution.

57. The solubility of AlF_3 in water is 6.7 g per liter of solution at 25 °C.
(a) Calculate the K_{sp} for AlF_3.
(b) Determine the solubility of AlF_3 in 1.0 M $Al(NO_3)_3$ solution.

58. Arrange the following in order of increasing solubility of $CaCO_3$:
(a) pure water (b) 0.02 M $CaCl_2$ solution
(c) 0.03 M Na_2CO_3 solution (d) 0.01 M NaCl solution
(e) 0.01 M HCl solution

59. Arrange the following in order of increasing solubility of PbI_2:
(a) pure water (b) 0.01 M $Pb(NO_3)_2$
(c) 0.01 M NaI (d) 0.01 M HNO_3
(e) 0.10 M $NaNO_3$

60. Predict which of the following compounds will dissolve in dilute HNO_3 but not in H_2O:
(a) $SrCO_3$ (b) $PbBr_2$ (c) MgF_2 (d) MnS
(e) CuI (f) $Fe(OH)_2$ (g) Hg_2Cl_2 (h) FeC_2O_4
(i) $PbCl_2$ (j) $CaCrO_4$

61. Many monuments and statues are made from marble, a thermodynamically stable mineral form of calcium carbonate, $CaCO_3$. Granite is another common stone used for monuments and is composed of quartz (SiO_2) and various nonreactive silicates. Acid rain is observed to severely weather marble, but not granite. Can you explain why?

62. Gravimetric analysis involves the formation of a solid precipitate that can be filtered, dried, and weighed. The weight of the precipitate can provide information on the original analyte concentration. Silver can be analyzed by reaction with chloride ion to form insoluble silver chloride. In an analysis, a 1.239-g sample of powder containing an unknown amount of silver is dissolved in 200.0 mL of water. To this sample, 200.0 mL of 0.08000 M Cl^- is added, precipitating all of the Ag as AgCl. The AgCl is then filtered and washed with 400 mL of water, providing 0.3454 g of AgCl.
(a) Calculate the weight percent of silver in the original sample.
(b) Calculate the relative error in the described gravimetric analysis procedure due to the solubility losses of silver.
(c) After performing the analysis a white-to-purple film is observed on the glassware used for the precipitation reaction. Cleaning with soap and water fails to remove the film, but a solution of dilute ammonia cleans the glassware with little effort. Explain why the ammonia was the more effective cleaning agent in this problem.

63. As an employee for a company that processes silver ore into silver metal to be used in jewelry, you suggest the following procedure for recovering the silver from the ore. The ore sample is crushed, dissolved in strong acid, and treated with a solution of sodium phosphate to isolate the silver as silver phosphate salt. The precipitate is dried and collected for further processing into silver metal. The procedure is tested by obtaining 5.6921 g of ore, dissolving and treating in a total solution volume of 2.5 L. The PO_4^{-3} concentration in this solution is monitored and determined to be 0.12 *M*. The precipitate is filtered and washed with an additional 500.0 mL of water.

(a) How many grams of Ag_3PO_4 would you expect to recover if the ore were originally 21.6% silver by weight?

(b) How many grams of silver would be lost in the isolation process?

(c) How many grams of silver would be lost if the process were scaled up to an industrial level and 5000 kg of ore were processed in the manner described above?

(d) If silver is selling for $5.00 per ounce, how much money would be lost in the treatment of 5000 kg of ore?

(e) You would like to reduce the amount of silver lost. Several modifications of the procedure are proposed. Indicate if each would increase or decrease silver loss and why.

1. Make the treatment solution acidic.
2. Make the wash solution acidic.
3. Add a greater excess of phosphate anion.
4. Reduce the volume of wash solution and precipitation solution.

(f) What other cations may coprecipitate with the silver phosphate, causing a mixture of salts?

64. Elemental lead is known to be hazardous when ingested, especially for infants and young children. Before its hazards became known, lead was also an ingredient in the solder commonly used to plumb homes. Tap water from these systems often has lead concentrations in excess of that considered to be harmful, approximately 20 parts per billion or $\approx 1 \times 10^{-7}\ M\ Pb^{2+}$. Having just purchased an older home that may have lead solder in the plumbing, you contact a local company that has advertised a method to remove lead from home water systems. The salesman arrives at your home and proceeds to describe their system, in which they claim the lead can be removed by precipitation with chloride ions. In order to test the accuracy of their claims, calculate the concentration of lead in the tap water if no excess of chloride ion is present, and calculate the concentration of excess chloride ion that would be necessary to reduce the Pb^{2+} concentration to a level considered to be safe. After doing these calculations, you should politely refuse their offer. Explain why you would not accept the offer.

16

Proton-Transfer Reactions

Of the many types of matter that have engaged chemists over the centuries, surely among the most important are acids, bases, and salts. These substances and the theories concerning their nature have played a vital role not only in the development of chemistry, but also in the history of civilization. Think, for example, of the impact that saltpeter (KNO_3), a constituent of gunpowder, has had on the political histories of various nations; or of the value of carbonates and hydroxides of potassium and sodium in the ceramics, glass and soap industries; or of the need for nitric, acetic, and sulfuric acids as precursors to the products of our vast chemical industry.

Salt as a category of matter probably had its origin in the work of the alchemists on the interrelationships of what they considered to be the four basic elements—fire, water, earth, and air. When certain solids, "earths," were mixed with water, some portion was found to dissolve in the water and was labeled "salt." By the seventeenth century many salts had been discovered and their properties characterized. Moreover, after numerous experiments on the effects of water and that very potent element, fire, on these substances, it was found that some salts could be decomposed into two different substances.

Investigation of the properties of these two new types of matter—acids and bases—led to the conclusion that they were chemical opposites. Acids were known to have a sour taste, to turn some blue plant dyes red, and to dissolve numerous substances; in contrast, bases have a bitter taste, turn some red plant dyes blue, and have a slippery feel. Moreover, the reaction of an acid with a base results in the mutual neutralization of their properties.

The similarity of the chemical and physical effects of all known acids suggested the presence of some common "acidifying principle." Since the chemistry of the latter part of the eighteenth century was dominated by experiments on combustion and Lavoisier's demonstration that oxygen is consumed in this process, it is not surprising that Lavoisier and his followers believed this common acidifying principle to be oxygen. Indeed, Lavoisier derived the name *oxygen* from the Greek word for "acid former." According to this theory, acids are binary compounds, with one of the elements being oxygen and the other being the acid radical. Sulfuric acid, for example, was believed to consist of sulfur (the radical) plus oxygen (the acidifying principle). All of the known acids were classified in this way.

Subsequent investigations on the composition of hydrochloric acid by the English chemist Humphry Davy in the early nineteenth century showed that this acid does not contain oxygen. By 1830, more than ten acids that did not contain oxygen had been discovered and characterized, and it became obvious that the one element all acids had in common was not oxygen, but hydrogen.

By 1850, the accumulated evidence for the ideas of Davy and other investigators was overwhelming, and the "hydrogen theory" was accepted. Attention was then directed to the nature of the hydrogen in acids. Since many compounds contain hydrogen, what makes some of them acids, while others exhibit none of these characteristics? In the late nineteenth century, Svante Arrhenius and Wilhelm Ostwald used Faraday's earlier results on the dissociation of electrolytes (Chapter 10) to show that acids, bases, and salts are

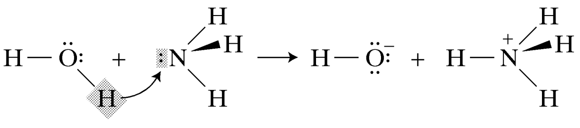


Figure 16.1 The proton transfer from water to ammonia.

electrolytes. They further demonstrated that in water, acids dissociate to form hydrogen ions, while bases produce hydroxide ions. Thus, when gaseous hydrogen chloride dissolves in water, molecules of HCl dissociate into hydrogen ions and chloride ions:

$$\mathrm{HCl} \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{Cl^-}(aq)$$

On the other hand, methane does not dissociate into ions and therefore is not an acid in water. When solid potassium hydroxide dissolves, it enters the solution as potassium ions and hydroxide ions. Since some bases do not contain hydroxide ions, these substances must produce OH^- ions by reaction with the water. For example,

$$\mathrm{NH_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

Moreover, the Arrhenius theory recognized that some acids are strong electrolytes and are therefore extensively dissociated into ions in water, while other acids are weak electrolytes and are therefore only partly dissociated into ions. The same is true for bases.

The Arrhenius concept is limited to the behavior of acids and bases in water. Later chemists proposed other definitions of acids and bases that incorporate many more compounds and reactions within their confines. One of the most useful of these more general definitions is the one advanced almost simultaneously by the Danish chemist J. N. Brønsted and the English chemist T. M. Lowry in 1923. The **Brønsted-Lowry definition** is a logical extension of the Arrhenius concept:

An acid is a substance that can release a proton (hydrogen ion), while a base is a substance that can combine with a proton.

Hence, when gaseous ammonia is dissolved in water, the water (acid) releases a hydrogen ion to the ammonia (base), forming a hydroxide ion and an ammonium ion (Figure 16.1).

$$\mathrm{H_2O} + \mathrm{NH_3} \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{NH_4^+}(aq)$$

The Brønsted-Lowry definition, then, is independent of the solvent. For example, hydrogen sulfide functions as an acid in releasing a proton to ammonia in liquid ammonia:

$$\mathrm{H_2S} + \mathrm{NH_3} \rightleftharpoons \mathrm{HS^-} + \mathrm{NH_4^+}$$

Another very useful definition, which we will explore in greater detail in Chapter 17, was suggested by G.N. Lewis in 1923, but was not widely received until the latter part of the 1930s. The Lewis definition is much more general than either the Arrhenius or Brønsted-Lowry definition. According to Lewis, an acid is a species capable of accepting a pair of electrons, while a base is a species that can provide a pair of electrons. Because the proton can accept a pair of electrons and is therefore a Lewis acid, all Brønsted-Lowry acids are also Lewis acids; the same holds true for bases. In addition to the proton, however, there are vast numbers of ions and molecules that can also function as Lewis acids.

16.1 PROTON-TRANSFER REACTIONS

Since the Brønsted-Lowry definition of acids and bases encompasses the Arrhenius definition but is not restricted to reactions carried out in water, it is generally the more useful concept, and the remainder of this chapter will be devoted to an exposition of its many features. The definition of an acid as a species capable of releasing a proton and a base as a species capable of accepting a proton leads to the conclusion that a Brønsted-Lowry acid-base reaction involves a *transfer* of a proton from the acid to the base. For example, in the reaction of acetic acid with ammonia, a proton is transferred from an acetic acid molecule (acid) to an ammonia molecule (base), resulting in the formation of an acetate ion and an ammonium ion:

$$\mathrm{CH_3CO_2H} + \mathrm{NH_3} \rightleftharpoons \mathrm{CH_3CO_2^-} + \mathrm{NH_4^+}$$

The reverse reaction is also a proton-transfer reaction between the acid NH_4^+ and the base $CH_3CO_2^-$.

The species formed when an acid loses its proton is called its **conjugate base**. For example,

$$\text{Acid} \longrightarrow \text{Base} + H^+$$

$$CH_3CO_2H \longrightarrow CH_3CO_2^- + H^+$$

Similarly, the species that results when a base accepts a proton is called its **conjugate acid**:

$$\text{Base} + H^+ \longrightarrow \text{Acid}$$

$$NH_3 + H^+ \longrightarrow NH_4^+$$

Every proton-transfer reaction is therefore of the type

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Base}_1 + \text{Acid}_2$$

where Acid_1—Base_1 and Acid_2—Base_2 are conjugate acid-base pairs.

Methodology 16.1

Complete the following proton-transfer reaction and identify the conjugate acid-base pairs.

$$HF + OH^- \rightleftharpoons$$

The first step is to identify the reactant acid and base.

> You should recognize HF as a weak electrolyte from Chapter 11 and as an acid from Chapter 6, where you learned that it is named hydrofluoric acid. The base is the hydroxide ion, which has three pairs of nonbonded electrons on the oxygen.

HF has nonbonded electrons on the fluorine, and, moreover, the hydroxide ion also has a hydrogen. So, how do you know that HF will be the proton donor and OH^- will be the proton acceptor?

> In addition to the fact that HF is called hydrofluoric acid, the hydroxide ion has a negative charge, which makes it difficult to remove a positively charged hydrogen ion.

Complete the equation.

$$HF + OH^- \rightleftharpoons F^- + H_2O$$

Identify the conjugate base of HF and the conjugate acid of OH^-.

> The species that is left behind after the HF loses a proton is the conjugate base; this is the fluoride ion, F^-. The species that is formed when OH^- accepts a proton is its conjugate acid; this is water.

Problem 16.1

Complete the following proton-transfer reaction and identify the conjugate acid-base pairs.

$$NO_2^- + H_2O$$

Solution:

The nitrite ion has no hydrogen and can only act as a proton acceptor (a base).

$$NO_2^- + H_2O \rightleftharpoons HONO + OH^-$$

The conjugate base-acid pairs are: NO_2^-/HONO and OH^-/H_2O.

Although by definition an acid must contain hydrogen, not all compounds that contain hydrogen are acids. Whether or not a compound containing hydrogen functions as an

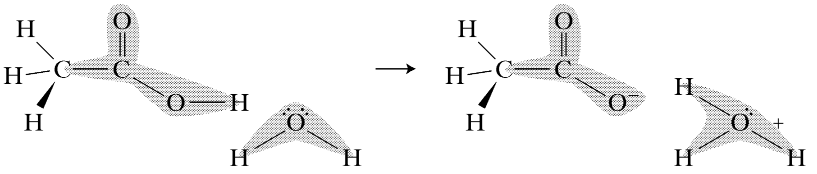
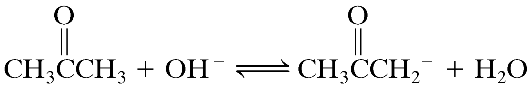


Figure 16.2 Changes in electron density during proton transfer in acetic acid.

acid depends on the strength and polarity of the bond to hydrogen, and on the ability of the base with which it is reacting to accept the proton. Acetic acid, for example, contains a hydrogen atom bonded to the very electronegative oxygen atom. This bond is quite polar (Figure 16.2), and therefore dissociation into $CH_3CO_2^-$ and H^+ is moderately easy. When acetic acid is mixed with water, protons are released to water molecules,

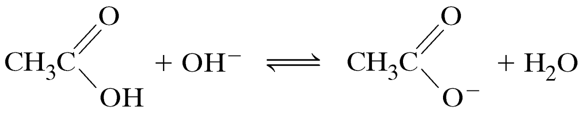
$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$$

Acetone, on the other hand, contains hydrogen atoms bonded to carbon atoms, and because of the small electronegativity difference, these bonds are not very polar. Acetone is therefore a nonelectrolyte and shows no acidic properties in water. However, if acetone is treated with a stronger base than water—for example, hydroxide ion—the attraction of the hydroxide for the proton is sufficiently great to cause the transfer to occur to some extent,

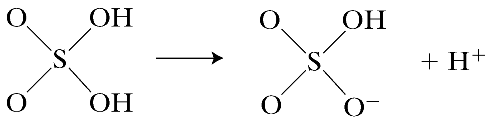


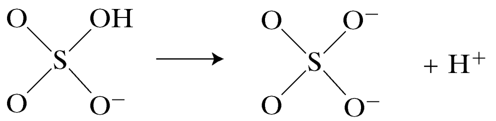
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + OH^- \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}CH_2^- + H_2O$$

The reaction of acetic acid with hydroxide ion also occurs to a greater extent than the reaction with water.



Some acids are able to provide more than one proton. For example, sulfuric acid, $O_2S(OH)_2$, has two very polar O—H bonds.





The same is true for acids such as hydrosulfuric, phosphorus, carbonic, oxalic, and so forth. These acids are referred to as **polyprotic acids**. Acids that can provide only one proton per molecule are called **monoprotic acids**.

The sole criterion for a base is that it be able to accept a proton. Because a proton is extremely small, the attraction between a base and a proton is more than a simple electrostatic attraction; the extreme smallness of the proton distorts the electron density of the base, and a covalent bond is formed. Since the proton has no electrons, the base must supply a *pair* of electrons for this bond. Any species with a nonbonded pair of electrons is therefore a potential base. Tables 16.1 and Table 16.2 list a number of common acids and bases.

Bases that can accept more than one proton also exist: the carbonate ion, the phosphate ion, and the oxalate ion are good examples:

$$C_2O_4^{2-} + H^+ \longrightarrow HC_2O_4^-$$

$$HC_2O_4^- + H^+ \longrightarrow H_2C_2O_4$$

These are **polyprotic bases**, while those that can accept only one proton per molecule or ion are **monoprotic bases**. Moreover, some species, such as H_2O, HS^-, and HCO_3^-, can react as both acids and bases. Hydrogen sulfide ion, for example, has a fairly polar H—S bond, and there are also nonbonded electron pairs on the sulfur. When mixed with a base such as hydroxide ion, hydrogen sulfide ion functions as an acid:

$$HS^- + OH^- \rightleftharpoons S^{2-} + H_2O$$

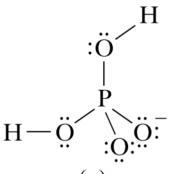
But when mixed with an acid such as hydrochloric acid, it behaves as a base:

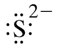
$$HS^- + HCl \rightleftharpoons Cl^- + H_2S$$

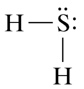
Species that function as both Brønsted-Lowry acids and bases are termed **amphiprotic**.

Visualization 16.1

Categorize each of the following as base, diprotic acid, or amphiprotic:


(a)


(b)


(c)

Solution:

(a) is a diprotic acid because it has two hydrogens attached to oxygens; it is also a base because it contains many lone pairs and one oxygen, the most basic site, has a negative charge; it is also amphiprotic because it can function as either an acid or as a base.
(b) has no hydrogen so it can not be an acid. It is a base.
(c) is a diprotic acid; it has the potential to be a base because of the lone pairs on sulfur. It is, however, a very weak base. It also has the potential to be amphiprotic, but generally does not function as an amphiprotic species in water.

16.2 ACID AND BASE STRENGTHS

The extent to which an acid donates a proton to a given base is a measure of its strength as an acid. Conversely, the extent to which a base accepts a proton from a given acid is a measure of its strength as a base. Because of the convenience of working with water, the fact that it is amphiprotic, and the great abundance of aqueous solutions, acid and base strengths are often measured relative to water.

Suppose, for example, that one mole of each of four acids—acetic, nitrous, chlorous, and hydrochloric—were separately mixed with one liter of water. An analysis of each mixture at equilibrium would show that in the acetic acid solution, only 0.4% of the acetic acid dissociates; that is, only 0.004 mol of hydronium ions and 0.004 mol of acetate ions are present. In the nitrous acid solution, 2% of the nitrous acid molecules dissociate to form 0.02 mol of nitrite ions and 0.02 mol of hydronium ions. In the chlorous acid solution, 10% of the acid dissociates, and in the hydrochloric acid mixture, almost 100% of the molecules are dissociated into hydronium ions and chloride ions. Thus, HCl is far superior to the other three acids in its ability to release a proton. Therefore the proton-releasing abilities, or acid strengths, vary in the order

$$HCl > HClO_2 > HNO_2 > HC_2H_3O_2$$

Data from this type of experiment can also be used to calculate the equilibrium constants for the dissociation of acids (except for very strong or very weak acids):

(1) $$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

TABLE 16.1 Acid Dissociation Constants in Water at 25 °C

$HClO_4$	$>10^{10}$	HNO_2	4.6×10^{-4}
HI	10^{10}	$p\text{-}NO_2C_6H_4CO_2H$	3.9×10^{-4}
HBr	10^9	HF	3.5×10^{-4}
HCl	10^8	$m\text{-}ClC_6H_4CO_2H$	1.5×10^{-4}
H_2SO_4	10^3	H_2Se	2.0×10^{-4}
HNO_3	10^2	$p\text{-}ClC_6H_4CO_2H$	1.0×10^{-4}
$HClO_3$	10	$C_6H_5CO_2H$	6.5×10^{-5}
CF_3CO_2H	6.0×10^{-1}	$p\text{-}CH_3C_6H_4CO_2H$	4.2×10^{-5}
CCl_3CO_2H	2.0×10^{-1}	$p\text{-}CH_3OC_6H_4CO_2H$	3.4×10^{-5}
$CHCl_2CO_2H$	3.3×10^{-2}	CH_3CO_2H	1.8×10^{-5}
$HClO_2$	1.0×10^{-2}	H_2S	1.0×10^{-7}
H_2Te	2.5×10^{-3}	HClO	3.0×10^{-8}
$o\text{-}ClC_6H_4CO_2H$	1.2×10^{-3}		

Because these equilibrium constants refer to reactions of the type given in equation (1), they are particularly useful as measures of relative extents of reaction and therefore relative acid strengths. Table 16.1 lists the constants for a set of selected acids. The strongest acid listed in the table is the one with the highest equilibrium constant—$HClO_4$; the weakest acid listed is the one with the lowest constant—HClO.

The same approach can be used to determine relative base strengths. For example, suppose that one-mole quantities of amide ion, ammonia, and acetate ion are each mixed with one liter of water. When the amount of base that has accepted protons from the water is determined after equilibrium has been established, the following percent conversions are attained:

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^- \qquad 100\% \text{ conversions}$$

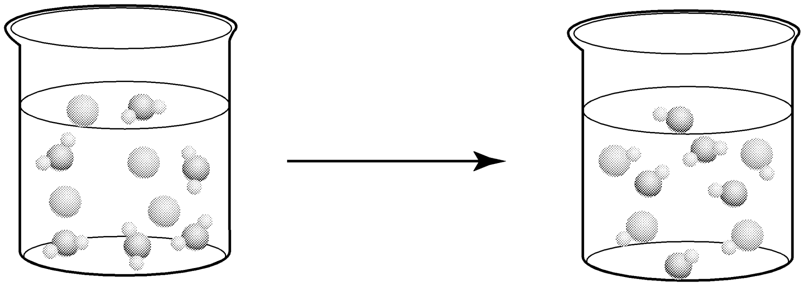
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad 0.4\% \text{ conversion}$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \qquad 2 \times 10^{-3}\ \% \text{ conversion}$$

In other words, in water the amide ion (NH_2^-) is a very strong base, whereas the acetate ion is a rather weak base.

Visualization 16.1

Is the reaction below characteristic of a strong or weak base?



Solution:

Each spherical base reacts with a water molecule to form a hydroxide ion. The reaction can be represented as

$$B + H_2O \rightleftharpoons HB^+ + OH^-$$

or as

$$B^- + H_2O \rightleftharpoons HB + OH^-$$

Because all of the base molecules have reacted, the base is strong.

TABLE 16.2 Equilibrium Constants for Selected Bases in Water at 25 °C

H^-	$>10^{23}$	HS^-	1.0×10^{-7}
NH_2^-	$\sim 10^{21}$	$(C_2H_5)_3P$	5.0×10^{-8}
OH^-	1	H_2NOH	1.1×10^{-8}
$(C_2H_5)_3N$	4.0×10^{-4}	C_5H_5N	1.4×10^{-9}
NH_3	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}
CN^-	2.0×10^{-5}	$C_6H_5NH_2$	3.8×10^{-10}
H_2NNH_2	1.0×10^{-6}	F^-	2.9×10^{-11}

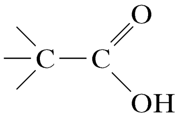
Equilibrium constants for the reaction of selected bases with water are listed in Table 16.2. These reactions are of the following types:

$$\text{(2a)} \qquad B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$\text{(2b)} \qquad B^- + H_2O \rightleftharpoons BH + OH^-$$

Additional equilibrium constants are provided in Appendix 5.

The data in Tables 16.1 and Table 16.2 indicate that acidities and basicities vary widely. Even when the bonds involved in the dissociation of acids are the same, say O—H, the equilibrium constants of species containing this bond vary over many orders of magnitude. For example, perchloric acid (O_3ClOH) is a very strong acid with an equilibrium constant of 10^{10}, while hypochlorous acid (ClOH) is quite weak and has a constant of 10^{-8}. Furthermore, consider two structurally similar acids such as acetic and trifluoroacetic acid, both of which contain the skeleton



The equilibrium constants of these two acids differ by 10^5. Clearly, the composition and structure of acids and bases influence their reactivities markedly. (Figure 16.3 portrays the distribution of the electron density in the two acids.)

Effect of Structure on Acidity

Let us begin our analysis of the effect of structure on acidity (basicity will be considered later) by attempting to determine what factors enhance the ease with which an acid, generalized as HA, dissociates to a proton and its conjugate base A^-:

$$\text{(3)} \qquad HA \rightleftharpoons H^+ + A^-$$

If the dissociation occurs in the gas phase or in a solvent that does not solvate either the acid or its conjugate base, the dissociation can be visualized as occurring in three steps: (a) the dissociation of the bond to the hydrogen atom, (b) the loss of an electron from the hydrogen atom, and (c) the gain of an electron by A.

$$\text{(a)} \qquad HA \rightleftharpoons H + A$$

$$\text{(b)} \qquad H \rightleftharpoons H^+ + e^-$$

$$\text{(c)} \qquad A + e^- \rightleftharpoons A^-$$

Because for the most part we shall be interested only in *relative* acidities, and since step (b) is common to all acid dissociations, only steps (a) and (c) need to be considered. If en-

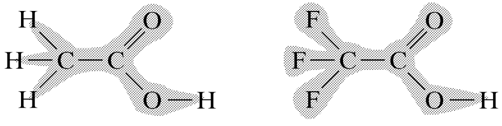


Figure 16.3 A schematic representation of the electron density in acetic and trifluoroacetic acid.

Figure 16.4 The effect of a neighboring atom on the electron density in the O—H bond.

tropy changes are assumed to be similar for a series of acids, the free-energy change and therefore the extent of reaction (3) will depend on the strength of the H—A bond and the electron affinity of A. The greater the H—A bond energy, the greater the energy required for step (a) and the lower the extent of the reaction. But, the greater the electron affinity, the greater the amount of energy given off in step (c) and the greater the extent of reaction. It is the *sum* of the bond energy and electron affinity that determines the relative extent of reaction (3).

When reaction (3) is carried out in a solvent that can interact with the acid or its conjugate base, two other steps must also be considered—solvation of the acid and solvation of its conjugate base. Nevertheless, the relative dissociations of acids in water are usually *controlled* by the bond energy and electron affinity steps. Consequently, relative acidities can be determined with the following two guidelines:

1. The relative acidities of two or more acids that contain the acidic proton bonded to a given atom, say oxygen, are determined by the affinity of that given atom in each acid for an electron. In the two acids shown in Figure 16.4, the Z portion of the acid ZOH appears to be pulling more electron density toward it, presumably giving the oxygen in that molecule the lower electron density.

   For example, the relative acidities of perchloric acid (O_3ClOH) and hypochlorous acid (ClOH) (both of which contain an O—H bond) are determined by the relative affinities of the oxygen of the O_3ClO group and the ClO group for an electron. As we shall see, the oxygen in the O_3ClO group has a greater affinity for an electron, and perchloric acid is therefore the stronger acid. This rule has its basis in the fact that the H—X bond energies of two acids will be similar when X is the same atom. That is, the bond energies are not very dependent upon the remainder of the acid. The relative acidities will then be controlled by the electron affinity of the atom X (which is considerably affected by the remainder of the acid molecule).

   Since the polarity of the H—X bond is determined by the electron affinity of X, the ease with which the H—X bond in a given acid dissociates can also be related to the polarity of that bond. Hence, the O—H bond in perchloric acid is more polar than the O—H bond in hypochlorous acid, and perchloric acid is therefore the stronger acid (see Figure 16.5).
2. The relative acidities of two acids that contain the acidic proton bonded to different atoms are determined by the relative bond energies and electron affinities (and possibly also the relative hydration energies). If the difference in bond energies between the two acids is greater than the difference in electron affinities, the acid with the weaker H—X bond will be the stronger acid, and vice versa. This case can be illustrated by the binary acids of the elements in a given periodic group, for example, Group VI. The H—Te bond for H_2Te is much weaker than the H—S bond in H_2S and thus, in spite of the fact that sulfur is more electronegative and therefore has a greater affinity for an electron, H_2Te is the stronger acid.

Let us now use these guidelines to explain the relative acidities of the species in Table 16.1. One of the more obvious patterns in these data is that for acids of general structure $O_nQ(OH)_m$—for example, O_3ClOH, O_2ClOH, OClOH, and ClOH—an in-

Figure 16.5 The effect of neighboring atoms on the electron density in the O—H bond.

crease in the number of oxygens (n) attached to a given central atom (Q) increases the acidity of the acid. Thus, in the series O_nClOH, the acidities vary in the order

$$O_3ClOH > O_2ClOH > OClOH > ClOH$$

Similarly, nitric acid (O_2NOH) is stronger than nitrous acid (ONOH) and sulfuric acid, $O_2S(OH)_2$, is stronger than sulfurous acid, $OS(OH)_2$. Since all these acids have the same X—H bond, the first rule can be applied. Accordingly, nitric acid is stronger than nitrous acid because the oxygen of the group O_2NO has a greater affinity for an electron than the group ONO. Stated in terms of bond polarity, the O—H bond in O_2NOH is more polar than the O—H bond in ONOH.

This difference in electron affinity (and bond polarity) can be explained as follows. In ONOH, two oxygens are attached to the nitrogen; in O_2NOH the third oxygen removes more electron density from the OH oxygen. This removal of electron density exposes a greater amount of nuclear positive charge at the nitrogen, which in turn attracts electron density from the oxygen of the O—H bond. The oxygen of this bond is therefore more electron-deficient and has a greater affinity for an electron than the corresponding oxygen in ONOH. (Consequently, the O—H bond in O_2NOH is more polar than that in ONOH.) The same reasoning indicates that in the series O_3ClOH, O_2ClOH, OClOH, and ClOH, the successive addition of oxygen to the chlorine central atom results in the removal of electron density from the oxygen of the O—H bond, thereby increasing its affinity for electrons.

Visualization 16.3

Which diagram best represents the relative electron densities in ClOH and BrOH?

(a)

(b)

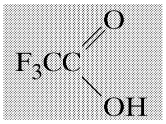
(c)

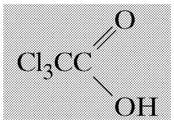
Solution:

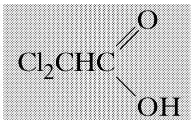
The chlorine removes more electron density than the bromine does from the oxygen. Therefore, representation (a), which shows more electron density around the oxygen in BrOH, is the best description of the electron density.

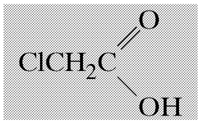
A variation of the central atom in series of the type $O_nQ(OH)_m$ also affects the acidity. In the series LiOH, H_3COH, and ClOH, the electronegativities of the atoms Li, C, and Cl increase in the order Li < C < Cl. Thus, the most polar O—H bond occurs in ClOH and this compound is the strongest acid. In LiOH, the electronegativity difference between lithium and oxygen is so large that this linkage is almost totally ionic. Hence, LiOH is a source of hydroxide ions, ClOH is a weak source of hydronium ions, and H_3COH is a source of neither.

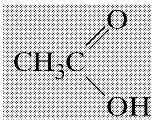
The same rule can be applied to the following series of substituted acetic acids:


$F_3CC(=O)OH$

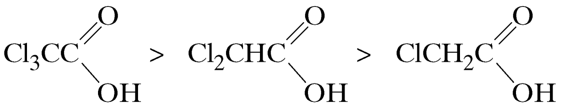

$Cl_3CC(=O)OH$


$Cl_2CHC(=O)OH$


$ClCH_2C(=O)OH$


$CH_3C(=O)OH$

In these compounds the substituent responsible for alteration of the electron density at the oxygen of the O—H group is three bonds away from the oxygen. Replacement of a hydrogen in the methyl group of acetic acid by the more electronegative chlorine results in decreased electron density at the carbon to which it is attached. Thus the nuclear positive charge at the carbon becomes more exposed, and it attracts electron density from the carbon of the carbonyl group (C═O), which then also has an increased, partially positive charge. The final result is electron withdrawal from the oxygen of the O—H group, which gives it a greater affinity for electrons. Thus the electron-withdrawing effect of the electronegative chlorine is passed, bond by bond, through the three intervening bonds to the oxygen. As more hydrogens are replaced by chlorines, more and more density is removed, and the oxygen obtains a greater and greater affinity for electrons (the O—H bond becomes more polar). Hence, the acidities of the chloroacetic acids vary as follows:


$$Cl_3CC(=O)OH > Cl_2CHC(=O)OH > ClCH_2C(=O)OH$$

Because fluorine is an even better electron-withdrawing group than chlorine, trifluoroacetic acid is an even stronger acid than trichloroacetic acid. The alteration of electron density at a given atom by an atom or group one or more bonds removed, which results from changes induced in the electron density of intervening bonds, is termed the **inductive effect**.

The relative acidities of the binary acids of the Group VI and VII elements are amenable to interpretation with the second rule. That is, the bond energies of the H—X bonds of HF, HCl, HBr, and HI decrease markedly in going down the group, and this change outweighs the increase in electron affinity in going up the group. Thus, the acidity orders HI > HBr > HCl > HF and $H_2Te > H_2Se > H_2S > H_2O$ can be attributed to variations in the H—X bond energies.

Methodology 16.2

Predict which acid is stronger—$ClCH_2CO_2H$ or $ClCH_2CH_2CO_2H$.

For these two acids, which factor, electron affinity or bond energy, will control the acidities?

Because these acids both have the acidic proton on an oxygen of the carboxyl group (CO_2H), the electron affinity of the OH oxygen will control the acidity.

How do the two acids differ?

3-Chloropropanoic acid has one more CH_2 group than chloroacetic acid.

How does this difference affect the electron affinity of the oxygen of the OH group?

In 3-chloropropanoic acid, the chlorine is farther from the oxygen and therefore has less effect on the electron density of that oxygen.

Which compound has an oxygen with the greater electron affinity?

Chloroacetic acid

Which compound is more acidic?

Chloroacetic acid

Effect of Structure on Basicity

Let us begin our discussion of relative basicities with an important generalization:

The stronger the base, the weaker its conjugate acid;
the stronger the acid, the weaker its conjugate base.

That is, the greater the basicity of a base, B, the more readily it accepts a proton, and the higher the extent of reaction (4):

$$(4) \qquad \underset{\text{base}}{B} + H^+ \rightleftharpoons \underset{\text{conjugate acid}}{BH^+}$$

The higher the extent of reaction (4), the smaller the degree to which the conjugate acid dissociates back to the base. Table 16.1 and Table 16.2 provide a number of examples of this generalization: HCl is a very strong acid, and its conjugate base, Cl^-, is extremely weak; HF is a weaker acid, and its conjugate base, F^-, is stronger than Cl^-; acetic acid is a weaker acid than HF, and its conjugate base, $C_2H_3O_2^-$, is therefore a stronger base than F^-; and hydrocyanic acid is weaker than acetic acid, and consequently its conjugate base is stronger than acetate ion.

One of the advantages of this generalization is that it allows an analysis of basicity in terms of the acidity of the conjugate acid. Those characteristics that enhance the strength of an acid (low H—X bond energy and high electron affinity of X) diminish the basicity of its conjugate base. Hence, a strong base will be one whose conjugate acid has a strong H—X bond and whose X atom has a low affinity for electrons. The guidelines for relative basicities, then, are the following:

1. The relative basicities of two bases that have the same basic atoms (atoms to which the protons become attached) are determined by the relative affinities of those atoms for an electron: the lower the affinity, the stronger the base. For example, ammonia is a stronger base than hydroxylamine (H_2NOH) because substitution of the electronegative OH for a hydrogen increases the affinity of the nitrogen for an electron.
2. The relative basicities of two bases whose basic atoms are different are usually determined by the strength of the bond to those atoms in their conjugate acids: the stronger the bond, the stronger the base. For example, triethylamine, $(C_2H_5)_3N$, is a stronger base than triethylphosphine, $(C_2H_5)_3P$, because the N—H bond of the conjugate acid $(C_2H_5)1_3NH^+$ is stronger than the P—H bond of the conjugate acid $(C_2H_5)_3PH^+$ (even though nitrogen has a greater affinity for electrons than phosphorus).

Problem 16.2

Which is the stronger base—OH^- or SH^-?

Solution:

We first establish which conjugate acid is stronger—H_2O or H_2S. Because the acidic hydrogen is attached to different atoms, the acidities are determined by the strength of the bond between oxygen and hydrogen relative to that between sulfur and hydrogen. The hydrogen-sulfur bond is longer and therefore weaker; H_2S is the stronger acid. Using the generalization that the stronger the acid the weaker the conjugate base, we can conclude that SH^- is the weaker base.

16.3 EXTENTS OF PROTON-TRANSFER REACTIONS

Although the extents of the reactions of acids and bases with water have already been discussed, it is frequently necessary to have at least a qualitative knowledge of the extent of reaction between any acid and base:

$$\mathrm{A + B \rightleftharpoons C + D}$$

$$\mathrm{acid_1 + base_2 \rightleftharpoons acid_2 + base_1}$$

For such a reaction, the extent is determined by the relative acidities of the two acids A and C and the relative basicities of the bases B and D. In fact, the reaction can be viewed as a competition between the two sets of acids and bases for the most proton transfers. If A, B, C, and D are present in equal concentrations at the beginning of the reaction, and if A and B are stronger than their conjugates, more protons will be transferred from A to B than from C to D and the equilibrium will lie on the product side ($K > 1$). If the stronger set is the product acid and base, more transfers will occur from C to D than from A to B, and the equilibrium constant will be less than 1.

The determination of which is the stronger acid and which is the stronger base can be accomplished by using the relative acidities and basicities listed in Table 16.1 and Table 16.2 and the generalization about the strengths of the conjugates. As a first example, let us consider the reaction between acetic acid and the fluoride ion,

$$\mathrm{CH_3CO_2H + F^- \rightleftharpoons HF + CH_3CO_2^-}$$

Table 16.1 shows that HF is a stronger acid than acetic acid, and Table 16.2 shows that the acetate ion is a stronger base than the fluoride ion. Therefore, a greater number of proton transfers between HF and the acetate ion will occur than between acetic acid and the fluoride ion, and the extent of reaction is less than 50% ($K < 1$).

As another example, let us consider the reaction of chlorous acid with the cyanide ion:

$$\mathrm{HClO_2 + CN^- \rightleftharpoons HCN + ClO_2^-}$$

The stronger acid is $HClO_2$, and its conjugate base must therefore be weaker than the conjugate base of HCN. The stronger acid and base therefore appear as reactants, and the extent of the reaction is high.

16.4 QUANTITATIVE ASPECTS OF PROTON-TRANSFER EQUILIBRIA IN AQUEOUS SOLUTIONS

Self-Ionization of Water

Because of the amphiprotic nature of water, protons are transferred between water molecules in liquid water:

$$\mathrm{H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-}$$

Since the hydronium ion is a much stronger acid than water, and the hydroxide ion is a much stronger base than water, the extent of this reaction is very small. Indeed, at 25 °C its equilibrium constant, designated K_w, has a value of 10^{-14}. The equilibrium expression for this reaction does not contain the concentration of water because so little water is consumed by the reaction that its concentration remains constant:

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 10^{-14} \tag{5}$$

Both hydronium ions and hydroxide ions exist in pure water, and because every proton transfer results in one hydronium ion and one hydroxide ion, their concentrations are equal. The value of this concentration can be calculated by letting x represent the hydronium ion concentration, which must also be equal to the hydroxide ion concentration:

$$x = [H_3O^+] = [OH^-]$$

$$K_w = [H_3O^+][OH^-] = 10^{-14} = (x)(x) = 10^{-14}$$

$$x = 10^{-7}\ M$$

Thus the hydronium ion and hydroxide concentrations in pure water are 10^{-7} *M*.

Because of the paramount importance of the hydronium and hydroxide ion concentrations in aqueous solution, and the inconvenience of writing very small numbers in exponential form, these concentrations are frequently expressed as their negative logarithms. The negative logarithm of the hydronium ion concentration is designated pH, while the negative logarithm of the hydroxide concentration is pOH. Indeed, the symbol p can be used to designate the negative logarithm of any variable:

$$\text{pH} = -\log[H_3O^+]$$

$$\text{pOH} = -\log[OH^-]$$

$$\text{pQ} = -\log[Q], \qquad Q = \text{some variable}$$

The pH of pure water is then $-\log[10^{-7}] = -(-7) = 7$. The pOH of pure water is, of course, also 7. A graphic representation of the relationship between pH, pOH, $[H_3O^+]$, and $[OH^-]$ is shown in Figure 16.6. If the negative logarithms* of both sides of equation (5) are taken, the useful relationship that pH + pOH = 14 at 25 °C is obtained.

Regardless of what is added to water, the relationship between the concentrations of hydronium ions and hydroxide ions as expressed by equation (5) is maintained. If a substance that produces hydronium ions is added, the concentration of hydroxide ions will decrease so that the product $[H_3O^+][OH^-]$ remains at its constant value of 10^{-14}. The same effect can be expressed in terms of Le Châtelier's Principle: the additional hydronium ions place a stress on the system, which can only be relieved by the reaction of H_3O^+ with OH^- to form more H_2O.

When hydronium ions dominate an aqueous solution—that is, when $[H_3O^+] > [OH^-]$—the solution is said to be acidic. Conversely, when $[OH^-] > [H_3O^+]$, the solution is basic or alkaline. When $[H_3O^+] = [OH^-]$, the solution is neutral. Thus, an acidic solution has a pH less than 7.00, a basic solution has a pH greater than 7.00, and a neutral solution has a pH equal to 7.00.

The pH of a solution can be estimated by placing some of the solution on litmus or some other pH indicator paper. These strips of paper are treated with dyes that change

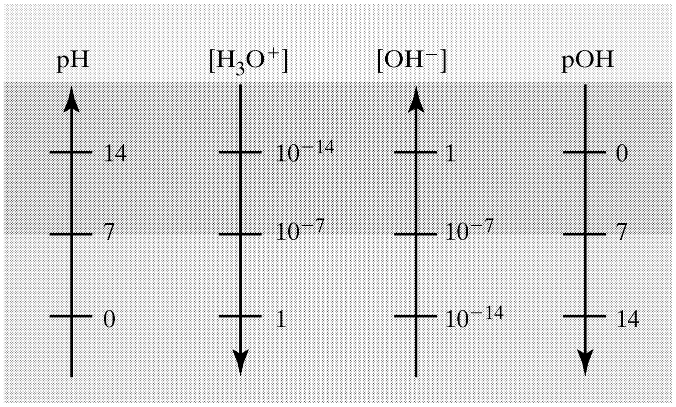


Figure 16.6 The relationship between pH, pOH, $[H_3O^+]$, and $[OH^-]$.

$$* \quad K_w = [H_3O^+][OH^-] = 10^{-14}$$
$$-\log[H_3O^+][OH^-] = -\log 10^{-14}$$
$$-\log[H_3O^+] - \log[OH^-] = 14$$
$$\text{pH} + \text{pOH} = 14$$

color as the pH of the solution changes. [Compounds whose color depends on pH will be discussed in Section 6 of this chapter.] For example, the dye extracted from the litmus plant turns blue if the $pH > 7$ and red if the $pH < 7$. For more accurate measurements, a pH meter is used.

Problem 16.3

Calculate the pH and pOH of a solution that has a hydronium ion concentration of $5.0 \times 10^{-9}\ M$.

Solution:

$$[H_3O^+] = 5.0 \times 10^{-9}\ M$$

$$pH = -\log(5.0 \times 10^{-9})$$

$$\log(5 \times 10^{-9}) = -8.30$$

$$pH = 8.30$$

$$pOH = 14.00 - 8.30 = 5.70$$

Problem 16.4

Calculate the hydroxide ion concentration in a solution of pH = 4.70.

Solution:

$$pOH = 14.00 - 4.70 = 9.30$$

$$9.30 = -\log[OH^-]$$

$$\log[OH^-] = -9.30$$

$$[OH^-] = \text{antilog}(-9.30) = 10^{-9.30} = 5.0 \times 10^{-10}$$

✓ Check Point 16.1

Calculate the hydronium ion concentration in a solution that has a pH of 8.37.

Solution:

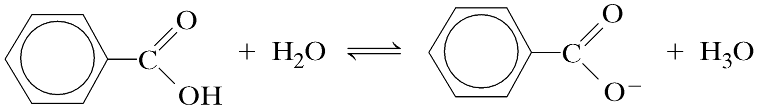
4.3×10^{-9}

◇ ◇ ◇ ◇ ◇

Equilibrium Constants for Molecular Acids and Bases

Equilibrium constants for the reaction of molecular acids with water are designated K_a, while constants for molecular bases are designated K_b. For many acids and bases, these constants can be determined by a direct measurement of the hydronium ion concentration with a pH meter.

For example, suppose that we have dissolved 0.100 mol of benzoic acid in sufficient water to make 1.00 L of solution. We then determine the pH of the solution to be 2.60. In order to calculate K_a for benzoic acid, we first write an equation for the reaction of benzoic acid with water:



The corresponding equilibrium expression is

$$K_a = \frac{[H_3O^+][C_6H_5CO_2^-]}{[C_6H_5CO_2H]}$$

Note that the concentration of water does not appear in this expression. The reaction is carried out in a large excess of water, and the amount of water consumed is so small that the concentration of water remains constant.

Strictly speaking, there are two sources of hydronium ion in this solution: the reaction of the acid with water and the self-ionization of water. Since the pH of the solution is low, the acid has produced vastly more hydronium ions than the self-ionization of water (which would be less than 10^{-7} because of suppression of the self-ionization by the added hydronium ion). Consequently, the concentration of H_3O^+ from the self-ionization of water can be neglected. The concentration of H_3O^+ from the acid can be calculated from the pH.

$$\begin{aligned} pH = 2.60 &= -\log[H_3O^+] \\ \log[H_3O^+] &= -2.60 \\ [H_3O^+] &= 10^{-2.60} = 2.5 \times 10^{-3}\ M \end{aligned}$$

According to the equation for the reaction, every acid molecule that dissociates produces one benzoate ion and one hydronium ion. Therefore, the concentration of benzoate ion at equilibrium is also 2.5×10^{-3} *M*. The concentration of the acid at equilibrium is its original concentration minus the amount consumed during the reaction.

	$C_6H_5CO_2H$ +	$H_2O \rightleftharpoons$	$^{-}C_6H_5CO_2$ +	H_3O^+
Start (mol/L)	0.100	constant	0	0
Change (mol/L)	-2.5×10^{-3}		2.5×10^{-3}	2.5×10^{-3}
Equilibrium (mol/L)	$0.100 - 2.5 \times 10^{-3} = 9.75 \times 10^{-2}$		2.5×10^{-3}	2.5×10^{-3}

Finally, the equilibrium concentrations are inserted into the equilibrium expression:

$$K_a = \frac{(2.5 \times 10^{-3}\ M)(2.5 \times 10^{-3}\ M)}{9.75 \times 10^{-2}\ M} = 6.4 \times 10^{-5}$$

When the equilibrium constant is low (10^{-5} and lower), the calculation can usually be simplified by assuming that the equilibrium concentration of the acid is its initial concentration. The validity of such an assumption is totally dependent, however, upon the number of significant figures in the data. Values for pH are usually given to the nearest one-hundredth of a pH unit, which when translated into the hydronium ion concentration usually results in a value for $[H_3O^+]$ of two significant figures. Consequently, a 2 to 5 percent error can generally be tolerated.

Problem 16.5

When 0.10 mol of propanoic acid is mixed with sufficient water to give 1.00 L of solution, the pH of the solution is 2.94 after equilibrium has been established. Calculate K_a for propanoic acid.

Solution:

Propanoic acid reacts with water according to the equation

$$CH_3CH_2CO_2H + H_2O \rightleftharpoons CH_3CH_2CO_2^- + H_3O^+$$

The equilibrium expression is

$$K_a = \frac{[CH_3CH_2CO_2^-][H_3O^+]}{[CH_3CH_2CO_2H]}$$

Continued on the next page

Problem 16.5 *Continued*

Solution: *Continued*

Assuming that the amount of H_3O^+ from the self-ionization of water is negligible, the concentration of H_3O^+ resulting from the dissociation of the acid is given by

$$\text{pH} = 2.94 = -\log[H_3O^+]$$
$$[H_3O^+] = 1.15 \times 10^{-3}\ M$$

The concentration of propanoate ion is the same, $1.15 \times 10^{-3}\ M$. The concentration of the acid at equilibrium is 0.10 − 0.00115, which to two significant figures is 0.10 *M*.

	$CH_3CH_2CO_2H + H_2O \rightleftharpoons$	$CH_3CH_2CO_2^- +$	H_3O^+
Start (mol/L)	0.10	0	0
Change (mol/L)	-1.15×10^{-3}	1.15×10^{-3}	1.15×10^{-3}
Equilibrium (mol/L)	$0.10 - 1.15 \times 10^{-3} = 0.10$	1.15×10^{-3}	1.15×10^{-3}

The equilibrium constant is therefore

$$K_a = \frac{(1.15 \times 10^{-3})^2}{0.10} = 1.3 \times 10^{-5}$$

Problem 16.6

The pH of a solution made by mixing 0.050 mol of diethyl amine with enough water to make 1.00 L of solution is 11.82. Calculate K_b for diethyl amine.

Solution:

Diethyl amine reacts with water according to the equation

$$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$$

for which the equilibrium expression is

$$K_b = \frac{[(C_2H_5)_2NH_2^+][OH^-]}{[(C_2H_5)_2NH]}$$

The hydroxide ion concentration can be obtained by first converting pH to pOH with the relationship pH + pOH = 14:

$$\text{pOH} = 14 - 11.82 = 2.18$$
$$-\log[OH^-] = 2.18$$
$$[OH^-] = 6.6 \times 10^{-3}$$

	$(C_2H_5)_2NH + H_2O \rightleftharpoons$	$(C_2H_5)_2NH_2^+ +$	OH^-
Start (mol/L)	0.050	0	0
Change (mol/L)	-6.6×10^{-3}	6.6×10^{-3}	6.6×10^{-3}
Equilibrium (mol/L)	4.3×10^{-2}	6.6×10^{-3}	6.6×10^{-3}

Finally, we have

$$K_b = \frac{(6.6 \times 10^{-3})^2}{4.3 \times 10^{-2}} = 1.0 \times 10^{-3}$$

Check Point 16.2

The pH of a 0.10 *M* solution of chloroacetic acid ($ClCH_2CO_2H$) is 2.0. Calculate the K_a for chloroacetic acid.

Solution:

1.1×10^{-3}

◇ ◇ ◇ ◇ ◇

When an acid or base is very strong or very weak, the determination of its equilibrium constant is more difficult. Consider, for example, two very strong acids, such that 99.9% of the molecules of the first and 99.99% of the second are dissociated in water. The second acid is clearly stronger and has $K_a = 10^4$, as opposed to $K_a = 10^3$ for the first acid. However, because both are so close to being completely dissociated in water, their strengths are *experimentally indistinguishable*; that is, no experimental technique is capable of distinguishing between the two in water. The strengths of the two can be determined, however, if they are allowed to react in a nonaqueous medium with a base that is not as basic as water—for example, acetic acid:

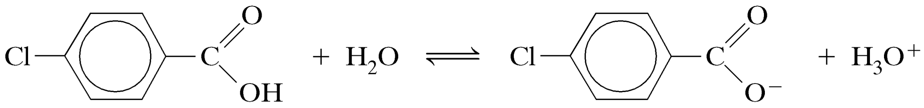
$$HA + CH_3CO_2H \rightleftharpoons CH_3CO_2H_2^+ + A^-$$

In this very weak base, these two strong acids are dissociated to a much smaller extent, and the difference between the two can be measured.

When the acid is very weak, the hydronium ions that result from the self-ionization of water cannot be ignored. That is, both dissociation of the acid and ionization of the water contribute to the total hydronium ion concentration. This situation also complicates the determination of the equilibrium constant, and the K_a for such an acid is often obtained indirectly from the equilibrium constant for the reaction of its moderately strong conjugate base with water.

Once the equilibrium constant for an acid or base is known, it can be used to calculate the concentrations of all the species in a solution of given concentration. For example, let us calculate the concentrations of all the species present in a 1.0×10^{-2} *M* solution of *p*-chlorobenzoic acid.

This acid reacts with water according to the following equation:



In addition to the four species shown in the equation, there is also OH^- from the self-ionization of water. But since the concentration of water remains constant, we need to calculate only the concentrations of four species.

If we use x to represent the equilibrium concentration of H_3O^+ and that of the *p*-chlorobenzoate ion, the stoichiometry of the equation dictates that the equilibrium concentration of *p*-chlorobenzoic acid is $1.0 \times 10^{-2} - x$.

	$ClC_6H_4CO_2H + H_2O \rightleftharpoons$	$ClC_6H_4CO_2^-$	$+ H_3O^+$
Start (mol/L)	1.0×10^{-2}	0	0
Change (mol/L)	$-x$	x	x
Equilibrium (mol/L)	$1.0 \times 10^{-2} - x$	x	x

The K_a as obtained from Table 16.1 is rather large, and it is therefore likely that the x in the equilibrium concentration of the free acid cannot be ignored. When these concentrations are inserted, the equilibrium expression becomes

$$k_a = 1.0 \times 10^{-4} = \frac{[H_3O^+][ClC_6H_4CO_2^-]}{[ClC_6H_4CO_2H]} = \frac{x^2}{1.0 \times 10^{-2} - x}$$

Solving for x with the quadratic formula, we obtain

$$x^2 + 1.0 \times 10^{-4}\ x - 1.0 \times 10^{-6} = 0$$

$$x = \frac{-1.0 \times 10^{-4} \pm \sqrt{1.0 \times 10^{-8} + 4.0 \times 10^{-6}}}{2} = 9.5 \times 10^{-4}, 1.05 \times 10^{-3}$$

Thus,

$$[H_3O^+] = 9.5 \times 10^{-4}\,M$$

$$[ClC_6H_4CO_2^-] = 9.5 \times 10^{-4}\,M$$

$$[ClC_6H_4CO_2H] = 1.0 \times 10^{-2} - 9.5 \times 10^{-4} = 9 \times 10^{-3}\,M$$

And, finally, $[OH^-]$ can be obtained from the relationship for K_w:

$$K_w = 10^{-4} = [H_3O^+][OH^-]$$

$$[OH^-] = \frac{10^{-14}}{9.5 \times 10^{-4}} = \frac{10 \times 10^{-15}}{9.5 \times 10^{-4}} = 1.1 \times 10^{-11}\,M$$

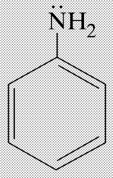
The x in the denominator can usually be ignored unless the equilibrium constant is high or the initial concentration of the acid or base is low. As stated before, the decision of whether to ignore the amount of acid or base that has dissociated in calculating its concentration must be based on the accuracy desired. Frequently, a quick calculation ignoring the x in the denominator will serve to indicate the approximate percentage of error involved (see Methodology 16.3).

Methodology 16.3

Calculate the concentration of all species in a $1.0 \times 10^{-1}\,M$ solution of aniline ($C_6H_5NH_2$). The equilibrium constant for this reaction is 3.8×10^{-10}.

Is aniline an acid or a base relative to water?

The nitrogen of the amino group attached to the benzene ring has a lone pair of electrons



that it can use to attract a hydrogen ion from water. Indeed, the reaction is analogous to the reaction of ammonia with water. Therefore, aniline is a base relative to water.

Write the equation and equilibrium expression for the reaction of aniline with water.

$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$$

$$K_b = 3.8 \times 10^{-10} = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

Let x represent the hydroxide ion concentration at equilibrium, and set up the equilibrium table:

	$C_6H_5NH_2 + H_2O \rightleftharpoons$	$C_6H_5NH_3^+$ +	OH^-
Start (mol/L)	0.10	0	0
Change (mol/L)	$-x$	x	x
Equilibrium (mol/L)	$0.10 - x$	x	x

Continued on the next page

Methodology 16.3 Continued

Therefore:

$$\frac{(x)(x)}{(1.0 \times 10^{-1}) - x} = 3.8 \times 10^{-10}$$

Assume that x will be negligibly small relative to 1.0×10^{-1} and solve the equilibrium expression.

We drop the x in the denominator and solve the equation as follows:

$$\frac{x^2}{1.0 \times 10^{-1}} = 3.8 \times 10^{-10}$$

$$x = 6.2 \times 10^{-6}$$

Is x really negligible compared to 0.10 M?

Clearly, x is about one ten-thousandth as large as 1.0×10^{-1}, and the equilibrium concentration of aniline is indeed 1.0×10^{-1}, to two significant figures. In other words, the solution to the exact equation would give the same answer to two significant figures.

Determine the concentrations of all species in the solution.

The concentrations are

$$[OH^-] = 6.2 \times 10^{-6}\ M$$

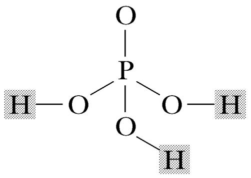
$$[C_6H_5NH_3^+] = 6.2 \times 10^{-6}\ M$$

$$[C_6H_5NH_2] = 1.0 \times 10^{-1}\ M$$

$$[H_3O^+] = \frac{10^{-14}}{6.2 \times 10^{-6}} = 1.6 \times 10^{-9}\ M$$

Equilibrium Constants for Polyprotic Acids

The dissociation of a polyprotic acid, which by definition can release more than one proton per molecule, occurs in a stepwise fashion. For each step, there is a corresponding equilibrium constant. The constant for the removal of one proton from the neutral acid is referred to as K_{a1}, the constant for the removal of a proton from the resulting negatively charged species is K_{a2}, and so on. For phosphoric acid, a triprotic acid, the steps and their corresponding constants are



$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a1}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a2}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_{a3}$$

It is generally true that $K_{a1} > K_{a2} > K_{a3}$, and so on.

The calculation of the concentration of all species present in a solution of a polyprotic acid is somewhat more complex. Consider, for example, a 1×10^{-1} M solution of H_2S. This species reacts with water as a diprotic acid, and dissociates in two steps according to the equations

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad K_{a1} = 1 \times 10^{-7}$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-} \qquad K_{a2} = 1 \times 10^{-13}$$

The equilibrium constants for the two steps are quite different, the first being a million times (10^6) as large as the second. Because of this great difference in extents, the amount of hydronium ion resulting from the reaction of H_2S with water can be assumed to result almost totally from the first step. Moreover, the amount of hydrogen sulfide ion consumed in the second step will be negligible compared with the amount produced in the first step. Thus, $[H_3O^+]$ and $[HS^-]$ can be obtained in the usual way from K_{a1}.

	$H_2S + H_2O \rightleftharpoons$	$HS^- +$	H_3O^+
Start (mol/L)	0.1	0	0
Change (mol/L)	$-x$	x	x
Equilibrium (mol/L)	$0.1 - x$	x	x

$$K_{a1} = 1 \times 10^{-7} = \frac{[H_3O^+][HS^-]}{[H_2S^-]} = \frac{(x)(x)}{1 \times 10^{-1} - x}$$

If it is assumed that x is negligible relative to the one significant figure of 1×10^{-1}, x can be dropped from the denominator and the equation can be simplified to

$$\frac{x^2}{1 \times 10^{-1}} = 1 \times 10^{-7}$$

$$x = 1 \times 10^{-4}\,M$$

Hence, $[H_3O^+]$ and $[HS^-]$ in a $1 \times 10^{-1}\,M$ H_2S solution are both $1 \times 10^{-4}\,M$.

The equilibrium concentration of sulfide ion can now be obtained from the expression for K_{a2}:

$$K_{a2} = 1 \times 10^{-13} = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

The concentration of HS^- (just calculated) is $1 \times 10^{-4}\,M$. The value used for $[H_3O^+]$, however, must reflect the fact that H_3O^+ is produced in both steps. Because the amount of H_3O^+ produced in the second step is assumed to be negligible, the concentration of H_3O^+ in the solution is taken as equal to $[H_3O^+]$ from the first step, $1 \times 10^{-4}\,M$.

	$HS^- + H_2O \rightleftharpoons$	S^{2-} +	H_3O^+
Start (mol/L)	1×10^{-4}	0	1×10^{-4}
Change (mol/L)	$-x$	x	x
Equilibrium (mol/L)	$1 \times 10^{-4} - x$ $= 1 \times 10^{-4}$	x	$1 \times 10^{-4} + x$ $= 1 \times 10^{-4}$

Thus:

$$K_{a2} = \frac{1 \times 10^{-4}[S^{2-}]}{1 \times 10^{-4}}$$

and

$$[S^{2-}] = K_{a2} = 1 \times 10^{-13}\,M$$

The concentration of sulfide also may be determined by first adding the equations for the two dissociations to give an equation representing the overall dissociation to sulfide ion.

$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	K_{a1}	1×10^{-7}
$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$	K_{a2}	1×10^{-13}
$H_2S + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + S^{2-}$	$K_{a1} \times K_{a2}$	1×10^{-20}

The equilibrium constant for this overall reaction is the product of K_{a1} and K_{a2}, or 1×10^{-20}. Then $[S^{2-}]$ can be obtained from the corresponding equilibrium expression

$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_{a1} \times K_{a2} = 1 \times 10^{-20}$$

This expression can be somewhat misleading, however, because $[H_3O^+]$ is not twice $[S^{2-}]$ (which would imply that all of the HS^- formed in the first step dissociates in the second step), but is instead the value calculated earlier, 1×10^{-4} *M*. The sulfide concentration is

$$\frac{(1 \times 10^{-4})^2[S^{2-}]}{1 \times 10^{-1}} = 1 \times 10^{-20}$$

$$[S^{2-}] = 1 \times 10^{-13}\ M$$

which is identical with the value obtained in the preceding calculations.

The overall expression is particularly valuable in dealing with saturated solutions of H_2S to which an acid has been added. Qualitatively, the addition of acid to a saturated solution (approximately 0.1 *M*) of H_2S decreases the concentration of sulfide ion and forms more H_2S:

$$S^{2-} + 2\,H^+ \rightleftharpoons H_2S$$

The initial concentration of sulfide is so low, however, that the increase in concentration of H_2S that results from the addition of any amount of hydronium ion is totally negligible. Hence, in a saturated solution, the concentrations of sulfide and hydronium ions are related by the expression

$$\frac{[H_3O^+]^2[S^{2-}]}{0.1} = 1 \times 10^{-20}$$

or

$$[H_3O^+]^2[S^{2-}] = 1 \times 10^{-21}$$

For example, the sulfide concentration in a 1 *M* HCl solution saturated with H_2S is

$$[S^{2-}] = \frac{1 \times 10^{-21}}{(1)^2} = 1 \times 10^{-21}\ M$$

This control of the sulfide ion by the hydronium ion concentration makes possible the analytical separation of certain metal ions. This can be illustrated by the separation of zinc(II) and cadmium(II) through the precipitation of their sulfides. The concentration of sulfide necessary for their precipitation is calculated from their respective solubility product expressions:

$$\underline{ZnS} \rightleftharpoons Zn^{2-}\,(aq) + S^{2-}\,(aq) \qquad K_{sp} = [Zn^{2+}][S^{2-}] = 1 \times 10^{-23}$$

$$\underline{CdS} \rightleftharpoons Cd^{2+}\,(aq) + S^{2-}\,(aq) \qquad K_{sp} = [Cd^{2+}][S^{2-}] = 1 \times 10^{-28}$$

If we suppose that a separation is required for a solution that is 0.1 *M* in Zn^{2+} and 0.1 *M* in Cd^{2+}, the required sulfide concentrations are

$$[Zn^{2+}][S^{2-}] = 1 \times 10^{-23}$$

$$[S^{2-}] = \frac{1 \times 10^{-23}}{1 \times 10^{-1}} = 1 \times 10^{-22}\ M \text{ for } Zn^{2+}$$

and

$$[Cd^{2+}][S^{2-}] = 1 \times 10^{-28}$$

$$[S^{2-}] = \frac{1 \times 10^{-28}}{1 \times 10^{-1}} = 1 \times 10^{-27}\ M \text{ for } Cd^{2+}$$

In order to precipitate cadmium but not zinc, a solution with a sulfide concentration of less than 1×10^{-22} M but greater than 1×10^{-27} M is required. The concentration of H_3O^+ necessary to produce a sulfide concentration of 1×10^{-22} M in a saturated H_2S solution is

$$[H_3O^+][S^{2-}] = 1 \times 10^{-21}$$

$$[H_3O^+]^2 = \frac{1 \times 10^{-21}}{1 \times 10^{-22}} = 10$$

$$[H_3O^+] = 3\ M$$

That is, when the concentration of H_3O^+ is slightly greater than 3 M, cadmium sulfide will precipitate and zinc sulfide will not.

Problem 16.7

Calculate the pH of a 1×10^{-3} M solution of carbonic acid.

Solution:

The reaction of carbonic acid with water occurs stepwise according to the following equations:

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad K_{a2} = 4.8 \times 10^{-11}$$

Most of the hydronium ion produced from the carbonic acid is a result of the first step. Therefore,

$$\frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = K_{a1} = 4.2 \times 10^{-7}$$

The difference in the equilibrium constants is sufficient to allow us to assume that almost all of the hydronium ion in the solution will be produced in the first step. Therefore,

$$\frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = K_{a1} = \frac{x^2}{0.001 - x}$$

Solving for x we obtain $x = 2 \times 10^{-5}$ M and therefore the pH is 4.7.

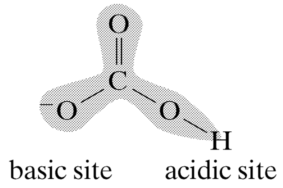
Acid-Base Equilibria for Ions

Neutral molecular compounds are not the only substances that behave as acids or bases. Ions also function as acids and bases, and several examples of such ions have already been given. The ammonium ion is a monoprotic acid in water and the acetate ion is a monoprotic base,

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

while the hydrogen carbonate ion can behave as both an acid and a base,



$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Since the conjugates of ions are in many cases molecular acids or bases, the relative acidity or basicity of an ion can often be ascertained qualitatively from the K_a or K_b of its conjugate. For example, the chloride ion can theoretically function as a base,

$$Cl^- + H_2O \rightleftharpoons HCl + OH^-$$

However, its conjugate acid is one of the very strong acids, and the generalization that "the stronger the acid, the weaker the conjugate base" would predict that Cl^- should therefore be a very weak base. In fact, the chloride ion shows no basic properties relative to water. In other words, the chloride ion does not affect the pH of an aqueous solution. In general, then, ions that are the conjugate bases of the very strong* acids do not function as bases relative to water.

The conjugate bases of the weak acids—for example, acetate ion, fluoride ion, and nitrite ion—are basic relative to water and react to form hydroxide ions. Cyanide ion, whose conjugate is the very weak hydrocyanic acid, is a much stronger base than the fluoride ion, whose conjugate acid is only moderately weak.

The acidity of acidic ionic species can also be predicted from the relative K_b values of their conjugate bases. Thus, the anilinium ion ($C_6H_5NH_3^+$), which is the conjugate acid of the weak base aniline, is a stronger acid than the ammonium ion (NH_4^+), which is the conjugate acid of the stronger base ammonia (see Table 16.2).

A variety of metal cations also act as acids. These cations are generally small and highly charged and are very strongly attracted to water molecules. Indeed, discrete species such as $Al(H_2O)_6^{3+}$ usually result from such interactions. The formation and characteristics of such Lewis acid-base adducts will be discussed in the next chapter. The significant point here is that the bond to the metal cation withdraws enough electron density to increase the polarity of the O—H bonds and thereby increase their acidity. These adducts then donate protons to water, as illustrated by the equation

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$$

Some common cations that produce hydronium ions in aqueous solutions are Be^{2+}, Al^{3+}, Sn^{4+}, Pb^{4+}, Sn^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, and Ni^{2+}. Except for Be^{2+}, the alkali and alkaline earth cations do not react with water.

We are now in a position to evaluate the relative acidities of aqueous solutions of salts. If the salt has a low solubility in water or is a weak electrolyte, it will affect the pH of water very little. If, however, it is soluble and a strong electrolyte, its effect on the pH of water can be predicted from our knowledge of the acidity and basicity of its constituent ions. Sodium chloride is a soluble, strong electrolyte, but as we have seen above, neither the sodium ion nor the chloride ion has any acidic or basic properties. An aqueous solution of NaCl is therefore neutral (pH = 7).

Sodium acetate is also a soluble, strong electrolyte. The sodium ion does not react with water, but the acetate ion is the conjugate base of the weak acid acetic acid and therefore has some basic properties. The reactions of sodium acetate with water can be summarized as

$$Na^+ + H_2O \longrightarrow \text{no reaction}$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \tag{6}$$

Since hydroxide ions are produced by the reaction of the acetate ion with water, an aqueous solution of sodium acetate is basic. However, a comparison of the acidity of the species in equation (6) shows that the stronger acid and base lie on the product side, and therefore the extent of this reaction is low.

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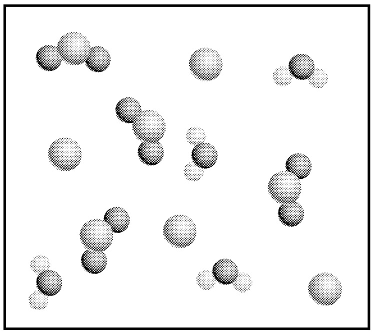
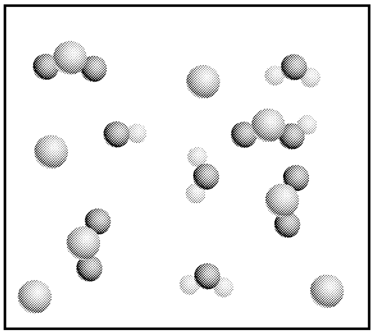
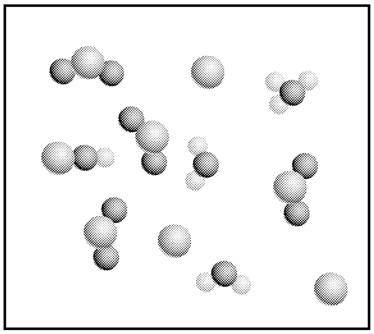
* Remember that the common strong acids are hydrochloric, hydrobromic, hydroiodic, nitric, sulfuric, and perchloric acids.

Visualization 16.4

Which diagram best portrays the reaction of KNO_2 with water?


(a)


(b)


(c)

Solution:

(a) shows only potassium ions, nitrite ions and water, (b) shows that one nitrite ion has reacted with water to form nitrous acid and hydroxide ion (thereby making the solution basic), and (c) shows that a water molecule has reacted with a potassium ion to form the molecular species KOH, which does not exist, and a hydronium ion, which would make the solution acidic. (b) is the best depiction of a solution of KNO_2.

Ammonium chloride provides an example of a salt that contains an acidic cation. The ammonium ion is the conjugate acid of the weak base ammonia and therefore possesses acidic properties:

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3 \tag{7}$$

$$Cl^- + H_2O \longrightarrow \text{no reaction}$$

A comparison of the relative acidities of the species of equation (7) shows that the stronger acid and base are on the product side of the equation, and the extent of this reaction is therefore also low. Since the chloride ion does not react with water, an aqueous solution of NH_4Cl is acidic.

In an aqueous solution of ammonium acetate, both the cation and anion react with water. Whether the solution is acidic or basic depends on which reaction has the greater extent:

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

To evaluate the equilibrium constant for the reaction of an ion with water, we make use of the close relationship of the ion to its conjugate. The conjugate base A^- of the weak acid HA reacts with water according to the equation

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

We must first evaluate the equilibrium constant for this reaction. This equilibrium constant is the K_b for the anion A^-, but it is not listed in the table of K_b values for *molecular* bases. If the equation representing the dissociation of HA in water is subtracted from the equation for the self-ionization of water we obtain

$$\begin{array}{c} H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \\ -(HA + H_2O \rightleftharpoons H_3O^+ + A^- \\ \hline H_2O + H_2O - HA - H_2O \rightleftharpoons H_3O^+ + OH^- - H_3O^+ - A^- \end{array}$$

Upon collecting terms and rearranging* the final equation, we obtain the desired equation:

$$A^- + H_2O \rightleftharpoons HA + OH^- \ K_b$$

The equilibrium constant K_b can therefore be obtained by dividing K_w by K_a.

$$K_b = \frac{K_w [\cancel{H_3O^+}][OH^-]}{K_a \ \dfrac{[\cancel{H_3O^+}][A^-]}{[HA]}} = \frac{[HA][OH^-]}{[A^-]}$$

The same result is obtained for the reaction of an acidic cation, HB^+, with water:

$$HB^+ + H_2O \rightleftharpoons B + H_3O^+ \ K_a$$

$$K_a = \frac{K_w}{K_b}$$

where K_b is the equilibrium constant for the reaction of the uncharged conjugate base with water. In general, then, the equilibrium constants for an acid and its conjugate base (or a base and its conjugate acid) are given by the expression

$$K_aK_b = K_w$$

As specific illustrations, let us consider the reactions of the ammonium ion and the acetate ion with water. For the ammonium ion, the equilibrium constant K_a is obtained as

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \ K_a$$

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

where K_b is the equilibrium constant for the reaction of ammonia with water.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = 1.8 \times 10^{-5}$$

For the acetate ion, the equilibrium constant K_b is obtained from the relationship

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^- \ K_b$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

where K_a is the equilibrium constant for the reaction of acetic acid with water, which coincidentally, is numerically identical to K_b for ammonia. Thus, we can conclude that the ammonium ion and the acetate ion react to the same extent with water. Consequently, the concentration of H_3O^+ produced by the hydrolysis of NH_4^+ is equal to the concentration of OH^- produced by the hydrolysis of the acetate ion, and an aqueous solution of ammonium acetate is therefore neutral ($[H_3O^+] = [OH^-]$).

Methodology 16.4

Determine whether an aqueous solution of NH_4F is acidic, basic, or neutral.

First we must determine if NH_4F is soluble in water.

Like sodium and potassium salts, most ammonium salts are water soluble. When NH_4F dissolves, the solution contains ammonium ions (NH_4^+) and fluoride (F^-) ions. In other words, ammonium fluoride is a soluble, strong electrolyte.

Continued on the next page

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* Notice that those species with a negative coefficient appear on the opposite side of the rearranged equation.

Methodology 16.4 Continued

Next we consider how each of the ions—NH_4^+ and F^-—react with water. The ammonium ion reacts with water as follows:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

Evaluate the equilibrium constant for this reaction.

The ammonium ion is an acid, but because it is not a molecular (neutral) species we cannot look it up in the K_a table. We can calculate the K_a value as

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now write the equation for the reaction of the fluoride ion with water.

The fluoride ion reacts with water by the following equation:

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

The constant for this reaction is K_w/K_a, where K_a is the acid dissociation constant for HF ($K_a = 3.5 \times 10^{-4}$).

$$K_b = \frac{10^{-14}}{3.5 \times 10^{-4}} = 2.9 \times 10^{-11}$$

Which reaction has the greater extent?

Because the equilibrium constant for the reaction of ammonium ion with water is larger than that for the reaction of the fluoride ion with water, there are more hydronium ions than hydroxide ions present in an aqueous solution of NH_4F.

Is the solution acidic or basic?

Because the hydronium ion concentration is greater than the hydroxide concentration, the solution is acidic.

The equilibrium constant for hydrolysis (reaction with water) can also be used to determine the behavior of an amphiprotic ion in water. The hydrogen carbonate ion can react both as an acid

$$(8) \qquad HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

and as a base

$$(9) \qquad HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

If the first reaction has a greater extent than the second, the hydrogen carbonate ion will produce more hydronium ions than hydroxide ions. The relative extents of the two reactions can be judged from their respective equilibrium constants. The constant for (8) is the second dissociation constant,* K_{a2}, for carbonic acid, whereas the constant for (9) is K_w/K_{a1}. To verify that the constant for (9) is indeed K_w/K_{a1} rather than K_w/K_{a2}, let us actually divide the appropriate equilibrium expressions:

$$K_w = [H_3O^+][OH^-]$$

$$K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} \qquad (\text{for } H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-)$$

$$\frac{K_w}{K_{a1}} = \frac{[H_3O^+][OH^-][H_2CO_3]}{[H_3O^+][HCO_3^-]} = \frac{[OH^-][H_2CO_3]}{[HCO_3^-]}$$

---

* Be sure that you understand that a diprotic acid dissociates in two steps and that the equilibrium constants for both of these steps are listed in the K_a table (Appendix 5). For carbonic acid, the steps are

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad K_{a1}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad K_{a2}$$

That K_w/K_{a1} rather than K_w/K_{a2} is the correct constant can be recognized at a glance because of the presence of H_2CO_3 in equation (9), which could only be a part of the expression for the first dissociation of carbonic acid.

From Appendix 5 we find that K_{a1} for carbonic acid is 4.2×10^{-7}, while K_{a2} is 4.8×10^{-11}. Hence, the equilibrium constants for (8) and (9) are 4.8×10^{-11} and $10^{-14}/(4.2 \times 10^{-7}) = 2.4 \times 10^{-8}$, respectively. Thus, equation (9) has the greater extent of reaction, and therefore the reaction of HCO_3^- with water has the net effect of producing more hydroxide ions than hydronium ions, making the solution basic.

Problem 16.8

Determine whether an aqueous solution of sodium hydrogen sulfite is acidic, basic, or neutral.

Solution:

Sodium hydrogen sulfite is soluble in water and is a strong electrolyte. In solution there are sodium ions, hydrogen sulfite ions, and the products of any reaction of these ions with water. Because the sodium ion does not react with water, only the two possible reactions of the amphiprotic species HSO_3^- with water need be considered.

(10) $$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$$

(11) $$HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$$ +

From Appendix 5 we find that for sulfurous acid, $K_{a1} = 1.3 \times 10^{-2}$ and $K_{a2} = 5.6 \times 10^{-8}$. The equilibrium constant for equation (10) is then 5.6×10^{-8}, and for equation (11) the constant is

$$\frac{K_w}{K_{a1}} = \frac{10^{-14}}{1.3 \times 10^{-2}} = 7.7 \times 10^{-13}$$

The acid strength of HSO_3^- is therefore greater than its base strength, and as a result, an aqueous solution of $NaHSO_3$ contains an excess of hydronium ions (the solution is acidic).

Once the equilibrium constant has been evaluated, the concentration of all the species present in a salt solution can be calculated. If both the cation and the anion of the salt react with water, the calculation becomes more complex; this situation will not be discussed here. For example, let us determine the concentration of all species present in a 0.10 *M* solution of ammonium chloride.

We first need to recognize that the chloride ion does not react with water because it is the conjugate base of the strong acid HCl. On the other hand, the ammonium ion behaves as an acid, according to the equation

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

The equilibrium constant for this process is

$$\frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

which means that

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

The problem is now solved in the usual way, letting $x = [H_3O^+]$.

	$NH_4^+ + H_2O \rightleftharpoons$	NH_3	$+ H_3O^+$
Start (mol/L)	0.10	0	0
Change (mol/L)	$-x$	x	x
Equilibrium (mol/L)	$0.10 - x = 0.10$	x	x

Thus,

$$\frac{x^2}{0.10} = 5.6 \times 10^{-10}$$

$$x = 7.5 \times 10^{-6}\,M$$

Hence, at equilibrium

$$[H_3O^+] = 7.5 \times 10^{-6}\,M$$

$$[NH_3] = 7.5 \times 10^{-6}\,M$$

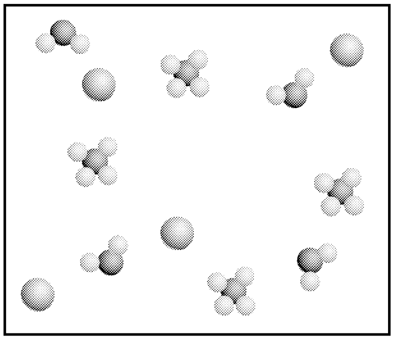
$$[NH_4^+] = 1.0 \times 10^{-1}\,M$$

$$[OH^-] = \frac{10^{-14}}{7.5 \times 10^{-6}} = 1.3 \times 10^{-9}\,M$$

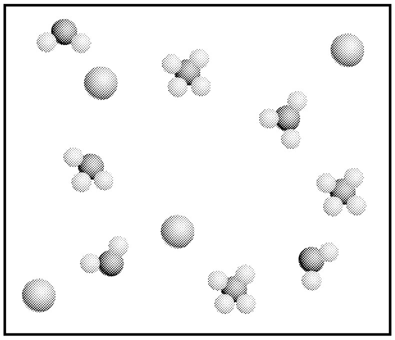
$$[Cl^-] = 1.0 \times 10^{-1}\,M$$

Visualization 16.5

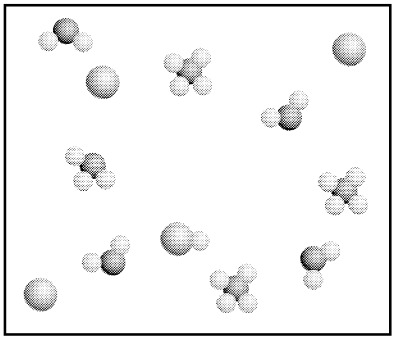
Which of the following is the best representation of an aqueous solution of NH_4Cl?



(a)



(b)



(c)

Solution:

(a) shows only ammonium ions, chloride ions, and water molecules in solution, (b) indicates that one ammonium ion has transferred a proton to a water molecule, thereby producing the hydronium ion and making the solution acidic, and (c) indicates that the transfer of the proton occurred to a chloride ion, thereby producing molecular HCl. Because HCl is a strong acid (and chloride ion is a very weak base), this is not a likely occurrence. (b) is the best representation of a solution of ammonium chloride.

Check Point 16.3

Calculate the pH of a 0.1 M sodium acetate solution.

Solution:

8.9

◇ ◇ ◇ ◇ ◇

16.5 THE COMMON ION EFFECT AND BUFFER SOLUTIONS

In accordance with Le Châtelier's Principle, the addition of the conjugate base (the common ion) to a weak acid inhibits its dissociation. Similarly, the addition of the conjugate acid to a weak base inhibits its production of hydroxide ions. Quantitatively, the effect can be calculated with either the equilibrium expression for the dissociation of the weak acid (or the weak base), or the expression for the reaction of the conjugate base (or the conjugate acid) with water. Let us consider the addition of the conjugate base A^- to a weak acid HA:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Since the concentration of hydronium ion will be the concentration of HA that has dissociated at equilibrium, we rearrange this equation as

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} \tag{12}$$

which emphasizes that the hydronium concentration and therefore the extent of dissociation of HA is a function of the ratio* of [HA] to $[A^-]$.

Now let us take the specific case of a 0.10 *M* solution of acetic acid to which has been added enough sodium acetate to make the solution 0.10 *M* in sodium acetate. The sodium acetate is a strong electrolyte, and this solution contains primarily molecular acetic acid, sodium ions, and acetate ions. Actually, there are two sources of acetate ion—the sodium acetate and the acetic acid (which dissociates slightly). The concentration of acetate ion resulting from the dissociation of 0.10 *M* acetic acid in pure water (with no excess acetate) is 1.3×10^{-3} *M*.

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$$

In the presence of acetate ion, this dissociation is repressed. Thus, the amount of acetate ion from the dissociation of acetic acid is negligible compared with the amount of acetate ion added as sodium acetate. Moreover, the amount of acetate ion consumed by the reaction with water to form acetic acid is also negligibly small compared with the 0.10 *M* concentration of the added acetate ion. The equilibrium concentrations can therefore be safely assumed to be

$$[HC_2H_3O_2] = 0.10\ M$$

$$[C_2H_3O_2^-] = 0.10\ M$$

and

$$[H_3O^+] = K_a \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]} = 1.8 \times 10^{-5}\ M \frac{(0.10\ M)}{(0.10\ M)} = 1.8 \times 10^{-5}\ M$$

---

* The same result can be obtained from the expression for the reaction of A^- with water:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{K_w}{K_a} = \frac{[HA][OH^-]}{[A^-]}$$

If we divide both sides of this equation by $K_w = [H_3O^+][OH^-]$, we obtain

$$\frac{K_w}{K_a K_w} = \frac{[HA][OH^-]}{[A^-][H_3O^+][OH^-]}$$

$$\frac{1}{K_a} = \frac{[HA]}{[A^-][H_3O^+]}$$

$$[H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

which is equivalent to equation (12).

The addition of the common ion has reduced the hydronium ion concentration from 1.3×10^{-3} *M* to 1.8×10^{-5} *M*, nearly a hundredfold reduction.

Methodology 16.5

A 25.0-mL portion of a 0.100 *M* HCl solution was added to 100 mL of a 0.100 *M* NH_3 solution. Calculate the hydronium ion concentration in the resulting solution.

With which base—ammonia or water—will the HCl react?

The HCl reacts preferentially with the stronger base, ammonia, to form ammonium chloride,

$$HCl + NH_3 \longrightarrow NH_4^+ + Cl_2$$

Does this reaction have a high extent?

We know that the reaction of HCl with water has a high extent because HCl is a strong acid. Ammonia is a stronger base than water and therefore the reaction of HCl with ammonia will have an even greater extent.

How many moles of ammonium ion are formed in this reaction?

The number of moles of HCl is less than the number of moles of NH_3:

$$\text{moles of HCl: } 0.0250\text{ L} \times 0.100\text{ mol/L} = 0.0025\text{ mol}$$

$$\text{moles of } NH_3\text{: } 0.100\text{ L} \times 0.100\text{ mol/L} = 0.010\text{ mol}$$

Because the extent of the reaction is high, the HCl is virtually completely converted to NH_4Cl. After the reaction, then, there are 0.0025 mol NH_4^+ and $0.0100 - 0.0025 = 0.0075$ mol NH_3.

What are the concentrations of ammonium ion and ammonia?

If the volumes are assumed to be additive, the total volume of solution is 125 mL. The concentrations are therefore

$$[NH_4^+] = \frac{0.0025\text{ mol}}{0.125\text{ L}} = 0.020\ M$$

$$[NH_3] = \frac{0.0075\text{ mol}}{0.125\text{ L}} = 0.060\ M$$

How do the concentrations of these two species affect the hydronium ion concentration in the solution?

The ratio of these two species controls the OH^- and H_3O^+ concentrations. Consider the reaction of NH_3 with H_2O,

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

We shall assume that the concentrations of NH_4^+ and NH_3 are those given above (that is, that the amount of NH_4^+ resulting from reaction of NH_3 with H_2O and the amount lost due to reaction of NH_4^+ with H_2O is negligible compared with the amount from the ammonium chloride).

Calculate the hydroxide ion concentration in the solution.

From the relationship

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Continued on the next page

Methodology 16.5 Continued

the hydroxide ion concentration can be given as

$$[OH^-] = \frac{[NH_3]}{[NH_4^+]} \times 1.8 \times 10^{-5} = \frac{0.060}{0.020} \times 1.8 \times 10^{-5}$$
$$= 5.4 \times 10^{-5}\,M$$

Finally, calculate the hydronium ion concentration.

$$[H_3O^+][OH^-] = K_w = 10^{-14}$$
$$[H_3O^+] = \frac{10^{-14}}{5.4 \times 10^{-5}} = 1.9 \times 10^{-10}\,M$$

Buffer Solutions

The operation of **buffer solutions**, which are of great importance in many biological and chemical processes, is based on the common ion effect. A buffer solution consists of nearly equal concentrations of a weak acid and a salt of that acid (its conjugate base) or a weak base and a salt of that base (its conjugate acid). Indeed, the acetic acid-acetate solution described previously is a buffer solution. The utility of these solutions lies in their ability to maintain an almost constant hydronium ion concentration when small amounts of even strong acids or bases are added. For example, when a strong acid is added to our acetic acid-acetate solution, the hydronium ion supplied by the strong acid reacts with the acetate ion, thereby converting it to acetic acid,

$$CH_3CO_2^- + H_3O^+ \longrightarrow CH_3CO_2H + H_2O$$

If a base is added, the hydroxide ions formed react with the acetic acid to form acetate ions,

$$CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$$

These additions serve merely to alter the concentration ratio of acetic acid to acetate ion, which in turn affects the hydronium ion concentration via equation (12).

As an illustration of the buffering ability of the solution, we will calculate (a) the change in hydronium ion concentration that occurs when 1.0×10^{-2} mol of HCl is added to 1.0 L of water and (b) the change in hydronium ion concentration that occurs when the same amount of HCl is added to 1.0 L of water containing 1.0×10^{-1} mol of acetic acid and 1.0×10^{-1} mol of sodium acetate. Because HCl is a strong acid, it is essentially completely dissociated in water, and the first solution therefore contains 1.0×10^{-2} mol of H_3O^+ per liter of solution. Pure water has a hydronium ion concentration of 10^{-7}; thus the change in $[H_3O^+]$ is from $10^{-7}\,M$ to $10^{-2}\,M$, a change of 10^5.

When the same amount of HCl is added to the buffer solution, the hydronium ions react with acetate ions according to the equation

$$CH_3CO_2^- + H_3O^+ \longrightarrow CH_3CO_2H + H_2O$$

Since H_3O^+ is a much stronger acid than acetic acid and the acetate ion is a much stronger base than water, this reaction has a very high extent. Thus, the 1.0×10^{-2} mol of H_3O^+ is converted to 1.0×10^{-2} mol of acetic acid. The initial concentrations of acetic acid and acetate ion were $1.0 \times 10^{-1}\,M$, and when equilibrium is reestablished the concentrations are

$$[HC_2H_3O_2] = 1.0 \times 10^{-1} + 1.0 \times 10^{-2} = 1.1 \times 10^{-1}\,M$$
$$[C_2H_3O_2^-] = 1.0 \times 10^{-1} - 1.0 \times 10^{-2} = 0.9 \times 10^{-1}\,M$$

The hydronium ion concentration can now be calculated with equation (12).

$$[H_3O^+] = 1.8 \times 10^{-5} \times \frac{1.1 \times 10^{-1}}{0.9 \times 10^{-1}} = 2.2 \times 10^{-5}\,M$$

The concentration of hydronium ion in the buffer solution before the HCl was added was 1.8×10^{-5} *M*. The change, therefore, is from 1.8×10^{-5} *M* to 2.2×10^{-5} *M*, a factor of $1.1/0.9 = 1.2$. When 1 mL of 0.1 *M* HCl was added to this solution, the pH did not change.

Since the weak acid (or base) and its conjugate base (or conjugate acid) must be present in nearly equal amounts in order to keep the concentration ratio of acid to conjugate base as constant as possible, a given buffer system can operate effectively over only a small pH range. An upper limit on the ratio of acid to conjugate base (or base to conjugate acid) is 10:1. For a given weak acid-conjugate base system, this means that buffering can occur between the hydronium ion concentrations of

$$[H_3O^+] = K_a = K_a \frac{10}{1} = 10\,K_a$$

and

$$[H_3O^+] = K_a = \frac{1}{10} = \frac{K_a}{10}$$

or, if everything is expressed as negative logarithms ($pK_a = -\log K_a$):

$$-\log[H_3O^+] = -\log K_a \pm \log 10$$

$$pH = pK_a \pm 1$$

Accordingly, the buffering action for the acetic acid-acetate system can be maintained at any pH between $p(1.8 \times 10^{-5}) - 1$ and $p(1.8 \times 10^{-5}) + 1$, or 4.74 ± 1.

If it is desirable, perhaps for some analytical procedure, to maintain a constant hydronium ion concentration at some other pH, the buffer system can be chosen by simply searching for a weak acid or weak base whose pK_a or pK_b has a value within ±1 of the desired pH.

Problem 16.9

What buffer system could be used to maintain a pH of 9.3?

Solution:

The desired pH is on the basic side; consequently we need to look for a weak base whose pK_b is $14 - 9.3 = 4.7 \pm 1$.

$$pOH = pK_b \pm 1$$

$$pOH = 14 - 9.3 = 4.7$$

$$pK_b = 4.7 \pm 1$$

$$K_b = 2 \times 10^{-4} \text{ to } 2 \times 10^{-6}$$

Table 16.2 reveals that NH_3 is one base with a K_b of approximately 2×10^{-5}. Thus, the buffer solution might be prepared from NH_3 and NH_4Cl. If the pH desired is exactly 9.30, the ratio of NH_3 to NH_4^+ can be determined as follows:

$$[OH^-] = K_b \frac{[NH_3]}{[NH_4^+]}$$

$$[OH^-] = \text{antilog}\,(-4.70) = 2.0 \times 10^{-5}$$

$$\frac{[OH^-]}{K_b} = \frac{2.0 \times 10^{-5}}{1.8 \times 10^{-5}} = 1.1 = \frac{[NH_3]}{[NH_4^+]}$$

If the solution is made to be 0.10 *M* in NH_3, the concentration of NH_4^+ should be $0.10/1.1 = 0.091$ *M*.

Probably the most important buffer system found in nature is the carbonic acid-hydrogen carbonate-carbonate equilibrium. When carbon dioxide is bubbled into water, a small percentage of it is slowly converted to carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

The carbonic acid can then behave as a normal diprotic acid and dissociate according to the equations

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad K_{a2} = 4.8 \times 10^{-11}$$

The importance of this buffer system in natural fluids can be illustrated by the equilibria present in sea water and blood plasma. In sea water, a buffering action is produced by the equilibrium between absorbed CO_2 and the vast carbonate sediments in the ocean beds. If alkaline materials appear in the water, CO_2 is converted to a hydrogen carbonate ion and is replenished by absorption of atmospheric CO_2 at the surface of the ocean. If acidic materials appear (for example, by volcanic eruptions), they react with carbonate and produce hydrogen carbonate. In this way the pH of the oceans is maintained at a fairly constant value.

In blood plasma, the control of pH is vital to the maintenance of life. Since plasma is just slightly basic (pH = 7.35 to 7.45), the rather strongly basic carbonate ion probably does not play a major role in the buffer. Consequently, the important species in the buffer are CO_2, H_2CO_3, and HCO_3^-.

16.6 ACID-BASE TITRATIONS

The neutralization of an acid with a base (or vice versa) is one of the oldest and most useful reactions in chemistry. The neutralization reaction, which we have previously defined as the reaction of an acid with a base to form a salt, has been used to determine the rates and extents of many reactions, but it is most often employed in quantitative analytical procedures. Some important applications are the determination of the percentage of carbonate in minerals, the percentage of phosphate in detergents, and the percentage of nitrogen in blood, proteins, foodstuff, and fertilizers.

The general procedure for the titration of a base with an acid is as follows. The base is added to distilled water in an Erlenmeyer flask, a few drops of an **indicator** solution are added, and the acid is placed in a buret (see Figure 16.7). The concentration of the acid is either known or has been previously determined to at least four significant figures. If the acid can be obtained pure, so that the concentration can be accurately known from the weight of acid used, the acid is called a **primary standard**. If a primary standard is not available, the concentration of the acid solution must be obtained by reacting a portion of

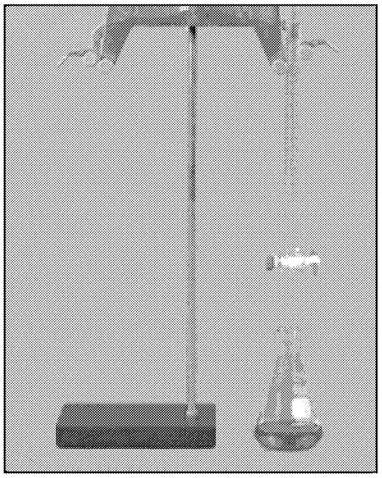


Figure 16.7 Equipment (Buret and Erlenmeyer) used in titrations.

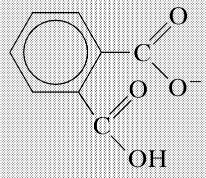
the solution with a base whose concentration is accurately known. This process is referred to as **standardizing** the acid.

The acid in the buret is added slowly to the base in the flask until the solution in the flask undergoes a marked change in color. This color change is due to reaction of the indicator with the acid and is the **endpoint** of the titration. If the indicator has been properly selected, this endpoint will also be very close to the **equivalence point** of the reaction—the point at which the number of equivalents of acid added from the buret is exactly equal to the number of equivalents of base present in the flask. In proton-exchange reactions, an **equivalent** is the amount of an acid that can supply one mole of protons or the amount of a base that can accept one mole of protons. Hence the number of equivalents (or moles) of acid can be calculated from the volume added and its concentration. This, in turn, allows calculation of the weight of base present in the flask. Methodology 16.6 and Problems 16.10 and 16.11 illustrate the calculations encountered in acid-base titrations.

Methodology 16.6

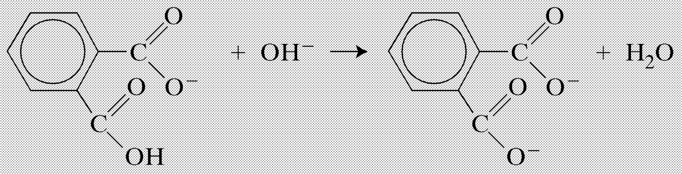
A solution of NaOH is standardized by using it to titrate a sample of pure, dry potassium hydrogen phthalate. When 0.3200 g of the potassium hydrogen phthalate is used, 32.78 mL of the NaOH solution is required. What is the molarity of the NaOH solution?

Presumably potassium hydrogen phthalate (KHP) is an acid, but what is its structure? Potassium hydrogen phthalate is a monoprotic acid. The cation is K^+, and the structure of the anion is



Give the equation for the reaction of KHP with hydroxide ion.

The reaction with OH^- proceeds according to the following equation



If we are to determine the molarity of the NaOH solution, we must know the number of moles of hydroxide ion added, and that requires us to know the number of moles of KHP. Determine the number of moles of KHP.

The number of moles of the acid is obtained by dividing the weight of acid used by its molecular weight (204.23),

$$\text{Moles of acid} = \frac{0.3200\ \text{g}}{204.23\ \text{g/mol}} = 1.567 \times 10^{-3}$$

This value must also be the number of moles of base added (moles of base $= 1.567 \times 10^{-3}$). Calculate the molarity of the base.

1.567×10^{-3} mol of the base is present in the volume of the titrant used (32.78 mL). Therefore, the molarity of the base is simply

$$M = \frac{1.567 \times 10^{-3}\ \text{mol}}{3.278 \times 10^{-2}\ \text{L}} = 0.04780\ M$$

Problem 16.10

What is the percentage of acetic acid in vinegar if a 10.0-g sample requires 35.00 mL of 0.09983 *M* NaOH for titration?

Solution:

Acetic acid reacts with NaOH according to the equation

$$CH_3CO_2H + OH^- \rightleftharpoons CH_3CO_2^- + H_2O$$

The number of moles of OH^- used is

$$0.09983 \text{ mol/L} \times 0.03500 \text{ L} = 3.494 \times 10^{-3} \text{ mol}$$

This must be the number of moles of acetic acid consumed in the reaction and therefore the number of moles in the sample titrated. Since the molecular weight of acetic acid is 60.03, the weight of acetic acid in the vinegar sample is

$$60.03 \text{ g/mol} \times 3.494 \times 10^{-3} \text{ mol} = 0.2097 \text{ g}$$

and the percentage is

$$\frac{0.2097}{10.0} \times 100 = 2.10\%$$

(Note that the answer should be expressed to only three significant figures.)

Problem 16.11

A 0.4157-g sample containing sodium carbonate and inert impurities requires 37.46 mL of 0.1023 *M* HCl for titration. Calculate the percentage of sodium carbonate in the sample.

Solution:

Carbonate ion reacts with hydronium ion according to the equation

$$CO_3^{2-} + 2\, H_3O^+ \rightleftharpoons H_2CO_3 + 2\, H_2O$$

from which it is evident that 2 mol of HCl is required for the complete conversion of 1 mol of carbonate ion to carbonic acid. The number of moles of HCl used is

$$0.03746 \text{ L} \times 0.1023 \text{ mol/L} = 3.832 \times 10^{-3} \text{ mol}$$

Since 2 mol of HCl are required to react with 1 mol of CO_3^{2-}, the number of moles of sodium carbonate present is half this amount, or

$$\frac{3.832 \times 10^{-3}}{2} \text{ mol} = 1.916 \times 10^{-3} \text{ mol}$$

Since the formula weight of Na_2CO_3 is 106.0, the weight of Na_2CO_3 in the sample is

$$1.916 \times 10^{-3} \text{ mol} \times 106.0 \text{ g/mol} = 0.2031 \text{ g}$$

The percentage of Na_2CO_3 in the sample is

$$\frac{0.2031 \text{ g}}{0.4157 \text{ g}} \times 100 = 48.86\%$$

A crucial facet of the acid-base titration is the determination of when the equivalence point is reached. In order to understand more fully the problems involved in this determination, let us now follow the hydronium ion concentration during the titration of 50.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH. At the beginning of the titration, when only 0.100 *M* HCl is present in the flask, the hydronium ion concentration is 0.100 *M* and the pH is 1.000. When hydroxide is added to the flask, the following reaction occurs:

$$OH^- + H_3O^+ \rightleftharpoons H_2O + H_2O$$

This reaction has a very high extent. When 25.0 mL of the hydroxide solution have been added, one-half of the 5.00×10^{-3} mol of HCl originally present has been converted to water, sodium ions, and chloride ions. At this point there is 2.50×10^{-3} mol of hydronium ions in a total of 75.0 mL of solution (assuming the volumes—50.0 mL + 25.0 mL—are additive). Thus, halfway through the titration the hydronium ion concentration is

$$\frac{2.50 \times 10^{-3}\ \text{mol}}{7.50 \times 10^{-2}\ \text{L}} = 0.0333\ M$$

and the pH is 1.478.

As we continue to titrate, we find that when 49.0 mL of hydroxide have been added, only 1.0×10^{-4} mol of hydronium ion remains; the other 4.9×10^{-3} mol has been converted to water by reaction with OH^-. This 1.0×10^{-4} mol is contained in 49 + 50 = 99 mL of solution, and the H_3O^+ concentration is then

$$\frac{1.0 \times 10^{-4}\ \text{mol}}{9.9 \times 10^{-2}\ \text{L}} = 1.0 \times 10^{-3}\ M$$

The pH of the solution one milliliter away from the equivalence point is therefore 3.00.

At the equivalence point, 50.0 mL of the hydroxide solution have been added to the acid solution, and all of the hydronium ions resulting from HCl have been converted to water. The solution at this point is simply an aqueous solution of sodium chloride.

$$Na^+ + OH^- + H_3O^+ + Cl^- \rightleftharpoons 2\,H_2O + Na^+ + Cl^-$$

Since neither sodium ions nor chloride ions react with water, the solution is neither acidic nor basic; that is, $[H_3O^+] = [OH^-] = 10^{-7}\ M$. The pH at the equivalence point is therefore 7.0.

If the titration is continued past the equivalence point, hydroxide ions are simply added to the solution of NaCl. At one milliliter past the equivalence point, where a total of 51.0 mL of hydroxide solution have been added, the amount of hydroxide ion is

$$1.0 \times 10^{-3}\ \text{L} \times 1.0 \times 10^{-1}\ \text{mol/L} = 1.0 \times 10^{-4}\ \text{mol}$$

in 101.0 mL of solution, or

$$\frac{1.0 \times 10^{-4}\ \text{mol}}{0.101\ \text{L}} = 1.0 \times 10^{-3}\ M$$

The pH at this point is therefore 11.00.

Figure 16.8 shows a plot of these five points and others. The titration of any strong acid with any strong base, both at 0.1 *M* concentration, will produce exactly the same curve. The one feature of the curve most relevant to our discussion of the determination of the equivalence point is the very fast rate at which the pH changes around this point and the large pH range over which this change occurs.

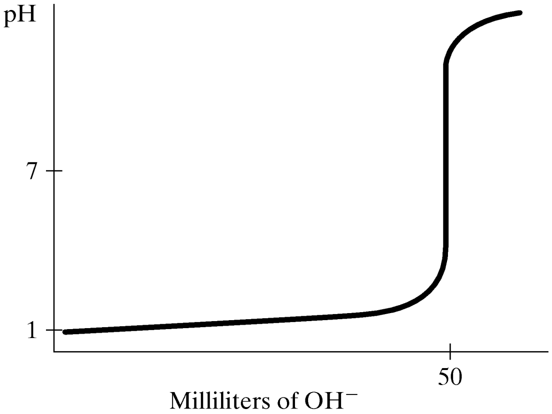


Figure 16.8 The curve for the titration of a strong acid with a strong base.

Theoretically, it would be desirable to find some chemical or physical process that would respond to a pH of 7, the exact pH at the equivalence point. However, the very abrupt change of pH near the equivalence point allows use of a process that responds over a wider, more practical range of pH (say 5 to 9) to detect the equivalence point. Chemically, this can be accomplished with a substance that changes color as the pH changes through the critical region.

Such substances, called indicators, are themselves acids or bases. For example, the indicator called phenol red (see Figure 16.9) can behave as an acid by releasing the proton of the —OH group. Thus, when sufficient hydroxide ions are present in the solution, the indicator reacts to form water and its conjugate base. Because the acid is yellow and the base red, the color of the indicator changes when the acid is converted to its conjugate.

The equilibrium expression for the reaction of the indicator, a weak acid, with water is given by

$$\mathrm{HIn} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{In^-}$$

$$K_a = \frac{[\mathrm{In^-}][\mathrm{H_3O^+}]}{[\mathrm{HIn}]}$$

If this is rearranged as follows, the relationship between the color of the solution and its pH becomes more obvious:

$$[\mathrm{H_3O^+}] = K_a \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]}$$

Thus, when the conversion of the weak acid to its conjugate has occurred to an extent of 50%, and there are therefore equal amounts of HIn and $\mathrm{In^-}$, the hydronium ion concentration will be equal to the indicator constant, K_a, and the color of the indicator will be the result of an equal mixture of red and yellow, i.e., orange. When the indicator reaction has occurred to an extent of 9%, the ratio of [HIn] to $[\mathrm{In^-}]$ will be approximately 10 : 1, the hydronium ion concentration will be 10 K_a, and the color of the solution will be yellow with a tinge of red. If the extent goes below 9%, the human eye is unable to distinguish further gradations in color; the color at 7% and that at, say, 1% will both appear to be yellow. The eye is also unable to distinguish between the color produced by a 90% extent and that produced by, say, a 99% extent. When the indicator reaction has proceeded to 90%, the ratio of [HIn] to $[\mathrm{In^-}]$ is approximately 1:10, the hydronium ion concentration is 0.1 K_a, and the color of the solution is red with a tinge of yellow. Hence, the visible change in indicator color will occur when the hydronium ion concentration is between 10 K_a and 0.1 K_a or, in negative logarithmic units, when

$$\mathrm{pH} = \mathrm{p}K_a \pm 1$$

Methyl orange is an example of a basic indicator. In acidic solution it is converted from its yellow basic form to its red conjugate acid (Figure 16.10). The expression relating the $\mathrm{OH^-}$ concentration in the region of color change to the K_b of the basic indicator is

$$\mathrm{pOH} = \mathrm{p}K_b \pm 1$$

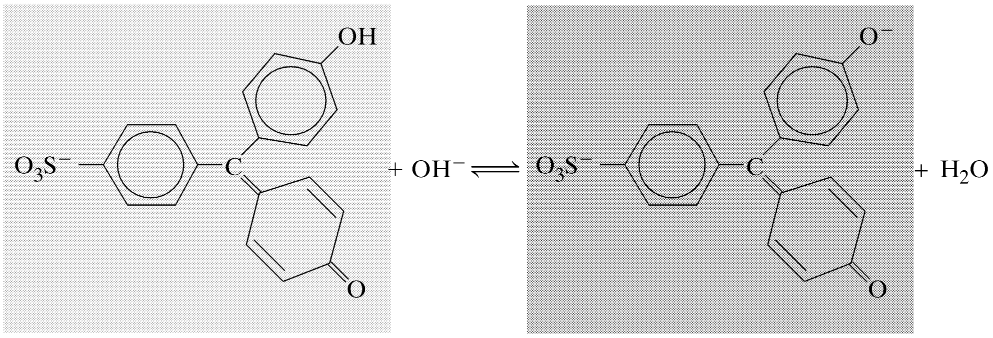


Figure 16.9 The acid-base behavior of phenol red, an indicator.

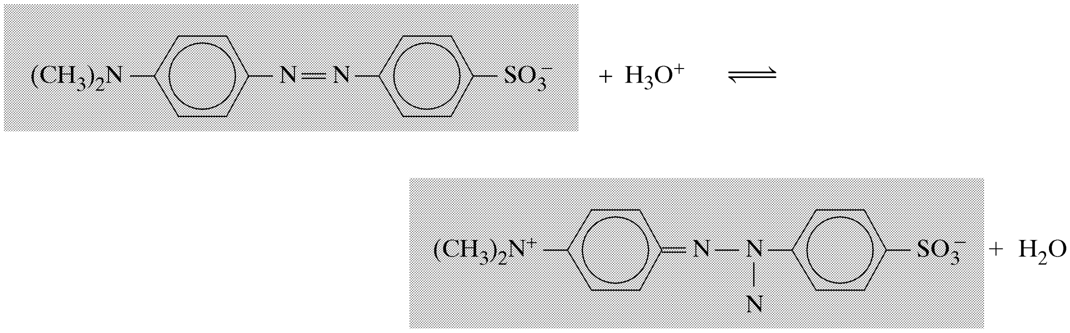


Figure 16.10 The basic indicator, methyl orange.

Table 16.3 lists some common indicators and the pH range in which the color change occurs. These pH ranges have been experimentally determined and in some cases do not extend over the theoretical range of two pH units.

We can now choose an indicator for our titration of HCl. Since the pH at the equivalence point is 7, an indicator changing in the range of 6 to 8 would be most satisfactory, therefore phenol red would be an appropriate choice. Since the change of pH is so abrupt near the equivalence point, indicators such as cresol purple, which changes in the pH region of 7.4 to 9.0, or chlorophenol red, which changes from 4.8 to 6.4, would also be appropriate. Clearly an indicator such as methyl orange, which changes over the range of 3.1 to 4.4, would produce too large an error in the determination of the equivalence point. That is, with methyl orange as the indicator, the endpoint would occur appreciably before the equivalence point was reached and an error would result.

The choice of an indicator becomes more critical in the titration of a weak acid with a strong base or vice versa. To illustrate this point, let us now derive the titration curve for the titration of 50.0 mL of a 0.100 *M* solution of the weak acid acetic acid with the 0.100 *M* solution of sodium hydroxide. At the outset of the titration, when no base has been added, the hydronium ion concentration in the flask is simply that which results from the dissociation of a 0.10 *M* acetic acid solution:

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$$

$$x = [H_3O^+] = [CH_3CO_2^-]$$

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

$$x = 1.3 \times 10^{-3}$$

$$\text{pH} = 2.89$$

As the hydroxide is added to the flask, it reacts with the acetic acid to form acetate ions. When the titration is halfway completed (that is, when 25.0 mL of 0.10 *M* NaOH have been added), half of the acetic acid has been converted to acetate ions. This solution is, of course, a buffer system, and since the ratio of the concentrations of weak acid to its con-

TABLE 16.3 Some Common Indicators

	ACID COLOR	BASIC COLOR	pH INTERVAL
methyl orange	red	yellow-orange	3.1–4.4
methyl red	red	yellow	4.2–6.2
chlorophenol red	yellow	red	4.8–6.4
phenol red	yellow	red	6.4–8.0
cresol purple	yellow	purple	7.4–9.0
phenolphthalein	colorless	red-violet	8.0–9.8
alizarine yellow	yellow	violet	10.1–12.0

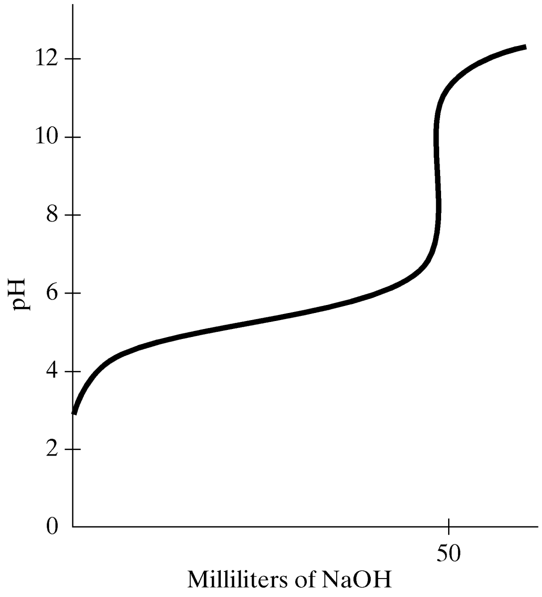


Figure 16.11 Curve for the titration of a weak acid with a strong base.

jugate base is 1, the hydronium ion concentration as given by equation (12) is equal to K_a. The pH at this point is then $-\log[1.8 \times 10^{-5}] = 4.74$.

At the equivalence point, the acetic acid has been converted to acetate ions, and the only source of acetic acid is the reaction of acetate ions with water. Hence, in 100.0 mL of solution there is 0.050 L × 0.100 mol/L = 5×10^{-3} mol of acetate ions and an equal amount of sodium ions. Thus, the hydronium ion concentration is best calculated by considering the reaction of a 0.0500 *M* solution (5×10^{-3} mol/0.100 L = 0.0500 *M*) of acetate ions with water.

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x}$$

$$x = 5.3 \times 10^{-6}$$

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14 - 5.28 = 8.72$$

Thus, at the equivalence point, the pH is 8.7. Figure 16.11 shows the complete titration curve. Comparison of this curve with that for the titration of a strong acid with a strong base reveals that for the weak acid, the pH is considerably higher when the region of rapid change in pH occurs around the equivalence point. Moreover, the pH at the equivalence point is higher, and therefore an indicator such as phenolphthalein, which undergoes its color change in the region 8 to 10, would be appropriate. An indicator such as chlorophenol red, which was perfectly adequate for the strong acid-strong base titration, is certainly not appropriate for this weak acid-strong base titration; its color change occurs in a pH region that is attained before the equivalence point is reached.

Problem 16.12

A 0.3700-g sample of an unknown monoprotic acid is dissolved in enough water to make a total of 50.00 mL of solution. This solution is titrated with a standard 0.1250 *M* NaOH solution, and 40.00 mL are required to reach the equivalence point. When 20.00 mL of the NaOH solution have been added, the pH of the solution is 7.00. Determine (a) the molecular weight of the acid and the molarity of the acid solution, (b) the K_a of the acid, and (c) the indicator that should be used for the titration.

Continued on the next page

Problem 16.12 *Continued*

Solution:

(a) The number of moles of OH^- required to reach the equivalence point is

$$0.0400 \text{ L} \times 0.1250 \text{ mol/L} = 5.000 \times 10^{-3} \text{ mol}$$

Since the acid is monoprotic, this is also the number of moles of acid present in the solution. The molecular weight can be determined as follows:

$$\frac{0.3700 \text{ g}}{\text{Molecular weight}} = 5.000 \times 10^{-3} \text{ mol}$$

$$\text{Molecular weight} = 74.00$$

The molarity of the solution is the number of moles per liter:

$$\frac{5.000 \times 10^{-3} \text{ mol}}{0.05000 \text{ L}} = 0.1000\ M$$

(b) At the midpoint of the titration, when 20.00 mL of the NaOH solution have been added, half of the acid has been converted to its conjugate base:

$$HA + OH^- \longrightarrow A^- + H_2O$$

At this point the ratio of [HA] to $[A^-]$ is 1, and therefore $K_a = [H_3O^+]$:

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

when

$$\frac{[A^-]}{[HA]} = 1, \text{then } K_a = [H_3O^+]$$

A pH of 7.00 corresponds to $[H_3O^+] = 1.0 \times 10^{-7}$ and thus $K_a = 1.0 \times 10^{-7}$.

(c) In order to determine the indicator that should be used for the titration, we must first calculate the pH of the solution at the equivalence point. At this point the acid has been converted to its conjugate base, which reacts with H_2O according to the equation

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

If the solution volumes are additive, the concentration of A^- is

$$\frac{5.000 \times 10^{-3} \text{ mol}}{0.0900 \text{ L}} = 0.056\ M$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$\frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$$

$$= \frac{x^2}{0.056 - x}$$

$$x = 7.5 \times 10^{-5}\ M$$

and

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-5}}$$

$$= 1.3 \times 10^{-10}$$

$$\text{pH} = 9.89$$

Ideally, an indicator whose midrange pH is 9.9 should be used for the titration. Of those listed in Table 16.3, probably phenolphthalein would be most appropriate, even though the pH lies slightly outside its range.

CHAPTER SUMMARY

In Chapters 11 and 15, your study of the concept of **acids** and **bases** was limited to aqueous systems; that is, until this point, acids and bases have been defined in terms of their chemical behavior relative to water. In this chapter the definition of acids and bases has been broadened to include many nonaqueous systems: *an acid is a substance that can release a proton (*hydrogen ion*) and a base is a substance that can accept a proton.* An acid-base reaction, then, is a reaction in which a proton is transferred from an acid to a base. The species formed when an acid releases a proton is called its **conjugate base**; the species formed when a base accepts a proton is called its **conjugate acid**. This view of acids and bases is known as the **Brønsted-Lowry concept**.

From the Brønsted-Lowry definition, it follows that acidity and basicity are entirely *relative* properties. A single substance may behave either as an acid or a base, depending on the other components of a particular reaction. The **acidity** of a substance—its strength as an acid—is a measure of the extent to which it donates a proton to a given base. Similarly, **basicity**—strength as a base—is the extent to which a base accepts a proton from a given acid. The stronger the acid, the weaker its conjugate base; the stronger the base, the weaker its conjugate acid.

Acid strength and base strength are functions of structure. Of particular importance are (1) the electron affinity of the atom to which the transferable proton is attached and (2) the energy of the bond between a transferable proton and the atom to which the proton is attached. You should carefully study the sections on the effect of structure on acidity and basicity until you are able to predict relative acid and base strengths for a variety of substances. Furthermore, you should be able to apply this knowledge of relative acid and base strengths in making qualitative predictions about the extent of proton-transfer reactions. (The reaction tends to move in the direction that produces the *weaker* acid and base.)

Since by far the most common proton-transfer reactions (both in the chemist's laboratory and in nature) are reactions that occur in aqueous solution, the quantitative aspects of aqueous proton-transfer reactions are emphasized. Although water is generally considered a nonelectrolyte, pure water does contain a low concentration of ions, due to the reaction

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

The extent of this reaction is described in terms of the constant K_w, which has a value of 1×10^{-14} at room temperature:

$$[H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$$

Any aqueous solution in which $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ is designated **neutral**. If $[H_3O^+] > [OH^-]$, the solution is said to be **acidic**, and if $[OH^-] > [H_3O^+]$, the solution is said to be **basic**, or alkaline. A common way to describe the acidity of a solution is in terms of the pH scale:

$$\mathrm{pH} = -\log[H_3O^+]$$

You should familiarize yourself with the pH scale and learn to make all the possible conversions between $[H_3O^+]$, $[OH^-]$, pH, and pOH. Because this requires the use of logarithms, you may find it helpful to review the section on logarithms in the Appendix.

One of the major goals in your study of this chapter should be to develop the ability to deal (both qualitatively and quantitatively) with the equilibria involved in a variety of electrolytic solutions. Be sure that you understand the equilibria discussed here, and that you can write the equations for them. You should also be able to calculate the concentrations of all species present and express the acidity of the solutions in terms of pH. The following list summarizes the various types of electrolytic solutions that you must deal with in your study of this chapter.

1. **Solutions of strong acids**: Recall that the common strong acids are HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4. Because these acids can be assumed to be completely dissociated into ions in aqueous solution, the concentration of each ion is

known from the concentration of the electrolyte. For example, in a 0.010 *M* HNO_3 solution, the concentrations of the hydronium and nitrate ions are each 0.010 *M*, and $pH = -\log 0.01 = 2$.

2. **Solutions of strong bases**: The common strong bases are the hydroxides of the alkali and the alkaline earth elements (except Be). Aqueous solutions of strong bases are completely dissociated into ions, and the ion concentrations are apparent from the concentration of the electrolyte. Thus, a 0.010 *M* $Ca(OH)_2$ solution is 0.010 *M* in Ca^{2+} and 0.020 *M* in OH^-.
3. **Solutions of weak acids**: Ion concentrations are not apparent from the concentration of a weak acid (a 0.01 *M* CH_3CO_2H solution, for example, is *not* 0.010 *M* in H_3O^+). Rather, ion concentrations depend on the magnitude of the equilibrium constant K_a. Using K_a, it is possible to calculate the molar concentration of each species present in the solution, as well as the pH and pOH of the solution.

   In the case of polyprotic acids (H2CO3, H3PO4, and so on), ion dissociation occurs in several steps. However, because Ka1 > Ka2 > Ka3, nearly all the hydronium ions come from the first step and the pH can be found using only Ka1.
4. **Solutions of weak bases:** The most commonly encountered weak bases are NH_3 and the amines. Using K_b values, we can calculate the concentrations of species present, including $[OH^-]$, from which we can then obtain the pOH and the pH.
5. **Solutions of salts**: Recall that (with few exceptions) all salts are strong electrolytes; in solution, salts exist only as ions. Therefore, the concentrations of the ions are known from the concentration of the salt. For example, a 0.010 *M* $BaCl_2$ solution contains 0.010 *M* in Ba^{2+} and 0.020 *M* Cl^-.

   When considering the acidity of salt solutions, it is convenient to divide salts into four categories:

   (a) **Salts consisting of the cation of a strong base and the anion of a strong acid**; examples include NaCl, KNO_3, and $CaBr_2$. In salts of this type neither of the ions reacts with water. Thus the equilibrium between water and its ions is unaffected, and the solution is neutral ($pH = 7$).

   (b) **Salts consisting of the cation of a strong base and the anion of a weak acid**; examples are $NaCH_3CO_2$, KNO_2, and $Ca(ClO)_2$. The anions of these salts undergo reaction with water, producing OH^- and making the solution basic ($pH > 7$):

   $$A^- + H_2O \rightleftharpoons HA + OH^-$$

   The ion concentrations and the pH can be calculated using the equilibrium constant derived from the conjugate acid, $K_b = \frac{K_w}{K_a}$.

   (c) **Salts containing the cation of a weak base and the anion of a strong acid**, such as NH_4Cl and NH_4NO_3. In this case, the cation reacts with water, making the solution acidic ($pH < 7$):

   $$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

   The ion concentrations and the pH can be calculated using the equilibrium constant derived from the conjugate base, $K_a = \frac{K_w}{K_b}$.

   (d) **Salts containing the cation of a weak base and the anion of a weak acid**, such as $NH_4C_2H_3O_2$ and NH_4F. In solutions of these salts, both the cation and the anion react with water. The cation produces H_3O^+ and tends to make the solution acidic; the anion produces OH^- and tends to make the solution basic:

   $$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

   $$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

   Whether the solution is acidic or basic depends on which reaction occurs to the greater extent.

The salts in the four categories just listed are all salts of monoprotic acids. When the salts of polyprotic acids are examined, some additional factors must be considered. Polyprotic acids can produce more than one different kind of salt; for example, sulfurous acid (H_2SO_3) is the parent acid of two different sodium salts, Na_2SO_3 and $NaHSO_3$. Solutions of salts that contain hydrogen in the anion are somewhat more difficult to deal with quantitatively. Sodium hydrogen sulfite ($NaHSO_3$) is a strong electrolyte that is completely dissociated into Na^+ and HSO_3^- in solution. The anion, however, undergoes two different reactions with water:

$$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$$

$$HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$$

The first reaction makes the solution acidic; the second reaction makes the solution basic. Thus, whether a solution is acidic or basic depends on which one of these reactions occurs to the greater extent; that is, which of these reactions has the larger equilibrium constant.

6. **Buffer solutions**: Buffer solutions are solutions that contain either (a) a weak acid and a salt of that acid (for example, CH_3CO_2H and $NaC_2H_3O_2$) or (b) a weak base and a salt of that base (for example, NH_3 and NH_4Cl). You can treat buffer solutions quantitatively if you use the appropriate K_a or K_b and recognize the role of the common ion.

The final section of the chapter deals with acid-base titrations. You should understand the procedure followed in this technique, learn the pertinent terminology, and be able to carry out calculations. Note that the **equivalent weight** of an acid or a base is its formula weight divided by the number of protons it donates or accepts.

An understanding of acid-base indicators is essential to the understanding of acid-base titrations. It is not necessary for you to memorize the names, formulas, and pH intervals of specific indicators, but you should know how indicators function and understand the significance and the origin of the pH interval.

TERMS

Some important terms include

Monoprotic acid or base An acid or base that can provide or accept only one proton per molecule.

Polyprotic acid or base An acid or base that can provide or accept more than one proton per molecule. Polyprotic acids and bases can be further described as *diprotic*, *triprotic*, and so on.

Amphiprotic substance A substance that can function as both a Brønsted-Lowry acid and base. For example, water is amphiprotic, because it can either give up or accept a proton.

Inductive effect The alteration of electron density at a given atom by an atom (or group of atoms) that is one or more bonds away. The effect results from changes induced in the electron density of intervening bonds. For example, the fact that chloroacetic acid is a stronger acid than acetic acid can be explained by the inductive effect of the chlorine on the oxygen of the −OH group.

Ion product of water, K_w The equilibrium constant for the self-ionization of water:

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

In any aqueous solution, K_w is the product of the molar concentrations of hydronium ion and hydroxide ion. At room temperature, K_w has a value of approximately 1×10^{-14}:

$$[H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$$

pH The negative logarithm of the hydronium ion concentration; pH = $-\log[H_3O^+]$. Similarly, pOH = $-\log[OH^-]$; $pAg^+ = -\log[Ag^+]$; and so on.

Acid dissociation constant, K_a An equilibrium constant for the dissociation of a weak acid in water:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \text{ or}$$

the reaction of an acidic ion with water; for example,

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

In these cases, the K_a must be determined from the K_b of the conjugate base as

$$K_a = \frac{K_w}{K_b}$$

Base dissociation constant, K_b An equilibrium constant for the dissociation of a weak base in water:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}, \text{ or}$$

the reaction of a basic ion with water; for example,

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

In these cases, the K_b must be determined form the K_a of the conjugate acid as

$$K_b = \frac{K_w}{K_a}$$

Hydrolysis constant, K_h In some texts the equilibrium constant for the reaction of a cation or an anion with water is referred to as K_h. In this text we use the term K_a or K_b for the equilibrium constant for the reaction of ions with water. These K_a or K_b values, however, cannot be found in the K_a or K_b tables (the tables are generally restricted to molecular acids and bases).

Cation hydrolysis:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

$$\frac{[B][H_3O^+]}{[BH^+]} = K_h = \frac{K_w}{K_b}$$

Anion hydrolysis:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$\frac{[HA][OH^-]}{[A^-]} = K_h = \frac{K_w}{K_a}$$

Buffer solution A solution that tends to resist changes in pH. A buffer solution consists of a weak acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$; HCO_3^-/CO_3^{2-}; and so on), or a weak base and its conjugate acid (NH_3/NH_4^+).

Titration An analytical procedure whereby a solution of one reactant (the **titrant**) is slowly added from a buret to a solution of a second reactant. From the volume and the concentration of titrant used, the amount of the second reactant can be calculated.

Standard solution Any solution of accurately known concentration.

Equivalence point The point in a titration when the amount of titrant that has been added is exactly equivalent to the amount of the substance being titrated.

Indicator Any substance that produces a visible change to signal the end of a titration.

Endpoint The point in a titration at which the indicator undergoes a visible change. (Note that the terms "endpoint" and "equivalence point" are *not* synonymous.)

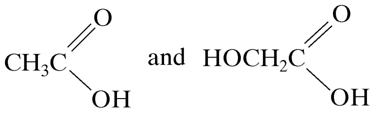
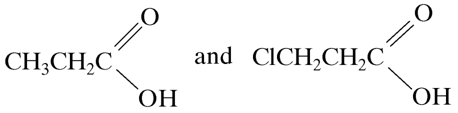
Acid-base indicators Compounds that undergo color changes at the endpoints in acid-base titrations. These indicators are weak acids or bases whose dissociated forms are not the same color as their undissociated forms. For example, if HIn represents an indicator that is a weak acid, then in aqueous solution

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

and HIn and In^- have different colors.

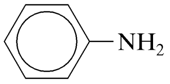
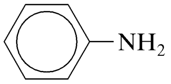
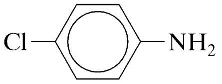
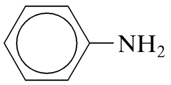
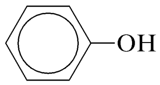
pH interval The pH range over which a given acid-base indicator changes completely from one color to another. This interval is approximately two pH units.

PROBLEMS

1. For each of the following pairs of acids, predict which is the stronger:
- (a) NH_3 and PH_3
- (b) $H_2C_2O_4$ and $HC_2O_4^-$
- (c) SiH_4 and PH_3
- (d) NH_3 and H_2O
- (e) HCl and HBr
- (f) 
- (g) 
- (h) $P(OH)_3$ and $As(OH)_3$
- (i) ClOH and BrOH
- (j) H_2CO_3 and H_2SO_3
- (k) NH_4^+ and NH_3
- (l) H_2S and HS^-

2. For each of the following pairs of bases, predict which is the stronger:
- (a) $B(OH)_3$ and $Al(OH)_3$
- (b) BeO and BaO
- (c) CH_3^- and NH_2^-
- (d) NH_3 and NH_2^-
- (e) F^- and Cl^-
- (f) S^{2-} and O^{2-}
- (g) PO_4^{3-} and HPO_4^{2-}
- (h) OH^- and O^{2-}
- (i) $HONH_2$ and $ClNH_2$
- (j) $NaNH_2$ and $ClNH_2$
- (k) PH_3 and AsH_3
- (l) HCO_3^- and HSO_3^-

3. Provide explanations for the following observations:
- (a) $HClO_3$ is a stronger acid than $HClO_2$.
- (b) H_2S is a stronger acid than H_2O.
- (c) NH_3 is a stronger base than PH_3.
- (d) LiOH is a base and ClOH is an acid.
- (e) HClO is a stronger acid than HIO.

4. For each of the following pairs of bases predict which is the stronger:
- (a) CH_3^-, NH_2^-
- (b) NH_3, NH_2^-
- (c) F^-, Cl^-
- (d) S^{2-}, O^{2-}
- (e) PO_4^{3-}, HPO_4^{2-}
- (f) OH^-, O^{2-}
- (g) $HONH_2$, CH_3NH_2
- (h)  , CH_3NH_2
- (i) $NaNH_2$, $ClNH_2$
- (j)  , 
- (k)  , 

5. Predict which acid in each of the following pairs of acids is stronger:
- (a) HIO_3 and HIO
- (b) $ClCH_2CO_2H$ and $ClCH_2CH_2CO_2H$
- (c) $HAsO_4^{2-}$ and H_3AsO_4
- (d) H_2SO_3 and H_2SeO_3
- (e) HClO and HIO

6. Predict which base in each of the following pairs of bases is stronger:
- (a) PO_4^{3-} and HPO_4^{2-}
- (b) NO_2^- and NO_3^-
- (c) NH_3 and $HONH_2$
- (d) HS^- and S^{2-}
- (e) $Be(OH)_2$ and $Ba(OH)_2$

7. Circle the species in each of the following pairs that is more acidic.
- (a) FCH_2CH_2COOH, $CH_3CHFCOOH$
- (b) HOCl, HOBr
- (c) NH_3, PH_3
- (d) trifluoroacetic acid, difluoroacetic acid

8. Explain the following decreasing order of base strength:

$$NH_3 > H_2NNH_2 > NH_2OH > NF_3$$

9. Phosphorous acid (H_3PO_3) behaves as a diprotic acid, with $K_{a1} = 1.6 \times 10^{-2}$ and $K_{a2} = 7 \times 10^{-7}$. Available x-ray data show that one of the P—O bonds is shorter than the other two P—O bonds.
(a) Suggest an electron dot structure for phosphorous acid.
(b) Determine whether a solution of NaH_2PO_3 is acidic, basic, or neutral.

10. Predict whether the extent of each of the following reactions is greater than or less than 50%:
(a) $H_2SO_4 + C_2H_3O_2^- \rightleftharpoons HSO_4^- + H_2C_2H_3O_2$
(b) $F^- + H_2O \rightleftharpoons HF + OH^-$
(c) $HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$
(d) $NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$
(e) $C_6H_5NH_2 + C_2H_5NH_3^+ \rightleftharpoons C_6H_5NH_3^+ + C_2H_5NH_2$

11. Predict whether each of the following reactions carried out in aqueous solution has $K > 1$ or $K < 1$ or $K = 1$.
(a) $BaCl_2 + Zn(NO_3)_2 \rightarrow Ba(NO_3)_2 + ZnCl_2$
(b) $BaSO_4 + Pb(NO_3)_2 \rightarrow PbSO_4 + Ba(NO_3)_2$
(c) $H_2SO_3 + 2\ KNO_3 \rightarrow K_2SO_3 + 2\ HNO_3$
(d) $HClO_3 + ClO_2^- \rightarrow HClO_2 + ClO_3^-$
(e) $HS^- + HS^- \rightarrow H_2S + S^{2-}$
(f) $HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$

12. For each of the following reactions, predict whether the extent is greater than or less than 50%:
(a) $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$
(b) $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
(c) $HCO_2H + NO_2^- \rightleftharpoons HNO_2 + HCO_2^-$
(d) $HNO_2 + HS^- \rightleftharpoons H_2S + NO_2^-$
(e) $H_2CO_3 + CO_3^{2-} \rightleftharpoons HCO_3^- + HCO_3^-$
(f) $NH_4^+ + CH_3CO_2^- \rightleftharpoons CH_3CO_2H + NH_3$
(g) $C_6H_5CO_2^- + CH_3CO_2H \rightleftharpoons C_6H_5CO_2H + CH_3CO_2^-$
(h) $C_6H_5OH + OCl^- \rightleftharpoons HOCl + C_6H_5O^-$

13. Estimate the extent ($K > 1$ or $K < 1$) of each of the following reactions:
(a) $CH_3CH_2CO_2H + H_2O \rightleftharpoons CH_3CH_2CO_2^- + H_3O^+$
(b) $CH_3CH_2CO_2H + OH^- \rightleftharpoons CH_3CH_2CO_2^- + H_2O$
(c) $CH_3CH_2CO_2^- + H_2O \rightleftharpoons CH_3CH_2CO_2H + OH^-$
(d) $SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$
(e) $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$
(f) $HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$

14. 30.50 mL of an HCl solution are required to titrate a dry sample of 0.5110 g of Na_2CO_3. Determine the molarity of the HCl solution.

15. You are given two beakers, each of which contains a solution of some acid. Although the acid in beaker A is different from the acid in beaker B, the pH of the solution in A is the same as the pH of the solution in B. Is it valid to state that the molar concentration of the acid in A equals the molar concentration of the acid in B? Give a thorough explanation of your answer.

16. Calculate the pH of solutions with the following hydronium ion concentrations:
(a) $1.5 \times 10^{-4}\ M$
(b) $5.0 \times 10^{-8}\ M$
(c) $8 \times 10^{-13}\ M$

17. Calculate the pH of solutions with the following hydroxide ion concentrations:
(a) $1.0\ M$ (b) $6.7 \times 10^{-6}\ M$ (c) $4 \times 10^{-10}\ M$

18. Calculate the hydronium ion concentrations for solutions with the following values for pH:
(a) 1.53 (b) 3.62 (c) 11.73

19. Calculate the pH and pOH of the following:
(a) 0.980 g of NaOH dissolved in 250 mL of water.
(b) 2.5 mL of 12 *M* HCl diluted to 200 mL with distilled water.
(c) 10.0 mL of 0.10 *M* KOH mixed with 5.0 mL of 0.20 *M* HCl.
(d) 150.0 mL of 0.10 *M* KOH mixed with 250.0 mL of 0.10 *M* HCl.
(e) 200 mL of 0.10 *M* NaOH mixed with 100 mL of 0.10 *M* KOH.

20. A 0.10 M solution of propanoic acid has a pH of 3.0. Calculate K_a for this acid.

21. When 5.1 g of trimethylacetic acid is dissolved in enough water to make one liter of solution, the pH of the solution is 3.2. Calculate the K_a for trimethylacetic acid.

22. A 1.0 *M* solution of *N*-methylaniline has a pH of 9.35. Calculate K_b for this base.

23. Determine the pH of a 0.0033 *M* ammonia solution.

24. Calculate the pH of a 0.16 *M* lactic acid solution ($C_3H_6O_3$, $K_a = 1.4 \times 10^{-4}$).

25. Calculate the concentrations of all species in each of the following solutions:
(a) 0.10 *M* formic acid
(b) 1.0 *M* dichloroacetic acid
(c) 0.010 *M* triethylamine
(d) 0.15 *M* aniline ($C_6H_5NH_2$)

26. 10.0 g of a monoprotic acid that has a molecular weight of 100.0 is dissolved in enough water to make 1.00 L of solution. The pH of the resulting solution is 4.00. Determine the K_a of the acid.

27. The pH of a $1.0 \times 10^{-2}\ M$ solution of a monoprotic acid (MW-135) is 5.00. Determine K_a for the acid.

28. Morphine is a weak monoprotic base. A 0.10 *M* solution of this compound has a pH of 10.43. What is the K_b of morphine?

29. Calculate the pH of each of the following solutions:
(a) 0.010 *M* HNO_2
(b) 0.10 *M* H_2S
(c) 0.010 *M* H_2NOH

30. The pH of a household cleaning solution is 11.87. This cleanser is an aqueous solution of ammonia with a density of 1.00 g/mL. What is the mass percentage of ammonia in the solution?

31. As a quality control chemist for a pickle processor, you find that the vinegar from a certain supplier is 4 wt-% acetic acid and has a density of 1.004 g/mL. If the process requires vinegar with a pH between 2.4 and 3.4, is this vinegar acceptable?

32. Explain the following observations:
- (a) In general, $K_{a1} > K_{a2} > K_{a3} \ldots.$
- (b) Barium carbonate dissolves in 1 M HCl, but barium sulfate does not.
- (c) Copper(II) carbonate dissolves in 1 M HCl, but copper(II) sulfide does not dissolve.
- (d) When an open bottle of HCl is brought close to an open bottle of aqueous NH_3, a "white smoke" forms.

33. If finely powdered limestone ($CaCO_3$) is thoroughly stirred with a solution that is 1.0×10^{-3} M in ferric ion, ferric hydroxide precipitates.
- (a) Why did ferric hydroxide rather than ferric carbonate precipitate?
- (b) Write chemical equations to explain the precipitation of ferric hydroxide.

34. Explain the fact that a 0.155-g sample of sodium oxide dissolved in 100 mL of water has pH of 12.70.

35. Calculate the concentration of H_3O^+ and S^{2-} in 1.0×10^{-2} M H_2S.

36. A certain solution is 1×10^{-1} M in each of the following ions: Fe^{2+}, Cu^{2+}, Hg^{2+}, and Co^{2+}. When the solution is saturated with H_2S, which sulfides will precipitate?

37. Calculate the sulfide ion concentration in a saturated solution of H_2S that is 5.0×10^{-2} molar in HCl. How much copper(II) sulfide would dissolve in one liter of this solution?

38. A solution is 1.0×10^{-2} M in Cd^{2+} and 5.0×10^{-2} M in Zn^{2+}. If this solution is saturated with H_2S, what hydronium ion concentration is required to allow the precipitation of ZnS to begin? What concentration of Cd^{2+} remains in solution at this pH?

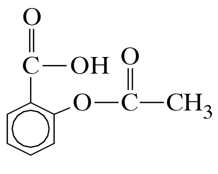
39. A 0.010 mole sample of an acid HA is dissolved in sufficient water to make a total of 1.0 liter of solution. The pH of this solution was 2.79.
- a. Calculate the K_a for the acid.
- b. Calculate the concentration of all species in a 1.0 M solution of the sodium salt of the conjugate base, NaA.

40. The pH of a 0.10 M aqueous solution of sodium hypobromite (NaOBr) is 10.84.
- (a) Calculate the equilibrium constant for the reaction of OBr^- with H_2O.
- (b) Calculate the K_a for HOBr.

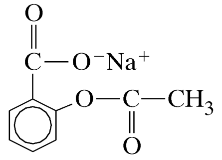
41. Provide the conjugate base of propanoic acid and its K_b value.

42. Provide the conjugate acid of ethyl amine and its K_a value:

43. Aspirin has an acid dissociation constant of 3×10^{-4}.



- (a) Calculate the pH of a 0.1 M aspirin solution.
- (b) Calculate the pH of a 0.1 M solution of



44. The pH of a 0.10 M aqueous solution of methylammonium chloride ($CH_3NH_3^+$, Cl^-) is 5.80.
- (a) Calculate K_a for methylammonium chloride.
- (b) Calculate K_b for methylamine.

45. Triphenylchlorosilane, $(C_6H_5)_3SiCl$, reacts with OH^- to form the silanol $(C_6H_5)_3SiOH$.
- (a) $(C_6H_5)_3SiOH$ is an acid. Write an equation showing it reacting with water.
- (b) When 1.0 mol of $(C_6H_5)_3SiOH$ is dissolved in 1.0 L of water, the pH of the resulting solution is 6.0. Calculate the K_a for $(C_6H_5)_3SiOH$.
- (c) Give the formula of the conjugate base of this acid and determine the equilibrium constant for the reaction of it with water.

46. The K_b for hydrazine (N_2H_4) is 1.0×10^{-6}.
- (a) What is the value of K_a for $N_2H_3^+$, the conjugate acid of hydrazine?
- (b) If the initial concentration of hydrazine is 0.20 M, what is the resulting pH of the solution after it has reached equilibrium?

47. What is the solubility and the pH of an aqueous solution when 78.0 g of calcium fluoride are mixed with 1.00 L water?

48. Calculate the concentrations of all species in each of the following solutions:

(a) 1.0 M NH_4Cl (b) 0.010 M $NaNO_2$ (c) 0.10 M KF

49. Calculate the pH of each of the following aqueous solutions:
- (a) 0.50 M NH_3
- (b) A solution prepared by dissolving 5.35 g of NH_4Cl in water and diluting to 500 mL.
- (c) A solution prepared by mixing 200 mL of the solution in (a) with 300 mL of the solution in (b).

50. Determine whether each of the following aqueous solutions is acidic, basic, or neutral. Also determine the equilibrium constants for all reactions.

(a) KBr (b) NH_4Br (c) KCN
(d) CsHS (e) NH_4CN

51. Determine whether a 0.1 M solution of each of the following is acidic, basic, or neutral:

(a) NH_4NO_2 (b) KHS

52. Determine whether 0.1 M solutions of each of the following salts will be acidic, basic, or neutral:

(a) NH_4Cl (b) $(NH_4)_2C_2O_4$ (c) $KHCO_3$
(d) Rb_3PO_4 (e) $Ba(NO_3)_2$ (f) K_2SO_3
(g) NaH_2PO_4 (h) NH_4CN (i) $Al(NO_3)_3$
(j) $NaHSO_3$ (k) $(C_6H_5NH_3)CN$ (l) $Fe_2(SO_4)_3$
(m) KBr

53. Determine whether an aqueous solution of NaH_2PO_4 is acidic, basic, or neutral. Show all appropriate equations and calculations.

54. Calculate the F^- concentration and the pH of a solution containing 0.20 *M* HF in 0.10 M HCl. K_a for HF = 6.8×10^{-4}.

55. Estimate the pH of a 0.12 *M* solution of ammonium nitrite. Show all work and clearly state any assumptions or approximations made.

56. A solution contains 0.17 mol of acetic acid and 0.050 mol of sodium acetate in 1.0 L of solution.
- (a) What is the pH of the solution?
- (b) What is the pH of this solution after 0.010 mol of OH^- is added?
- (c) How much would the addition of 0.01 mol of OH^- change the pH in 1.0 L of pure water?

57. If you had 100 mL of a 0.10 *M* solution of acetic acid, which of the following would increase the pH to the greatest extent? Assume that volumes are additive and give calculations to support your answers.
- (a) addition of 100 mL of a 0.10 *M* solution of sodium hydroxide
- (b) addition of 1860 mL of water
- (c) addition of 50 mL of a 0.10 *M* solution of sodium acetate

58. Describe how you would prepare an acetic acid-acetate buffer solution designed to maintain a pH of 5.0.

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

59. How many grams of NH_4Cl must be added to 100 mL of 0.25 *M* NH_3 in order to produce a pH of 8.2?

60. (a) What is the pH of one liter of a solution containing 0.10 mol of chloroacetic acid and 0.20 mol of sodium chloroacetate?

$$ClCH_2CO_2H + H_2O \rightleftharpoons H_3O^+ + ClCH_2CO_2^-$$

(b) What is the pH of the solution in (a) after the addition of 1.0×10^{-2} mol of HCl? After the addition of 1.0×10^{-2} mol of NaOH?

61. (a) Calculate the resulting pH when 5.0 mL of 1.0 *M* HCl is added to 100.0 mL of a buffer (pH = 9.25) that is comprised of 0.10 *M* NH_3 and 0.10 *M* NH_4Cl.

(b) For the same buffer solution, calculate the resulting pH if 5.0 mL of 1.0 *M* NaOH had been added instead of the HCl.

62. How many grams of NH_4Cl must be added to 100 mL of 0.1 *M* NH_3 in order to create a buffer that will maintain the pH at 9.25.

63. What concentration of sodium acetate is needed to prepare 1.00 L of a buffer which has a pH of 4.83 and an acetic acid concentration of 0.75 *M*?

64. A variety of chemicals, such as NaOCl, are used to chlorinate water in order to kill microorganisms. The agent responsible for the destruction of these organisms is hypochlorous acid, which is formed in the reaction:

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

With high pH, the solution contains mostly hypochlorite ion, which is inactive. If the pH is low, the major species will be HOCl, but the rate of corrosion and dissolution of swimming pool surfaces and tiles increases. As a compromise a pH of about 7.50 is usually maintained. Determine the ratio of HOCl to OCl^- at this pH.

65. Antacids used to neutralize excess acidity in the stomach generally contain either the water-insoluble hydroxides $Al(OH)_3$ and $Mg(OH)_2$ or calcium carbonate. Discuss the relative merits of the two types.

66. Calculate the pH of the solutions resulting from each of the following reactions:
- (a) 50 mL of 0.20 *M* HCl + 50 mL of 0.20 *M* KOH
- (b) 30 mL of 0.10 *M* HCl + 30 mL of 0.10 *M* NH_3
- (c) 25 mL of 0.20 *M* HCN + 25 mL of 0.20 *M* NaOH

67. Calculate the pH of the solution that results when the following are mixed:
- (a) 20 mL of 0.080 *M* ammonia mixed with 40 mL of H_2O.
- (b) 20 mL of 0.080 *M* ammonia mixed with 40 mL of 0.030 *M* NH_4Cl.
- (c) 20 mL of 0.080 *M* ammonia mixed with 40 mL of 0.040 *M* HCl.
- (d) 20 mL of 0.080 *M* ammonia mixed with 40 mL of 0.040 *M* NaOH.

68. Calculate the solubility of $Mg(OH)_2$ in an aqueous solution buffered at pH = 12.00.

69. If 10 mL of a solution 2.0 *M* in ammonia and 1.0 *M* in ammonium chloride is added to 10 mL of a 0.10 *M* solution of manganese(II) nitrate, will manganese(II) hydroxide precipitate? Assume additivity of volumes.

70. A solution of 3.15 g of an acid dissolved in 100 g of benzene boils at 80.985 °C (the boiling point of pure benzene is 80.099 °C). A 0.2145-g sample of the same acid requires 45.22 mL of a 0.1054 *M* sodium hydroxide solution for complete neutralization. Complete combustion of 1.004 g of the acid produced 0.9817 g CO_2 and 0.2007 g H_2O.
- (a) Calculate the equivalent weight of the acid.
- (b) Calculate the molecular weight and molecular formula of the acid.
- (c) Write an electron dot formula for the acid.

71. Complete combustion of 0.3045 g of a monoprotic base produced 0.5955 g of CO_2 and 0.4263 g of H_2O. A 0.1562-g sample, when analyzed for nitrogen, yielded 43.00 mL of nitrogen gas collected at 25 °C and 750 torr. A 0.1891-g sample of the base required 38.06 mL of a 0.1104 *M* HCl solution for complete neutralization. Determine the molecular formula of the base.

72. A 50.0 mL sample of 1.0 *M* NH_3 is titrated with 1.0 *M* HCl.
- (a) Calculate the pH at the beginning of the titration; i.e. before any titrant has been added.
- (b) Calculate the pH when 40.0 mL of HCl have been added.
- (c) Calculate the pH at the equivalence point.
- (d) If an indicator is chosen that changes color when 40.0 mL of HCl has been added, what is the K_a of that indicator?

73. For the titration of 50.0 mL of 0.100 M acetic acid with 0.100 M NaOH:
(a) Calculate the pH at the beginning of the titration
(b) Calculate the pH when 40.0 mL of 0.100 M NaOH have been added.
(c) Calculate the pH at the equivalence point.
(d) What indicator should be used for this titration.

74. This question concerns the titration of 50.00 mL of a 0.1000 M solution of m-FC_6H_4COOH (meta-fluorobenzoic acid) with 0.1000 M NaOH.
(a) At the beginning of the titration how many moles of m-FC_6H_4COOH are present?
(b) What is the pH of the solution at the beginning of the titration?
(c) What is the pH of the solution at the midpoint of the titration?
(d) What is the pH of the solution when 35 mL of titrant have been added?
(e) What is the pH of the solution at the equivalence point?
(f) What indicator should be used for this titration?
(g) If bromocresol green is used as the indicator, how many mL of titrant will have been added when the endpoint is reached?
(h) Carefully discuss and explain (rationalize) the difference in acidity of meta and parafluorobenzoic acid.

75. A 10.00-mL sample of table wine was diluted to 100.00 mL and titrated to a phenolphthalein end point with 25.62 mL of 0.04090 M aqueous NaOH. Assuming that both acidic hydrogens of tartaric acid ($H_2C_4H_4O_6$) completely react with the base, express the acidity of the wine in terms of grams of tartaric acid per 100 mL.

76. A titration of a 50.0-mL sample of 0.125 M NH_3 solution was done using 0.0250 M HCl.
(a) Calculate the volume a HCl required to reach the equivalence point.
(b) Calculate the equivalence point pH.
(c) Choose an indicator for this titration.

77. A 100.0-mL sample of a 0.020 M weak monoprotic acid solution was titrated with 0.050 M NaOH. If the pH of the solution is 6.00 after the addition of 20.0 mL of NaOH, find the K_a of the weak acid.

78. What mass of of a commercial antacid must be consumed to return 95.0 mL of 0.25 M stomach acid (HCl) to its usual proton concentration of 0.10 M? Assume that the antacid is composed of pure $NaAl(OH)_2CO_3$ and that the stomach is just a container for the reaction.

79. What volume of 0.125 M KOH(aq) is required to just neutralize 3.5 g of HCl(g) which has been dissolved in enough water to make 250.0 mL of acid solution?

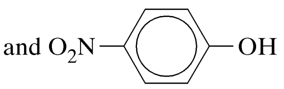
80. Calculate the pH at the equivalence point in each of the following titrations. In each case, choose a suitable indicator from Table 16.3 in your text.
(a) 25.0 mL of 0.080 M NH_3 is titrated with 0.10 M HCl
(b) 40.0 mL of 0.10 M HNO_2 is titrated with 0.20 M KOH
(c) 50.0 mL of 0.10 M NaOH is titrated with 0.085 M HNO_3.

81. A 20.00-mL sample of aqueous hydrazine, H_2NNH_2, was titrated with a 0.1000 M HCl solution. The equivalence point was reached when 25.00 mL of the HCl solution had been added to the hydrazine solution. (a) Determine the pH at the equivalence point. (b) Calculate the pH of the initial hydrazine solution. (c) Could an acid-base indicator with $K_a = 1 \times 10^{-7}$ be used effectively in this titration? Explain.

82. An analyst used exactly 35.13 mL of a solution of potassium hydroxide to neutralize 50.00 mL of a solution that contained 0.4924 g of potassium hydrogen sulfate ($KHSO_4$).
(a) Calculate the molarity of the KOH solution.
(b) Calculate the molarity of the $KHSO_4$ solution.
(c) Determine the pH of the solution at the equivalence point.

83. You are given 0.010 M solutions of the following acids:

HNO_3, $ClCH_2CO_2H$, and



Choose an indicator for each titration.

84. When 1.00×10^{-2} mol of p-chlorobenzoic acid is dissolved in enough water to make one liter of solution, the pH of the solution is 3.02.
(a) Calculate the K_a of p-chlorobenzoic acid.
(b) Calculate the pH of a 1.0 M solution of the acid.
(c) Calculate the pH of a 0.10 M solution of sodium p-chlorobenzoate.
(d) Calculate the concentration of all species in one liter of a solution that contains 1.0 mol of p-chlorobenzoic acid and 0.10 mol of sodium p-chlorobenzoate.

85. A 50.0-mL portion of a 0.100 M solution of p-chlorobenzoic acid is titrated with a 0.100 M NaOH solution.
(a) List all species present at the equivalence point and calculate their concentrations.
(b) Determine the pH at the equivalence point.
(c) Use Table 16.3 to select a suitable indicator for this titration.
(d) Assume that methyl orange is used as the indicator for the titration. How many milliliters of NaOH solution will have been added when the endpoint has been reached? (Assume the endpoint to occur in the middle of the indicator range.) What percentage of error would this produce?

86. Liquid ammonia is a fairly common nonaqueous medium for acid-base reactions. Since ammonia is similar to water in many of its properties, reactions in liquid ammonia are analogous to their counterparts in water (there are also some important differences). Fundamental to an understanding of reactions in ammonia is its self-ionization, which is strictly analogous to the self-ionization of water.
(a) Write an equation and equilibrium expression for the self-ionization of ammonia.
(b) The equilibrium constant for the self-ionization of liquid ammonia is 2×10^{-33} at −50 °C. Explain the difference between this value and the value for water (ignore the temperature difference) in terms of the

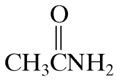
strength of H_2O as an acid and as a base relative to the strength of NH_3 as an acid and as a base. (*Hint:* Determine and compare the values of K_a and K_b for H_2O and K_a and K_b for NH_3 in water.)

(c) What are the ammonia analogs of H_3O^+ and OH^-? Define the ammonia analogs of pH [pH(NH_3)] and pOH, and calculate the pH(NH_3) of liquid ammonia.

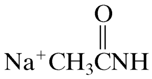
(d) What is the pH(NH_3) of an acidic liquid ammonia solution?

(e) Calculate the pH(NH_3) of a 1×10^{-3} *M* solution of $NaNH_2$ in liquid ammonia and a 1×10^{-3} *M* solution of NH_4Cl in liquid ammonia.

(f) Write an equation for a neutralization reaction carried out in liquid ammonia.

87. Ammonia is a stronger base than water and therefore can be used to differentiate the acidities of very weak acids. Acetamide  $CH_3\overset{\overset{O}{\|}}{C}NH_2$ is too weak an acid to affect the pH of a water solution, but it does lose protons in liquid ammonia.

(a) Write an equation and equilibrium expression for the reaction of acetamide with liquid ammonia. Assume the equilibrium constant for this reaction is 10^{-5} and calculate the pH(NH_3) of a 0.1 *M* solution of acetamide in liquid ammonia.

(b) Calculate the pH(NH_3) of a 0.1 *M* solution of  $Na^+CH_3\overset{\overset{O}{\|}}{C}NH^-$ in liquid ammonia.

88. Multiple-choice questions

1. Which aqueous solution has the highest pH?
   (a) 0.01 *M* HCl (b) 0.01 *M* HClO
   (c) 0.01 *M* NaCl (d) 0.01 *M* NaClO

2. Which requires the largest volume of 0.20 *M* NaOH for neutralization?
   (a) 50 mL of 0.10 *M* HCl
   (b) 50 mL of 0.10 *M* $HC_2H_3O_2$
   (c) 25 mL of 0.20 *M* HCN
   (d) all of the above require the same volume

3. Which of the following ions is the strongest base?
   (a) CN^- (b) ClO_4^-
   (c) NH_4^+ (d) Cl^-

4. From the following list of hypothetical acid-base indicators and their dissociation constants, choose the one that would be most satisfactory for the titration of 0.10 *M* HClO with 0.10 *M* KOH:
   (a) indicator A; $K_a = 1 \times 10^{-3}$
   (b) indicator B; $K_a = 1 \times 10^{-5}$
   (c) indicator C; $K_a = 1 \times 10^{-7}$
   (d) indicator D; $K_a = 1 \times 10^{-9}$

5. A solution of a salt of the type NaHX
   (a) is always acidic (b) is always basic
   (c) is always neutral (d) none of the above

6. According to the Brønsted-Lowry concept, HSO_4^- is
   (a) an acid (b) a base
   (c) amphiprotic (d) a salt

7. Of the four species H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, the strongest acid is
   (a) H_3PO_4 (b) $H_2PO_4^-$
   (c) HPO_4^{2-} (d) PO_4^{3-}

8. The equilibrium constant for the reaction

$$H_3BO_3 + ClO^- \rightleftharpoons H_2BO_3^- + HClO$$

   is 1.9×10^{-2}. The strongest acid is
   (a) H_3BO_3 (b) ClO^-
   (c) $H_2BO_3^-$ (d) HClO

89. Choose the most correct answer:

(a) Which acid is the strongest?

FCH_2COOH, $ClCH_2COOH$, $BrCH_2COOH$

(b) Which is acidic in aqueous solution?

NaF, K_2SO_3, KH_2PO_4

(c) Which is basic in aqueous solution?

$KHCO_3$, NH_4Br, KNO_3

(d) What is the approximate value of the equilibrium constant for the following reaction?

$$OCl^- + H_2O \longrightarrow HOCl + OH^-$$

10^{-6}, 10^{-8} 10^{-12}

(e) What is the approximate pH of a 1 *M* H_2SO_3 solution?

8, 7, 3, 1

(f) If a 1 M aqueous solution of a base has a pH of 12, what is the approximate value of the equilibrium constant for the reaction of that base with water?

10^{-10}, 10^{-8}, 10^{-6}, 10^{-4}

(g) Which of the following has the highest equilibrium constant?

$$F^- + H_2O \longrightarrow HF + OH^-$$

−

$$NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$$

(h) Which of the following is the strongest base?

F NO_2 - CN^-

(i) Which mixture should be used to buffer at a pH of 9

HOCl/NaOCl, NH_3/NH_4Cl, NaOH/NaCl

(j) What volume of 0.05 *M* HCl is required to reach the equivalence point in the titration of 50 mL of 0.1 *M* NaOH?

25 mL, 50 mL, 75 mL, 100 mL

17

Electron-Sharing Reactions

In the same year in which Brønsted and Lowry delineated the proton-transfer reaction, Gilbert Newton Lewis, one of the great American chemists, provided a more general definition of acids and bases. The **Lewis definition** is simply:

An acid is a substance that can accept a pair of electrons, and a base is a substance that can provide a pair of electrons.

A Lewis acid-base reaction occurs when one substance, the base, provides a pair of electrons to share with another substance, the acid. The product of the reaction—the species in which the pair of electrons is shared—is called the acid-base **adduct**, or **complex**. The simplest example of such a reaction is

(1) $$\underset{\text{acid}}{H^+} + \underset{\text{base}}{:H^-} \rightleftharpoons \underset{\text{adduct}}{H{-}H}$$

in which the hydrogen ion (H^+) is a Lewis acid, the hydride ion (H^-) is a Lewis base, and the product, H_2, is the Lewis adduct. When this reaction is carried out in water or in a similar polar solvent, the hydrogen ion bonds to the solvent, and the reaction can then be classified as a proton-transfer reaction:

(2) $$H_3O^+ + :H^- \rightleftharpoons H_2O + H_2$$

The water merely provides the vehicle necessary for the transfer of the proton. Hence, all proton-transfer reactions can also be classified as **electron-sharing reactions**.

Actually, equations (1) and (2) are examples of two different kinds of electron-sharing reactions. The first, of the type

(3) $$\underset{\text{acid}}{A} + \underset{\text{base}}{:B} \rightleftharpoons \underset{\text{adduct}}{A:B}$$

involves the addition of the base :B to the acid A and is therefore called an **addition reaction**. The second, of the type

(4) $$\underset{\text{adduct}}{A:B} + \underset{\text{base}}{:D} \rightleftharpoons \underset{\text{adduct}}{A:D} + \underset{\text{base}}{:B}$$

is the displacement of the base :B from the adduct A:B by another base :D to produce the new adduct A:D. Such **displacement reactions** can also occur by displacement of one acid by another,

$$\underset{\text{adduct}}{A:B} + \underset{\text{acid}}{C} \rightleftharpoons \underset{\text{adduct}}{C:B} + \underset{\text{acid}}{A}$$

Clearly, in the base-displacement reaction, two bases compete to provide the electron pair for the acid; in the acid-displacement reaction, two acids compete for the electron pair provided by the base.

17.1 ADDITION REACTIONS

Addition reactions can be conveniently categorized in terms of the types of species that function as the acid. Both the Lewis and Brønsted-Lowry definitions require that the base provide a pair of electrons, hence there is no difference between the two types of bases. Some common bases are listed in Table 16.2.

Problem 17.1

Which of the following are Lewis bases? BH_3, PH_3, OH^-.

Solution:

BH_3 has no nonbonding pairs of electrons. In fact, like BCl_3, it is an electron-deficient compound; it cannot be a Lewis base. Instead, it is such an efficient Lewis acid that it exists only as part of an adduct with other molecules such as ethyl ether.

PH_3, like its second-period neighbor, NH_3, has a nonbonding pair of electrons on the central atom. It therefore can behave as a Lewis base.

The hydroxide ion has three nonbonded pairs of electrons on the oxygen and is also negatively charged. In spite of oxygen's high electronegativity, which keeps the lone pairs tightly held, the hydroxide ion is a common Lewis base.

Although the proton is the simplest Lewis acid, the characteristics of Lewis acids are quite different from those of Brønsted-Lowry acids. A Brønsted-Lowry acid must contain a transferable proton; a Lewis acid must be able to accept a pair of electrons. The most obvious way in which an acid can accept a pair of electrons is to have an empty orbital that can accept and hold the electron pair.

Cations as Lewis Acids

All cations are potential Lewis acids. For example, the beryllium ion has four empty orbitals in its valence shell that may accept electron pairs—the 2*s* and the three 2*p* orbitals. When this ion is added to water, the following reactions take place:

$$Be^{2+} + H_2O \rightleftharpoons Be(H_2O)^{2+}$$

$$Be(H_2O)^{2+} + H_2O \rightleftharpoons Be(H_2O)_2^{2+}$$

$$Be(H_2O)_2^{2+} + H_2O \rightleftharpoons Be(H_2O)_3^{2+}$$

$$Be(H_2O)_3^{2+} + H_2O \rightleftharpoons Be(H_2O)_4^{2+}$$

Each reaction is an electron-sharing reaction, and together they portray the step-by-step formation of the adduct $Be(H_2O)_4^{2+}$. Some of each adduct is present in an aqueous solution of beryllium(II).

The behavior of Be^{2+} shows that more than one molecule of base may complex with a given acid. The number of bases bonded to the acid in a given adduct is called the **coordination number**. In $Be(H_2O)_2^{2+}$, for example, the coordination number of Be^{2+} is 2, and in $Be(H_2O)_4^{2+}$ it is 4. The maximum coordination number for a particular acid-base pair depends on the number of orbitals available in the acid, the size of both the acid and the base, and the strength of the adduct bond. The maximum coordination number of 4 for Be^{2+} is due to the presence of only four empty orbitals in its valence shell.

The structure of the adducts of ions of the representative elements can be described with the principles developed in Chapters 7 and 8. (Structures of adducts of transition-metal cations are more complex, and discussion of their bonding and geometry will be deferred until Chapter 22.) The electron dot* formula for the adduct $Be(H_2O)_4^{2+}$ is shown in Figure 17.1. Since there are four sigma-bonded electron pairs and no nonbonded pairs around the central atom, the geometry of the adduct can be predicted as tetrahedral.

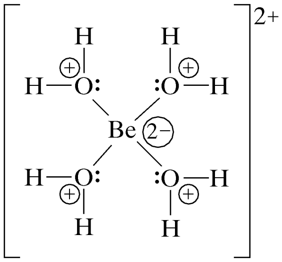


Figure 17.1 Electron dot formula for $Be(H_2O)_4^{2+}$.

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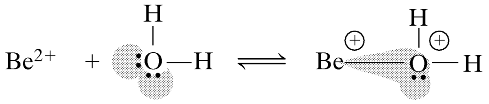
* Recall that the sum of the formal charges must equal the actual charge of the complex, in this case +2.

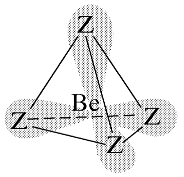
Problem 17.2

(a) Write an equation for the reaction of one water molecule with one beryllium ion. Show the available electron density on the water molecule. Also show the shared electron density in the adduct.

(b) Show the structure of the $Be(H_2O)_4^{2+}$ adduct using the symbol Z to represent a water molecule.

Solution:





Notice the formal charges given to Be and O in the adduct. The entire adduct has a +2 charge.

Because each water molecule supplies two electrons for each of the Be—O bonds, the oxygen atoms have *formal* positive charges. As a consequence of this and the strength of the Be—O bonds, sufficient electron density is removed from the oxygen-hydrogen bonds to increase their polarity. This increased polarity results in increased acidity of the hydrogens, and in water, reactions such as the following occur:

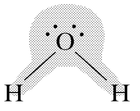
$$Be(OH_2)_4^{2+} + H_2O \rightleftharpoons [Be(OH_2)_3OH]^+ + H_3O^+$$

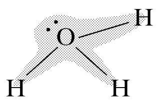
$$[Be(OH_2)_3OH]^+ + H_2O \rightleftharpoons Be(OH_2)_2(OH)_2 + H_3O^+$$

These proton-transfer reactions produce hydronium ions; hence, an aqueous solution of Be^{2+} is acidic. If the transfer of a second proton from the adduct occurs to a sufficient extent, the neutral hydroxide, $Be(OH_2)_2(OH)_2$, will precipitate out of the solution.

Visualization 17.1

Is the following picture a reasonable depiction of the electron density in an isolated water molecule relative to a water molecule bonded to a cation (M)?





Solution:

Yes, it shows that there is more electron density around the oxygen in an isolated water molecule than around the oxygen of water bonded to a metal ion.

TABLE 17.1 Stable Metal Ion-Water Complexes

$Be(OH_2)_4^{2+}$	$Ni(OH_2)_6^{2+}$
$Al(OH_2)_6^{3+}$	$Mn(OH_2)_6^{2+}$
$Cr(OH_2)_6^{3+}$	$Sn(OH_2)_4^{2+}$
$Co(OH_2)_6^{2+}$	$Pb(OH_2)_4^{2+}$
$Cu(OH_2)_6^{2+}$	$Zn(OH_2)_4^{2+}$
$Fe(OH_2)_6^{3+}$	

TABLE 17.2 Ammonia Complexes in Aqueous Solution

$Ag(NH_3)_2^{+}$	$Cu(NH_3)_4^{2+}$
$Zn(NH_3)_4^{2+}$	$Co(NH_3)_6^{2+}$
$Cd(NH_3)_4^{2+}$	$Ni(NH_3)_6^{2+}$

Some other metal ions also bond strongly to water. Insofar as they are known, the formulas for the adducts formed by some of the more common of these ions are given in Table 17.1. Because of the strong metal ion-oxygen bonds in the adducts, these ions also produce acidic aqueous solutions. A survey of the kinds of ions present in Table 17.1 shows that these are, in general, rather small, highly charged species. Such ions are more strongly attracted to the polar water molecules than larger, less highly charged ions.

Metal ions will also complex with bases other than water. For example, silver ion reacts with ammonia in liquid ammonia or water to form the adduct $Ag(NH_3)_2^{+}$.

$$Ag^{+} + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^{+}$$

Cadmium ion reacts with the same base to form the adduct $Cd(NH_3)_4^{2+}$:

$$Cd^{2+} + 4\,NH_3 \rightleftharpoons Cd(NH_3)_4^{2+}$$

while cobalt(II) forms the 6-coordinate complex $Co(NH_3)_6^{2+}$:

$$Co^{2+} + 6\,NH_3 \rightleftharpoons Co(NH_3)_6^{2+}$$

Some other ammonia complexes formed in aqueous solution are given in Table 17.2.

Problem 17.3

Predict the structures of $Ag(NH_3)_2^{+}$, $Cd(NH_3)_4^{2+}$, and $Co(NH_3)_6^{2+}$.

Solution:

If we assume that the d-electrons on the central atoms do not affect the geometry around the atom, we can use the valence shell electron pair repulsion model to predict the geometries. The silver complex has two pairs of electrons (these form the two bonds to the two ammonias) in its valence shell and these must be positioned at opposite ends of a straight line in order to minimize the repulsions between the pairs. Thus, the ammonia molecules are oriented at 180° to one another and the adduct is linear.

In the cadmium complex there are four pairs of electrons at the central atom and the adduct is therefore tetrahedral.

In the cobalt complex there are six pairs of electrons at the central atom and the complex is therefore octahedral.

Complex amines called porphyrins are complexed to Fe^{2+}, Mg^{2+}, and Co^{3+} in biologically vital systems such as hemoglobin, chlorophyll, and vitamin B_{12}. The heme group of hemoglobin is shown below in Figure 17.2.

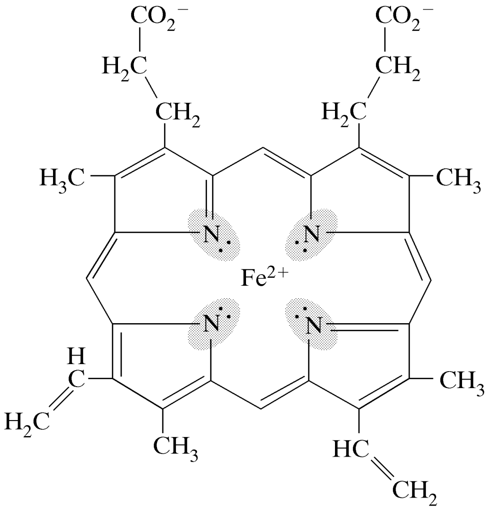


Figure 17.2 The Heme Group

TABLE 17.3 Some Common Amphoteric Hydroxides

HYDROXIDE	REACTION AS A BASE	REACTION AS A LEWIS ACID
$Zn(OH)_2$	$\underline{Zn(OH)_2} + 2\,H^+ \rightarrow Zn^{2+}\,(aq) + 2\,H_2O$	$\underline{Zn(OH)_2} + 2\,OH^- \rightarrow Zn(OH)_4^{\;2-}$
$Sn(OH)_2$	$\underline{Sn(OH)_2} + 2\,H^+ \rightarrow Sn^{2+}\,(aq) + 2\,H_2O$	$\underline{Sn(OH)_2} + 2\,OH^- \rightarrow Sn(OH)_4^{\;2-}$
$Pb(OH)_2$	$\underline{Pb(OH)_2} + 2\,H^+ \rightarrow Pb^{2+}\,(aq) + 2\,H_2O$	$\underline{Pb(OH)_2} + 2\,OH^- \rightarrow Pb(OH)_4^{\;2-}$
$Sb(OH)_3$	$\underline{Sb(OH)_3} + 3\,H^+ \rightarrow Sb^{3+}\,(aq) + 3\,H_2O$	$\underline{Sb(OH)_3} + OH^- \rightarrow Sb(OH)_4^{\;-}$
$Al(OH)_3$	$\underline{Al(OH)_3} + 3\,H^+ \rightarrow Al^{3+}\,(aq) + 3\,H_2O$	$\underline{Al(OH)_3} + OH^- \rightarrow Al(OH)_4^{\;-}$
$Cr(OH)_3$	$\underline{Cr(OH)_3} + 3\,H^+ \rightarrow Cr^{3+}\,(aq) + 3\,H_2O$	$\underline{Cr(OH)_3} + OH^- \rightarrow Cr(OH)_4^{\;-}$
$Sn(OH)_4$	$\underline{Sn(OH)_4} + 4\,H^+ \rightarrow Sn^{4+}\,(aq) + 4\,H_2O$	$\underline{Sn(OH)_4} + 2\,OH^- \rightarrow Sn(OH)_6^{\;2-}$

If the base is an anion, the Lewis acid-base reaction with the cation can also be classified as an ion-combination reaction. The addition of sufficient ions to balance the charge of the cation produces a neutral species that may precipitate from aqueous solution. Thus, when a solution of sodium cyanide is added dropwise to an aqueous solution of silver(I), a precipitate of silver cyanide soon forms. If the addition of cyanide is continued until the concentration of cyanide is quite high, the precipitate dissolves because of the formation of the ion $Ag(CN)_2^{\;-}$, whose alkali metal salts [for example, $NaAg(CN)_2$] are soluble.

$$Ag^+ + CN^- \rightleftharpoons \underline{AgCN}$$

$$\underline{AgCN} + CN^- \rightleftharpoons Ag(CN)_2^{\;-}$$

If a neutral Lewis acid can also participate in a proton-transfer reaction as a base, it is termed **amphoteric**. (Note that the term "amphiprotic" refers to a species that can behave as a Brønsted-Lowry acid and base, whereas "amphoteric" denotes a species that can function as a Brønsted-Lowry base and a Lewis acid.) Thus, the neutral precipitate AgCN is a Lewis acid because of its further reaction with the base CN^-, but it is also a Brønsted-Lowry base because it can accept a proton to form the weak electrolyte hydrocyanic acid.

$$\underline{AgCN} + H_3O^+ \rightleftharpoons Ag^+(aq) + HCN + H_2O$$

Among the most common amphoteric compounds are the water-insoluble hydroxides listed in Table 17.3. For example, zinc(II) hydroxide dissolves in a sodium hydroxide solution because of the formation of the adduct $Zn(OH)_4^{\;2-}$:

$$\underline{Zn(OH)_2} + 2\,OH^- \rightleftharpoons Zn(OH)_4^{\;2-}$$

and it also reacts with acid as a Brønsted-Lowry base:

$$\underline{Zn(OH)_2} + 2\,H^+ \rightleftharpoons Zn^{2+}(aq) + 2\,H_2O$$

Problem 17.4

Which of the following could be amphoteric and which could be amphiprotic?

(a) $NaHCO_3$
(b) $Ba(OH)_2$
(c) Sb_2S_3

Solution:

$NaHCO_3$ is definitely amphiprotic because the bicarbonate ion can accept a proton to form H_2CO_3 and can also release a proton to form $CO_3^{\;2-}$. Because the reaction of $HCO_3^{\;-}$ with water to give H_3O^+ and $CO_3^{\;2-}$ is a Brønsted-Lowry and Lewis reaction, $NaHCO_3$ could be classified as amphoteric. However, generally the term is applied to compounds in which the cation functions as a Lewis acid.

Continued on the next page

Problem 17.4 *Continued*

Solution: *Continued*

$Ba(OH)_2$ is a Brønsted-Lowry and Lewis base because it contains the OH^- ion, which reacts with acid to form water.

$$OH^- + H^+ \rightleftharpoons H_2O$$

It is not amphiprotic because the OH^- does not function as an acid; it is not amphoteric because the cation does not accept electron density (act as Lewis acid) from a base.

Sb_2S_3 is not amphiprotic because the sulfide ion does not have a proton to release to a base. It is amphoteric because the sulfide ion will react with acid (Sb_2S_3 will dissolve in acid)

$$2\,H^+ + S^{2-} \rightleftharpoons H_2S$$

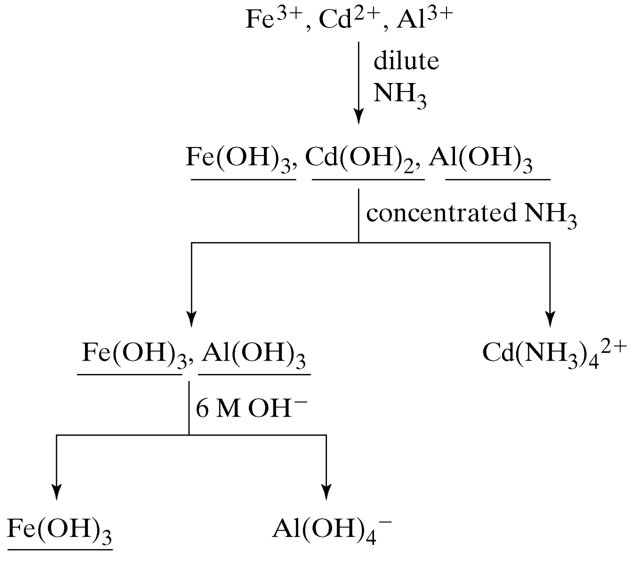
and the antimony can function as a Lewis acid and will react with excess sulfide ion.

$$Sb_2S_3 + S^{2-} \rightleftharpoons 2\,SbS_2^-$$

The Lewis acid properties of the cations can be utilized in the separation and identification of these ions. For example, the cations in a mixture of $Fe(NO_3)_3$, $Cd(NO_3)_2$, and $Al(NO_3)_3$ in water can be separated by recognizing that:

(a) Fe^{3+}, Cd^{2+}, and Al^{3+} all form insoluble hydroxides (see Chapter 15, Table 15.1).
(b) $Al(OH)_3$ is amphoteric and will therefore dissolve in moderately concentrated hydroxide solutions. Neither $Fe(OH)_3$ nor $Cd(OH)_2$ is amphoteric.
(c) Cd^{2+} forms a soluble ammonia complex (Table 17.2), whereas Fe^{3+} and Al^{3+} do not.

Thus, the addition of dilute aqueous ammonia to a solution of the three compounds will precipitate the three hydroxides*—$Fe(OH)_3$, $Cd(OH)_2$, and $Al(OH)_3$. If the mixture is then treated with concentrated ammonia, the $Cd(OH)_2$ will dissolve due to the formation of the soluble complex ion $Cd(NH_3)_4{}^{2+}$. The mixture will then consist of $Cd(NH_3)_4{}^{2+}$ in solution and $Fe(OH)_3$ and $Al(OH)_3$ as precipitates. The precipitate can be separated by centrifugation and then treated with 6 *M* NaOH. The $Al(OH)_3$ will react with OH^- to form the soluble hydroxy complex $Al(OH)_4{}^-$, and only $Fe(OH)_3$ will remain as a precipitate. The entire sequence can be summarized schematically as follows:



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* Remember that an aqueous solution of ammonia contains some hydroxide ions because of the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$$

Although the hydroxide concentration is low, it is sufficient to precipitate the hydroxides of many cations.

If the other solubility rules (Table 15.1) are also used, rather complex cation mixtures can be separated.

Methodology 17.1

Devise a scheme for the separation of the cations Ag^+, Zn^{2+}, Cu^{2+}, Sb^{3+}, Bi^{3+}, and Ba^{2+}.

First, use the data given in the general solubility rules (Table 15.1) to determine whether the cations differ in their solubility characteristics.

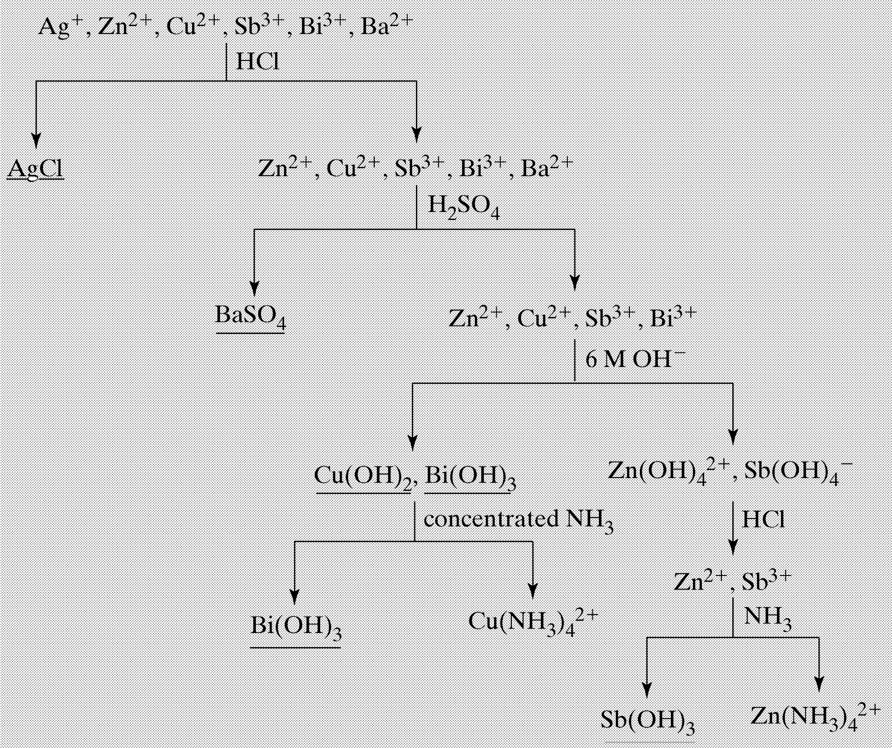
The solubility rules indicate that:

1. Only Ag^+ forms an insoluble chloride—AgCl. The chlorides of the other five ions are soluble in water.
2. Only Ba^{2+} forms an insoluble sulfate—$BaSO_4$.
3. The hydroxides of all but Ba^{2+} are insoluble.

Second, use Table 17.2 and Table 17.3 to determine which cations form ammonia complexes and which are amphoteric.

1. Ag^+, Zn^{2+}, and Cu^{2+} form ammonia complexes.
2. Zn^{2+} and Sb^{3+} have amphoteric hydroxides.

Construct a scheme to separate the ions:



Note that the zinc and antimony hydroxy complexes are destroyed with acid before the addition of NH_3 in the last step of the separation.

$$Zn(OH)_4^{2-} + 4H^+ \longrightarrow Zn^{2+}(aq) + 4\,H_2O$$

Problem 17.5

What reagent can be used to separate the components of each of the following mixtures:

(a) $BaCl_2$ and $CuCO_3$

(b) AgCl and $BaSO_4$

Solution:

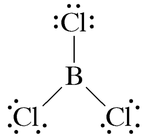
(a) Water because $BaCl_2$ is soluble in water whereas $CuCO_3$ is insoluble.

(b) Ammonia because both are insoluble in water, but AgCl will dissolve in ammonia because of the soluble ammonia complex formed by Ag^+.

$$AgCl + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2{}^+ + Cl^-$$

Molecules as Lewis Acids

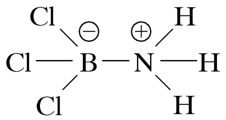
Some neutral *molecular* species also have empty orbitals, usually on the central atom, and can therefore function as Lewis acids. Consider the electron dot formula for boron trichloride, as an example:



The formula* shows only six electrons (three pairs) in the valence shell of boron; the boron can therefore accept two more electrons and fill its octet. Indeed, one of the classic examples of a Lewis acid-base reaction is the formation of an adduct between BCl_3 and NH_3,

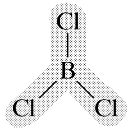
$$BCl_3 + :NH_3 \rightleftharpoons Cl_3B\!:\!NH_3$$

The lone pair of electrons on the base NH_3 is donated to the acid BCl_3 to form the covalent species $Cl_3B\!:\!NH_3$. The electron dot formula of the adduct shows four bonds about both boron and nitrogen and suggests sp^3 hybridization and bond angles of approximately 109° at both atoms. It is interesting to note the change in geometry of the acid in this reaction: from planar BCl_3 (sp^2 hybridization at boron) to tetrahedral bonds within the adduct.

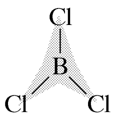


Visualization 17.2

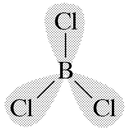
Which of the following is the most helpful representation of the electron density in stressing the Lewis acidity of BCl_3?



(a)



(b)



(c)

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* As we saw in Chapter 6, we can also draw electron dot formulas for BCl_3 that give the boron an octet of electrons. Because we are stressing the Lewis acid behavior of BCl_3, we show the formula with an electron-deficient boron.

Visualization 17.2 *Continued*

Solution:

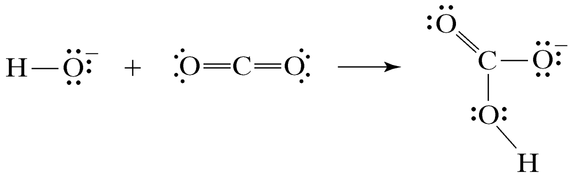
Only (c) shows that the chlorines have the greatest amount of electron density and that boron has relatively little.

Molecules that contain atoms that can expand their octet are also able to accept a pair of electrons. The central atom of tin tetrachloride has an octet of electrons in its valence shell, but because of the presence of empty d orbitals in the same quantum level, it can expand its octet, as in the reaction

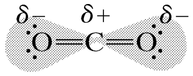
$$SnCl_4 + 2\,Cl^- \rightleftharpoons SnCl_6^{2-}$$

The hybridization utilized by tin in the adduct is presumably sp^3d^2, and the geometry is octahedral.

Neutral molecules that do not have empty orbitals can also function as Lewis acids if the bonding is such that an electron pair can be accommodated by a rearrangement of the electronic structure of the molecule. The electron dot formula for CO_2, for example, shows a completed octet for each of the atoms, and the molecule therefore has no empty orbitals. Carbon dioxide does react as a Lewis acid, however, with bases such as OH^- or H_2O. The reaction with OH^- may be portrayed as follows:

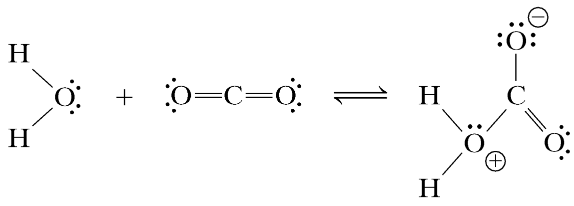


The electronegative oxygens remove sufficient electron density from the carbon to give it a partial positive charge that can attract the negative hydroxide ion. Because the

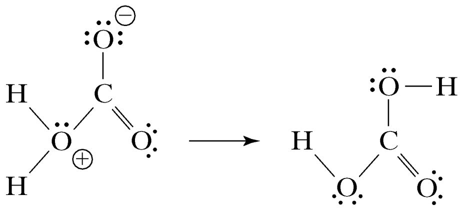


carbonyl carbon is attracted to sites that contain negative charge (electrons) the carbon is said to be **electrophilic** (*philos* comes from the Greek, meaning lover). Likewise, the negatively charged hydroxide ion is said to be nucleophilic (positive charge lover). As the hydroxide begins to bond to the carbon, one of the carbon-oxygen π-bonds breaks to allow formation of the new C—O bond.

The reaction of water with CO_2 can be explained in the same way.



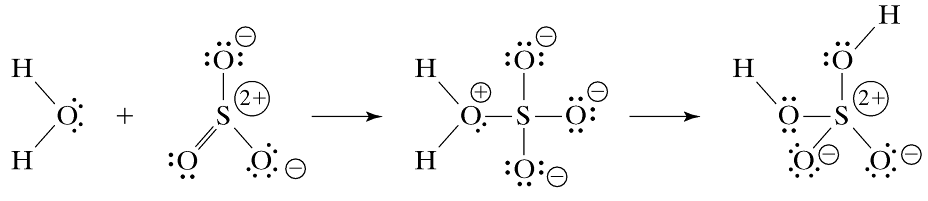
(5)



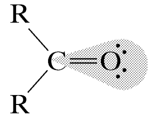
(6)

After the adduct is formed (equation 5), one of the hydrogens leaves the oxygen. Then the same hydrogen, or another one from a water molecule or a hydronium ion, attaches itself to the negatively charged oxygen (equation 6). The net result is the formation of carbonic acid; indeed, this is an example of the hydration of an acidic anhydride. The analogous hydration of another acidic anhydride, sulfur trioxide, is shown to produce sulfuric acid in equation (7).

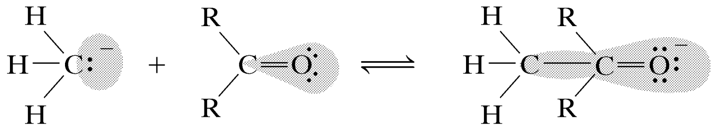
(7)



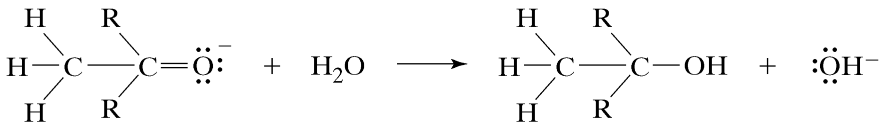
Compounds that contain the carbonyl group, such as ketones and aldehydes, function as Lewis acids in a manner analogous to that of carbon dioxide. The carbon of the carbonyl group has a partial positive charge (that is, it is electron-deficient) and therefore is a reasonably good electrophile.



Of the many known types of such reactions, we shall illustrate only one type of addition. The methide ion, $:CH_3^-$, which is a part of the essentially ionic compound $LiCH_3$, attacks the carbon of the carbonyl group to form an adduct containing a new carbon-carbon bond.



If this adduct is then added to water, it abstracts a proton, and an alcohol results.



Indeed, this is an important synthetic method for preparing alcohols.

Problem 17.6

Which of the following molecules can function as Lewis acids?

CCl_4, $SbCl_3$, NF_3, H_2CO

Solution:

CCl_4 and NF_3 do not have empty orbitals in their valence shells and therefore cannot accept electrons. The antimony in $SbCl_3$ can expand its octet because its valence shell contains empty *d*-orbitals. Methanal has a C=O bond, which has an electrophilic carbon that can undergo electron rearrangement (like CO_2). Both $SbCl_3$ and H_2CO can therefore function as Lewis acids.

17.2 EXTENT OF LEWIS ADDITION REACTIONS

Formation Constants

The extents of addition reactions vary considerably. The equilibrium constant for the formation of the AgI_2^- adduct is 10^{22}:

$$Ag^+ + 2I^- \rightleftharpoons AgI_2^- \qquad K = 10^{22}$$

whereas the constant for the formation of $PbCl_4^{2-}$ is 10:

$$Pb^{2+} + 4\,Cl^- \rightleftharpoons PbCl_4^{2-} \qquad K = 10$$

The formation of an adduct containing more than one mole of base per mole of acid is usually visualized as a step-by-step process. In some cases, the intermediate species can be detected and the equilibrium constants determined for each. For example, the overall **formation constant**, $\boldsymbol{K_f}$ for the complex $Cd(NH_3)_4^{2+}$ is 3×10^7. The sum of the four steps involved is the equation for the overall formation of the 4-coordinate complex, and the product of the stepwise constants (K_1 through K_4) is the overall formation constant.

$$\begin{array}{ll}
Cd^{2+} + NH_3 \rightleftharpoons Cd(NH_3)^{2+} & K_1 = 5 \times 10^2 \\
Cd(NH_3)^{2+} + NH_3 \rightleftharpoons Cd(NH_3)_2^{2+} & K_2 = 2 \times 10^2 \\
Cd(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cd(NH_3)_3^{2+} & K_3 = 30 \\
\underline{Cd(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cd(NH_3)_4^{2+}} & K_4 = 10 \\
Cd^{2+} + 4\,NH_3 \rightleftharpoons Cd(NH_3)_4^{2+} & K_f = K_1K_2K_3K_4 = 3 \times 10^7
\end{array}$$

Equilibrium constants for complex ions are also tabulated as **instability constants**. For $Cd(NH_3)_4^{2+}$, the instability constant is 3×10^{-8} and refers to the decomposition of the ion.

$$Cd(NH_3)_4^{2+} \rightleftharpoons Cd^{2+} + 4\,NH_3 \qquad K_{\text{instab}} = 3 \times 10^{-8}$$

Note that the instability constant is the reciprocal of the overall formation constant.

Either the formation constant or the instability constant can be used to calculate the equilibrium concentrations of the acid, base, and adducts in solution. However, these calculations are complicated by the existence of more than one adduct in solution and by the experimental uncertainty in the equilibrium constant for the formation of each adduct. The magnitude of the formation constant for each step is large; the extent of each reaction of the type $A + B \rightarrow C$ is more than 50%. Most of the reactants in each step are therefore converted to adduct, and at equilibrium the final adduct is the species present in the highest concentration. For example, when 4 mol of NH_3 are added to 1 mol of Cd^{2+} in aqueous solution, some of each of the following intermediate adducts is formed: $Cd(NH_3)^{2+}$, $Cd(NH_3)_2^{2+}$, and $Cd(NH_3)_3^{3+}$. The major species, however, is the final adduct $Cd(NH_3)_4^{2+}$. When an excess of the base is present, the concentration of the final adduct relative to the other adducts is even greater. For example, let us calculate the concentration of $Cd^{2+}(aq)$ after 1.0 mol of NH_3 has been added to 0.10 mol of Cd^{2+} in a total of 1.0 L of solution. The reaction of the ammonia with Cd^{2+} has a high extent and, consequently, the 0.10 mol of Cd^{2+} is converted almost completely to the adduct.

$$Cd^{2+} + 4\,NH_3 \rightleftharpoons Cd(NH_3)_4^{2+} \qquad K_f = 3 \times 10^7$$

The concentration of the adduct at equilibrium can therefore be assumed to be 0.10 M. The concentration of NH_3 remaining will be $1.0 - 0.4 = 0.6\ M$. (The amount of NH_3 produced by the dissociation of the adduct is very small and can be neglected.)

$$[Cd(NH_3)_4^{2+}] = 0.10\ M$$

$$[NH_3] = 0.6\ M$$

If we let the concentration of Cd^{2+} be x, the equilibrium concentrations may be summarized in the table

	$\mathrm{Cd^{2+}} + $	$4\,\mathrm{NH_3} \rightleftharpoons$	$\mathrm{Cd(NH_3)_4{}^{2+}}$
Start	0.10	1	0
Change	$-0.10 + x$	-0.40	0.10
Equilibrium	x	0.60	0.10

The equilibrium concentrations can then be inserted into the equilibrium expression:

$$\frac{[\mathrm{Cd(NH_3)_4{}^{2+}}]}{[\mathrm{Cd^{2+}}][\mathrm{NH_3}]^4} = 3 \times 10^7$$

$$\frac{0.10}{x(0.6)^4} = 3 \times 10^7$$

$$x = 3 \times 10^{-8}\,M$$

The value of x obtained, $3 \times 10^{-8}\,M$, shows that the amount of $\mathrm{Cd^{2+}}$ left in solution is very low.

The formation of complex ions is sometimes used to dissolve or prevent the precipitation of insoluble compounds (see Chapter 15). The two reactions involved—dissolution of the compound and formation of the complex ion—can be combined in order to simplify calculation of the equilibrium concentrations. For example, consider the two reactions involved in the dissolution of AgCl by $\mathrm{NH_3}$:

$$\underline{\mathrm{AgCl}} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-} \qquad K_{\mathrm{sp}} = 2 \times 10^{-10}$$

$$\mathrm{Ag^+} + 2\,\mathrm{NH_3} \longrightarrow \mathrm{Ag(NH_3)_2{}^+} \qquad K_{\mathrm{f}} = 2 \times 10^7$$

When these reactions are added, we have:

$$\underline{\mathrm{AgCl}} + 2\,\mathrm{NH_3} \rightleftharpoons \mathrm{Ag(NH_3)_2{}^+} + \mathrm{Cl^-}$$

The equilibrium constant for this reaction is the product of the K_{sp} and K_{f}. The equilibrium expression is

$$\frac{[\mathrm{Ag(NH_3)_2{}^+}][\mathrm{Cl^-}]}{[\mathrm{NH_3}]^2} = K_{\mathrm{sp}} \cdot K_{\mathrm{f}} = 4 \times 10^{-3}$$

Let us now determine how much ammonia will be required to dissolve 0.1 mol of AgCl in 1 L of solution. We can assume that the silver ion in AgCl will be converted completely to the complex; thus, at equilibrium

$$[\mathrm{Ag(NH_3)_2{}^+}] = 0.10\,M$$

$$[\mathrm{Cl^-}] = 0.10\,M$$

$$[\mathrm{NH_3}] = x$$

and

$$\frac{[0.10][0.10]}{(x)^2} = 4 \times 10^{-3}$$

$$x = 2\,M$$

Therefore, enough $\mathrm{NH_3}$ must be added to: (a) convert 0.10 mol of AgCl to $\mathrm{Ag(NH_3)_2{}^+}$ and (b) to provide an equilibrium concentration of 2 M. Because the adduct contains two moles of ammonia per mole of adduct, 0.20 mol of ammonia will be required just to form the adduct. Thus, the total amount required is

$$0.20 + 2 = 2.2\ \mathrm{mol}$$

Methodology 17.2

What is the concentration of silver ion after 1 mol of ammonia has been added to 0.1 *M* of $AgNO_3$ in 1 L of solution?

Write an equation for the reaction that occurs.

$$Ag^+ + 2\,NH_3 \longrightarrow Ag(NH_3)_2^+$$

Write the equilibrium expression for this equation.

$$\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = K_f = 2 \times 10^7$$

How do you know that two, rather than four or six, ammonia molecules bond to the silver?

> There is no easy way to determine the coordination number at this stage of your study of chemistry. Therefore, you must simply memorize the formulas of the adducts.

Can you assume that all of the silver ion is converted to the adduct $Ag(NH_3)_2^+$?

> Because the equilibrium constant is very large, you can assume that all but a very small amount of silver ion is converted to the adduct.

What is the concentration of $Ag(NH_3)_2^+$ in the solution?

> Because the process was begun with 0.1 *M* silver nitrate and we know that essentially all is converted to the adduct, $[Ag(NH_3)_2^+] = 0.1\ M$.

If 0.1 mol of $Ag(NH_3)_2^+$ is formed, how many moles of ammonia are used up?

> Each mole of adduct requires two moles of ammonia. Therefore, the formation of 0.1 mole uses up 0.2 mol of ammonia, leaving 0.8 mol of ammonia in the 1 L of solution.

Set up an equilibrium table.

	Ag^+	$+\ 2\,NH_3 \longrightarrow$	$Ag(NH_3)_2^+$
Start	0.1	1.0	0
Change	$-0.1 + x$	20.2	0.1
Equil	x	0.8	0.1

Insert the equilibrium concentrations into the equilibrium expression and solve for *x*.

$$\frac{[Ag)NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{(0.1)}{x(0.8)^2} = K_f = 2 \times 10^7$$

$$x = 8 \times 10^{-9}\ M$$

Problem 17.7

Calculate the silver ion concentration in a saturated solution of AgCl and then use the results of Methodology 17.2 to predict whether 0.1 mol of AgCl will dissolve in 1 *M* ammonia.

Solution:

The K_{sp} for AgCl is 2×10^{-10} and therefore

$$\underline{AgCl} \rightleftharpoons Ag^+ + Cl^- \quad K_{sp} = 2 \times 10^{-10}$$

$$[Ag^+][Cl^-] = K_{sp} = 2 \times 10^{-10}$$

$$x^2 = 2 \times 10^{-10}$$

$$x = 1.4 \times 10^{-5}\ M$$

From Methodology 17.2 we know that in 1 *M* ammonia the silver ion concentration will be reduced to $8 \times 10^{-9}\ M$, which is less than the silver ion concentration in a saturated solution of AgCl. AgCl will therefore dissolve in 1 *M* ammonia and form the ammonia adduct until the ammonia concentration decreases to the point where $[Ag^+][Cl^-] = K_{sp} = 2 \times 10^{-10}$.

✓ Check Point 17.1

When 0.01 mol of silver nitrate is added to 3 *M* ammonia in one liter of solution, what is the concentration of silver ion at equilibrium?

Solution:

$6 \times 10^{-11}\ M$

◇ ◇ ◇ ◇ ◇

The Effect of Structure on Extent

Let us now attempt to determine what factors influence the extent of addition reactions. A thorough analysis of the extent of any reaction must include a discussion of its entropy change and an examination of the components of its enthalpy change, such as bonding in the reactants and products, structural effects on the ground-state energies of the reactants and products, and so on. This type of analysis is difficult for most reactions, however, partially because the necessary data are unavailable.

In qualitative terms, addition reactions can be viewed as an attraction between an electron-rich species and an electron-deficient species. This aspect of the reaction can be emphasized by showing the richness of electron density of the base with a partial negative charge, $\delta-$, and the electron deficiency of the acid with a partial positive charge, $\delta+$.

$$\mathrm{B}:^{\delta-} + \mathrm{A}^{\delta+} \rightleftharpoons \mathrm{B}:\mathrm{A}$$

In other words, the base is attracted to positively charged centers and is therefore a nucleophile, whereas the acid is attracted to negatively charged centers and is sometimes referred to as an electrophile.

This view of addition reactions leads to the expectation that for a given acid, the extent of reaction should parallel the amount or availability of the electron density of the base. Similarly, for a given base, the extent should parallel the degree to which the acid is electron-deficient. For example, the attraction of a given acid for a negatively charged base, such as OH^-, is certainly greater than its attraction for a neutral species containing the same donor atom, such as H_2O. In other words, not only are the lone pairs of the OH^- more available than those of H_2O, but OH^- also has a negative charge and is therefore a stronger base. In the same way, the positively charged Be^{2+} ion is a stronger acid than the neutral species $BeCl_2$.

Problem 17.8

Make a drawing to show the difference in the lone pairs on OH^- as compared to H_2O.

Solution:

The lone pairs in OH^- are more extended because there is only one hydrogen to attract electron density, and the negative charge on the ion tends to repel the electrons.

Let us now determine the generality of this view, or model, of addition reactions. Table 17.4 lists equilibrium constants for the gas-phase interactions of boron trifluoride and trimethylboron with a variety of bases. The relative extents of the reaction of the bases with a given acid can be assumed to reflect the relative strengths of those bases

TABLE 17.4 Equilibrium Constants for the Formation of Adducts with BF_3 and $(CH_3)_3B$

ACID	BASE	K
BF_3	$(CH_3)_2O$	6
	$(CH_3)_2S$	0.2
	$(CH_3)_3N$	>15
	$(CH_3)_3P$	15
	$(CH_3)_3As$	2.5
	$(CH_3)_3Sb$	~0
$(CH_3)_3B$	$(CH_3)_3N$	2
	$(CH_3)_3P$	8
	$(CH_3)_3As$	0.6
	$(CH_3)_3Sb$	~0

toward the particular acid. For example, the reaction of $(CH_3)_2O$ with BF_3 has an equilibrium constant greater than that for the reaction of $(CH_3)_2S$ with BF_3, which reflects the fact that $(CH_3)_2O$ is a stronger base than $(CH_3)_2S$ toward BF_3. The same order of basicity, O > S, is observed in proton-transfer reactions such as the following:

$$H^+ + OH^- \rightleftharpoons H_2O \qquad K = 10^{14}$$

$$H^+ + SH^- \rightleftharpoons H_2S \qquad K = 10^{7}$$

The trends in basicity toward BF_3 can be rationalized roughly on the basis of the model just developed. The greater electronegativity of oxygen relative to nitrogen makes the lone pairs of $(CH_3)_2O$ less available than the lone pair of $(CH_3)_3N$. The same argument applied to $(CH_3)_2O$ relative to $(CH_3)_2S$ should make the sulfur derivative the stronger base. However, the lone pairs of sulfur are in the third rather than the second quantum level and are therefore considerably more diffuse. This diffuseness limits the interaction of the lone pair with the empty orbital of the electron-deficient boron. These three cases—$(CH_3)_2O$ versus $(CH_3)_3N$ and $(CH_3)_2S$—are shown pictorially in Figure 17.3.

The equilibrium constants given in Table 17.4 for the interaction of the Group V bases with $(CH_3)_3B$ reveal that $(CH_3)_3B$ is a weaker acid than BF_3 toward these bases. This observation can be explained as follows. Since fluorine is more electronegative than carbon, the fluorines in BF_3 remove more electron density from the boron, making it more electron-deficient (and therefore a better Lewis acid) than the boron in $(CH_3)_3B$.

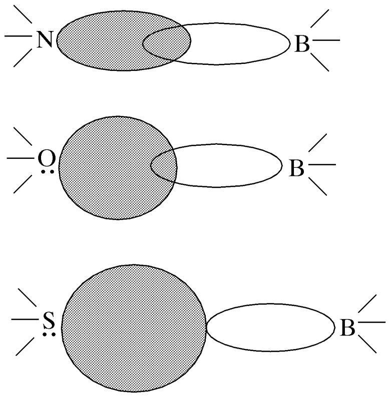
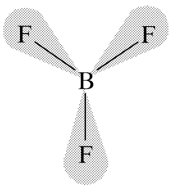


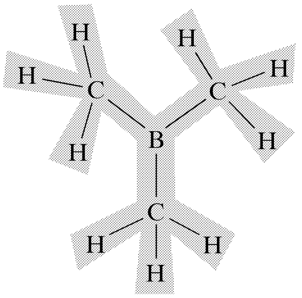
Figure 17.3 Relationship between the availability of the lone pair and basicity.

Problem 17.9

Represent the electron density in BF_3 and $B(CH_3)_3$.

Solution:





The equilibrium constants in the table also reveal that $(CH_3)_3P$ is a stronger base than $(CH_3)_3N$ toward $(CH_3)_3B$, which is opposite to the basicity order observed for BF_3. This observation can be explained by the argument that bumping of the methyl groups in the amine adduct $(CH_3)_3BN(CH_3)_3$ decreases the stability of the adduct and therefore decreases the extent of the reaction with $(CH_3)_3N$. The phosphorus base has a larger central atom and longer bonds to the methyl groups, which should alleviate this bumping to some extent and thereby make formation of the adduct more favorable.

Thus, with the possible exception of the interaction of $(CH_3)_3P$ with $(CH_3)_3B$, our model appears to explain the reactivity orders relative to BF_3 and $(CH_3)_3B$, and we can now continue to test its generality with data for some metal-ion complexes. Overall formation constants for some 4-coordinate halide complexes of Fe^{3+}, Hg^{2+}, and Cd^{2+} are listed in Table 17.5. When Fe^{3+} is the Lewis acid, the fluoride ion is a stronger base than the chloride ion, which is the basicity order predicted by our generalization about the availability of the lone pair. This same trend in basicity (in general, $F^- > Cl^- > Br^- > I^-$) is observed when the acid is Cr^{3+}, Al^{3+}, Be^{2+}, or another small and highly charged cation.

The opposite basicity order ($I^- > Br^- > Cl^- > F^-$) is observed for Hg^{2+} and Cd^{2+} and also holds for ions such as Ag^+, Cu^+, Pd^{2+}, and Pt^{2+}, which are larger and less highly charged than Fe^{3+}. This order is directly opposite to the one predicted by our model and cannot easily be explained. One theory links the greater basicity of I^- to the greater

TABLE 17.5 Overall Formation Constants for Some 4-Coordinate Halide Complexes

ACID	BASE	*K* FOR $A^{n+}(aq) + 4X^-(aq) \rightleftharpoons AX_4^{(4-n)-}(aq)$
Fe^{3+}	F^-	10^{15}
	Cl^-	10^{-1}
Hg^{2+}	Cl^-	10^{16}
	Br^-	10^{21}
	I^-	10^{30}
Cd^{2+}	Cl^-	10^{3}
	Br^-	10^{4}
	I^-	10^{6}

TABLE 17.6 Classification of Hard and Soft Bases

BASES			ACIDS		
Hard	*Soft*	*Borderline*	*Hard*	*Soft*	*Borderline*
H_2O	R_2S	$C_6H_5NH_2$	H^+	Cu^+, Ag^+	Fe^{2+}, Co^{2+}, Ni^{2+}
R_2O	PH_3	Br^-	Li^+, Na^+, K^+	Hg^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+}
OH^-	PR_3		Be^{2+}, Mg^{2+}, Ca^{2+}	Pt^{2+}	Sn^{2+}, $B(CH_3)_3$
O^{2-}	AsR_3		Sr^{2+}, Mn^{2+}	Cd^{2+}, Pd^{2+}	
NH_3	SbR_3		Al^{3+}, Ga^{3+}	$Ga(CH_3)_3$	
NR_3	I^-		Co^{3+}, Fe^{3+}	$Tl(CH_3)_3$	
F^-	H^-		BF_3, $AlCl_3$		
Cl−					

polarizability of its very diffuse lone pairs. This polarizability should result in a stronger covalent bond* between the more polarizable metal ions and the heavier halide ions.

Regardless of the reason, it would appear that acids can be classified into two groups: (1) those that bond most strongly to the fluoride ion and for which the basicity order $F^- > Cl^- > Br^- > I^-$ holds, and (2) those that bond most strongly to the iodide ion and for which the basicity order $I^- > Br^- > Cl^- > F^-$ holds. The acids in the first group also bond more strongly to nitrogen than to phosphorus and more strongly to oxygen than to sulfur. Conversely, those in the second group bond more strongly to phosphorus and sulfur. While these generalizations have been developed for ions, they also apply to molecular species. Thus, boron trifluoride, which bonds more strongly to $(CH_3)_2O$ and $(CH_3)_3N$ than to $(CH_3)_2S$ and $(CH_3)_3P$, can be placed in the first group. Trimethylboron, since it bonds more strongly to $(CH_3)_3P$ than to $(CH_3)_3N$, is normally placed in the second group (as we shall see later, it is actually a borderline case).

Bases such as I^-, $(CH_3)_2S$, and PH_3, which bond more strongly to the acids in the second group, can be categorized as **soft**, a description intended to portray the polarizable, diffuse character of their electron density. The acids that prefer these bases contain acceptor atoms or ions that are large in size, low in charge, and have unshared electrons in their valence shell. Since such properties result in high polarizability, these acids are classified as soft.

Bases such as F^-, OH^-, $(CH_3)_2O$, and NH_3 contain donor atoms or ions that are highly electronegative and rather unpolarizable. These are **hard** bases, and the acids that prefer them have properties that also allow them to be classified as hard: high positive or high partial positive charge and small size. Table 17.6 lists a number of hard and soft acids and bases. Some species have both hard and soft characteristics and are listed as borderline cases. The relative electron densities in an amine (a hard base) and a phosphine (a soft base) are shown in Figure 17.4.

With the hard and soft categories at hand, a great deal of experimental evidence can be summarized by the statement,

Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases

This important generalization (the hard/soft acid-base principle), first proposed by Ralph Pearson in 1963, does not involve a model that attempts to explain why certain acids pre-

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* The bonding in the adducts of many metal ions probably has considerable ionic character (see Chapter 22). For the moment, however, we will pretend that the bonding is mainly covalent.

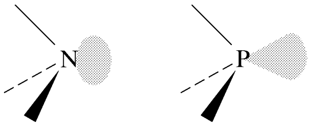


Figure 17.4 Relative Electron Densities of Hard and Soft Bases

fer to bind to certain bases, but is a simple summary of experimental fact. A reexamination of the data collected in Tables 17.4 and 17.5 shows that the hard acid BF_3 prefers to bond to the hard bases $(CH_3)_2O$ and $(CH_3)_3N$ rather than the soft bases $(CH_3)_2S$ and $(CH_3)_3P$; the borderline acid $(CH_3)_3B$ prefers the soft base $(CH_3)_3P$ over the hard base $(CH_3)_3N$; the hard acid Fe^{3+} bonds more strongly to the hard base F^-; the soft acids Hg^{2+} and Cd^{2+} bond more strongly to the soft base I^-.

The relative abundances of the mineral sources of metals provide an apt illustration of this principle. The hard metal ions occur much more frequently in nature combined with the hard base O^{2-} (that is, as oxides) rather than the softer base S^{2-} (that is, as sulfides), while the soft metal ions occur more frequently as sulfides. For example, the two major sources of aluminum are bauxite, a hydrated oxide of Al^{3+}, and corundum, which is mainly Al_2O_3. There are no major sulfide ores of aluminum. Similarly, the only abundant source of tin is cassiterite, which is primarily SnO_2. The soft metal ions Ag^+ and Hg^{2+}, on the other hand, occur as sulfides, their most abundant ores being argentite (Ag_2S) and cinnabar (HgS).

✓ Check Point 17.2

Which is more likely to be a major source of lead—PbO or PbS?

Solution:

PbS

◇ ◇ ◇ ◇ ◇

17.3 BASE-DISPLACEMENT REACTIONS

The displacement, or substitution, of one base by another is quite common. The reaction of fluoride ion with the Fe^{3+} ion in aqueous solution certainly proceeds by displacement of complexed water from the adduct $Fe(OH_2)_6{}^{3+}$:

$$\mathrm{Fe(OH_2)_6{}^{3+} + 6\,F^- \rightleftharpoons FeF_6{}^{3-} + 6\,H_2O}$$

Likewise, the reaction of chloride ion with the Co^{2+} ion in aqueous solution produces the blue $CoCl_4{}^{2-}$ ion. This reaction can be forced back to the blue $Co(OH_2)_6{}^{2+}$ adduct by simply adding water, which displaces chloride from the $CoCl_4{}^{2-}$ adduct.

$$\mathrm{Co(OH_2)_6{}^{2+} + 4\,Cl^- \rightleftharpoons CoCl_4{}^{2-} + 6\,H_2O}$$

Displacement reactions can also occur on the molecular species listed in Table 17.4. Indeed, a convenient way to establish whether an acid should be classified as hard or soft is to run a reaction such as

$$\mathrm{F_3B{:}O(CH_3)_2 + {:}S(CH_3)_2 \rightleftharpoons F_3B{:}S(CH_3)_2 + {:}O(CH_3)_2}$$

in which a hard base and a soft base compete for the acid. In this reaction, the hard acid BF_3 prefers the hard base $O(CH_3)_2$, and the equilibrium constant is less than 1. With $GaCl_3$ as the acid, on the other hand, the equilibrium constant for the reaction

$$\mathrm{Cl_3Ga{:}O(CH_3)_2 + {:}S(CH_3)_2 \rightleftharpoons Cl_3Ga{:}S(CH_3)_2 + {:}O(CH_3)_2}$$

is greater than 1. Gallium trichloride is categorized, therefore, as a soft acid.

One of the most common and useful types of base-displacement reaction occurs at carbon atoms. If methyl iodide is treated with hydroxide ion in a suitable solvent, the iodine is displaced as the iodide ion and methanol is formed:

$$\mathrm{H\ddot{\underset{\cdot\cdot}{O}}{:}^- \;+\; CH_3I \;\rightleftharpoons\; CH_3OH \;+\; {:}\ddot{\underset{\cdot\cdot}{I}}{:}^-}$$

The acid in this reaction is probably best visualized as the $CH_3{}^+$ ion, although methyl iodide is certainly not ionic and, as we shall see below, the mechanism for this reaction does not involve the CH_3^+ ion. However, this visualization has the advantage of making the analogy to other displacements more obvious. Methyl iodide, then, can be thought of as an adduct of the iodide ion and the CH_3^+ ion.

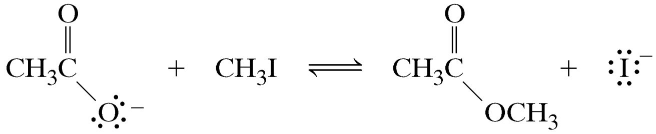
Numerous other bases can be used to displace the iodide ion in this reaction. For example, methoxide ion, CH_3O^-, reacts to form dimethyl ether:

$$CH_3\underset{\cdot\cdot}{\ddot{O}}:^- + CH_3I \rightleftharpoons CH_3OCH_3 + :\underset{\cdot\cdot}{\ddot{I}}:^-$$

Hydrogen sulfide ion produces methanethiol:

$$H\underset{\cdot\cdot}{\ddot{S}}:^- + CH_3I \rightleftharpoons CH_3SH + :\underset{\cdot\cdot}{\ddot{I}}:^-$$

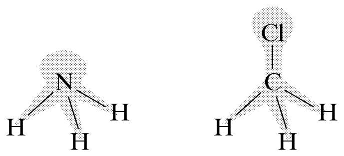
The acetate ion reacts to form the ester methyl acetate:



$$CH_3C(=O)\underset{\cdot\cdot}{\dot{O}}:^- + CH_3I \rightleftharpoons CH_3C(=O)OCH_3 + :\underset{\cdot\cdot}{\ddot{I}}:^-$$

Visualization 17.3

Is the following a good representation of the electron density at NH_3 and CH_3Cl?



Solution:

Yes, it shows the electron density at the lone pair on nitrogen and the polarization of electron density toward the nitrogen in the N—H bonds. In methyl chloride, the chlorine has attracted electron density from the carbon, thereby making the carbon electrophilic.

Problem 17.10

Write an equation for the reaction of ammonia with methyl iodide.

Solution:

When ammonia is used as the base, the product adduct is positively charged.

$$H_3N: + CH_3I \rightleftharpoons CH_3NH_3^+ + :\underset{\cdot\cdot}{\ddot{I}}:^-$$

If excess ammonia or some other base is present, a proton transfer from the adduct to the base will occur,

$$CH_3NH_3^+ + :NH_3 \rightleftharpoons CH_3NH_2 + NH_4^+$$

This type of reaction can be used as a method for the preparation of amines.

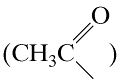
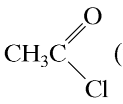
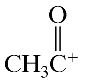
Displacements can also occur at adducts other than methyl iodide. Methoxide ion will react with methyl chloride, methyl bromide, or methyl iodide. In fact, the reaction of alkoxide ions, RO^-, with alkyl halides is a convenient general method for preparing ethers.

$$CH_3O:^- + CH_3Br \rightleftharpoons CH_3OCH_3 + :\underset{\cdot\cdot}{\ddot{Br}}:^-$$

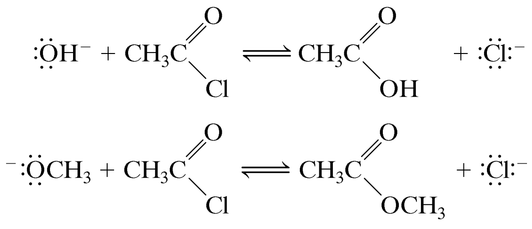
$$CH_3CH_2\underset{\cdot\cdot}{\ddot{O}}:^- + CH_3Cl \rightleftharpoons CH_3CH_2OCH_3 + :\underset{\cdot\cdot}{\ddot{Cl}}:^-$$

$$CH_3\underset{\cdot\cdot}{\ddot{O}}:^- + CH_3CH_2Br \rightleftharpoons CH_3CH_2OCH_3 + :\underset{\cdot\cdot}{\ddot{Br}}:^-$$

Problem 17.11

Compounds containing the acetyl group (), such as  (which can be visualized as the adduct of  $\overset{O}{\overset{\|}{CH_3C^+}}$ and $:\underset{\cdot\cdot}{\ddot{Cl}}:^-$), can also be used as adducts for base displacements. Write an equation for the reaction of hydroxide ion and methoxide ion with CH_3COCl.

Solution:



Rate of Base Displacements at Carbon

Unlike proton-transfer reactions, the rates of displacement reactions at carbon are generally slow. The rates (rather than the extents) of these reactions are therefore of prime importance, and the reactivity of the displacing base is measured in terms of its effect on the rate of the displacement reaction. How readily the base reacts in these terms is referred to as its **nucleophilicity**. Thus, the faster the rate of reaction between the base and the reactant adduct, the greater its nucleophilicity. This concept of nucleophilicity must be contrasted with the concept of basicity, which refers to reactivity as measured by the *extent* of a reaction. As mentioned earlier, a base can also be called a nucleophile, and an acid can also be called an electrophile. A base-displacement reaction can then be called a **nucleophilic-displacement**, or **nucleophilic-substitution reaction**. The reactant adduct is often referred to as the **substrate**.

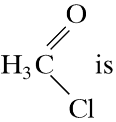
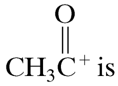
$$\begin{array}{ccccccc} B: & + & A:D & \rightleftharpoons & A:B & + & D: \\ \text{nucleophile} & & \text{substrate} & & \text{product} & & \text{leaving} \\ & & & & & & \text{nucleophile} \end{array}$$

Experimentally, it has been determined that the nucleophilicities of various bases toward the adduct methyl iodide (in hydrogen-bonding solvents such as CH_3OH) vary in the order

$$(C_2H_5)_3P > I^- > (C_2H_5)_3N > (CH_3)_2S > NH_3 > Cl^- > F^- > (CH_3)_2O$$

That is, of these bases, triethylphosphine, $(C_2H_5)_3P$, reacts most rapidly with CH_3I, while $(CH_3)_2O$ reacts most slowly. The nucleophilicity orders $(C_2H_5)_3P > (C_2H_5)_3N$, $(CH_3)_2S > (CH_3)_2O$, and $I^- > Br^- > Cl^- > F^-$ are clearly indicative of *soft* acid behavior: The third-row elements phosphorus, sulfur, and chlorine react more rapidly than their second-row counterparts, nitrogen, oxygen, and fluorine, with the acid portion of the substrate, CH_3^+. These reactivity orders depend somewhat on what solvent the reaction is carried out in, however, and in some solvents the halogen order is actually reversed to $F^- > Cl^- > Br^- > I^-$. For this reason, the acid CH_3^+ is classified as a borderline acid. Clearly, the hard and soft acid and base principle can be applied to both the extent and the rate of chemical reactions.

The nucleophilicity order given above demonstrates that the relative nucleophilicities of the hard bases NH_3 and $(CH_3)_2O$ are determined by the availability of the lone pair of electrons. Thus, the lone pair of NH_3 is more available than that of $(CH_3)_2O$, and NH_3 is therefore the better nucleophile. The availability of the lone pair also determines the relative nucleophilicities of the soft bases—for example, $(C_2H_5)_3P > (CH_3)_2S$.

When acetyl chloride,  $CH_3C(=O)Cl$ is used as the substrate, the reactivity order is quite different: The hard bases F^-, OH^-, $(CH_3)_2O$, NH_3, $(C_2H_5)_3N$, and so on, react more rapidly than the soft bases I^-, SH^-, $(CH_3)_2S$, $(C_2H_5)_3P$, and so on. The acid portion of the substrate,  $CH_3\overset{\overset{O}{\|}}{C}{}^+$, is therefore a *hard* acid. That  $CH_3\overset{\overset{O}{\|}}{C}{}^+$ is hard is quite understandable on the basis of the electronegativity of oxygen: The electronegative oxygen removes electron density from the carbon, making it less polarizable than the carbon of the borderline acid CH_3^+.

An altogether different reactivity order is encountered when a tertiary butyl halide is used as the substrate. The nature of the nucleophile does not affect the rate of the reaction at all!

$$(CH_3)_3CX + :B^- \rightleftharpoons (CH_3)_3C:B + X^-$$

This result cannot be explained by the hard and soft acids and bases principle, and we must look to the mechanism of the reaction for an explanation.*

Not only is the rate of this reaction independent of the nature and concentration of the nucleophile, but it is first-order with respect to the concentration of the substrate.

$$\text{rate} = k[(CH_3)_3CX]$$

The following two-step mechanism, in which the first step is rate determining, is consistent with this rate law:

$$(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^- \qquad \text{(slow)}$$

$$(CH_3)_3C^+ + B:^- \longrightarrow (CH_3)_3C:B \qquad \text{(fast)}$$

The rate-determining step is the dissociation of *tert*-butyl chloride to the $(CH_3)_3C^+$ (a carbocation) and Cl^- ions. The rate equation for this step is

$$\text{rate} = k[(CH_3)_3CCl]$$

which is in agreement with the experimentally determined rate law for the overall reaction. As soon as the $(CH_3)_3C^+$ ion is formed in the slow step, it is consumed in the fast step by the nucleophile. This mechanism has been given the abbreviation S_N1, which stands for "unimolecular nucleophilic substitution". Unimolecular refers to the molecularity of the rate-determining dissociation of the tert -butyl chloride.

A quite different mechanism has been postulated for nucleophilic displacements on methyl halides. Experimentally, the rate of these reactions is proportional to the concentrations of both the substrate and the nucleophile.

$$\text{rate} = k[CH_3X][B:]$$

A simple one-step mechanism identical to the overall equation

$$CH_3X + B:^- \rightleftharpoons CH_3B + X^-$$

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* This mechanism was also discussed in Chapter 12.

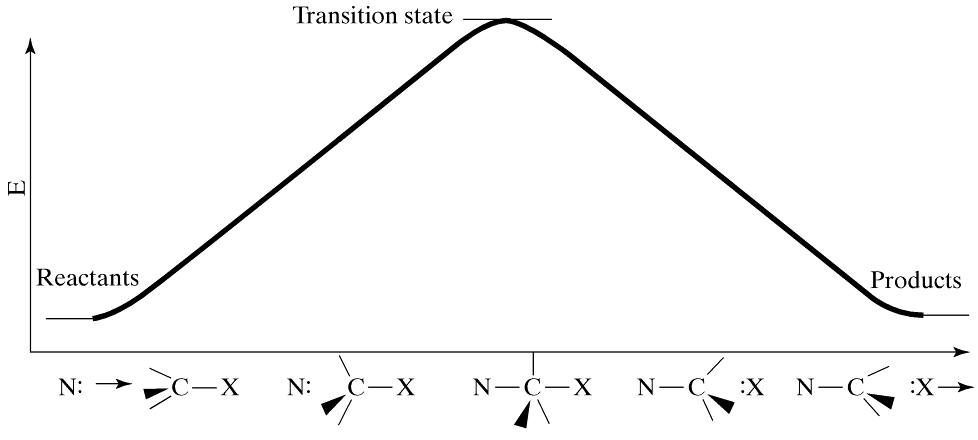


Figure 17.5 Reaction profile for the S_N2 mechanism.

is consistent with the rate equation. This process is bimolecular, and the mechanism is therefore abbreviated as S_N2.

The question now arises: Why should the replacement of the hydrogens in CH_3Cl by methyl groups to give $(CH_3)_3CCl$ result in a change in mechanism for displacements at the two substrates? The answer appears to lie at least in part in the structure of the transition state for the S_N2 reaction. Evidence based on the reactions of optically active substrates indicates that the nucleophile attacks the carbon of the substrate at a point directly opposite the leaving group. The structure of the activated complex, where the nucleophile is partially bonded and the leaving group has partially detached itself, is therefore:

A pictorial time sequence of events for the reaction, along with the corresponding energy profile, is shown in Figure 17.5. If the same transition state is imagined for *tert*-butyl chloride, the increase in repulsions between the nucleophile and the $C(CH_3)_3$ group and also between the leaving group and the $C(CH_3)_3$ group (due to the greater bulk of a methyl group relative to a hydrogen) are easily visualized. These repulsions increase the energy of the activated complex and, as a result of the increased activation energy, lead to a marked decrease in rate. Instead of proceeding by the relatively unfavorable S_N2 mechanism, the *tert*-butyl substrate utilizes the more favorable S_N1 mechanism.

This model suggests that most primary halides (for example, CH_3CH_2Cl) will undergo nucleophilic substitution via the S_N2 mechanism, while tertiary halides (for example, $(CH_3)_3CCl$ and $(C_6H_5)_3CCl$) will react by the S_N1 mechanism. This expectation has been verified by numerous experiments.

17.4 ACID-DISPLACEMENT REACTIONS

Whenever a reaction contains two potential Lewis acids, the possibility of an acid-displacement reaction exists. For example, if Zn^{2+} is added to an aqueous solution of the adduct $Cd(NH_3)_4{}^{2+}$, the following reaction (for which $K = 10^3$) will occur:

$$Zn^{2+} + Cd(NH_3)_4{}^{2+} \rightleftharpoons Zn(NH_3)_4{}^{2+} + Cd^{2+}$$

Here the borderline acid Zn^{2+} and the soft acid Cd^{2+} compete for the lone pair provided by the hard base NH_3. The ammonia prefers to bind to the harder acid, in agreement with the hard and soft acid and base principle.

The destruction of ammonia adducts with acids, a procedure frequently encountered in the qualitative analysis of transition metal salts, can also be thought of as a competition between the acid H^+ and the transition metal cation for the ammonia. The ammonia again prefers the harder acid, the proton.

$$4\,H^+ + Cu(NH_3)_4{}^{2+} \rightleftharpoons 4\,NH_4{}^+ + Cu^{2+}$$

CHAPTER SUMMARY

In electron-sharing reactions, one reactant possesses an unshared pair of electrons, and the other reactant is capable of accepting a pair of electrons because it has an empty orbital. The two reactants therefore share the electron pair, forming a covalent bond.

Electron-sharing reactions are viewed as acid-base reactions, according to the **Lewis concept**. This concept, which is broader in its definition of acids and bases than the Brønsted-Lowry concept, defines an **acid** as a substance that can accept a pair of electrons and a **base** as a substance that can provide a pair of electrons. Electron-sharing reactions are of two main types: addition reactions and displacement reactions.

In **addition reactions**, the electron-pair donor (also called the **nucleophile**, meaning "nucleus lover") and the electron-pair acceptor (or **electrophile**, the "electron lover") combine and share the electron pair to form a single product called the **adduct**.

The electron donor in addition reactions may be any species that contains an unshared pair of electrons; therefore, all Brønsted-Lowry bases are also Lewis bases. Electron acceptors (Lewis acids) can be classified into the following four major categories (note that in each equation, the acid is the first reactant):

1. Cations:

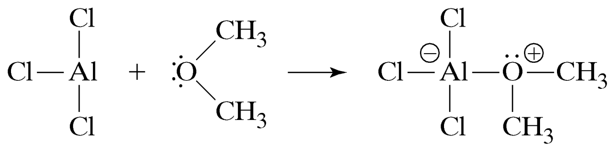
$$Ag^{+} + 2\,NH_3 \longrightarrow Ag(NH_3)_2{}^{+}$$

$$Hg^{2+} + 4\,I^{-} \longrightarrow HgI_4{}^{2-}$$

$$Zn^{2+} + 4\,OH^{-} \longrightarrow Zn(OH)_4{}^{2-}$$

2. Molecules whose central atoms have incomplete octets:

$$BCl_3 + NH_3 \longrightarrow Cl_3B - NH_3$$



3. Molecules in which the octet of the central atom can be expanded:

$$SnCl_4 + 2\,Cl^{-} \longrightarrow SnCl_6{}^{2-}$$

$$SiF_4 + 2\,F^{-} \longrightarrow SiF_6{}^{2-}$$

4. Molecules with multiple-bonded central atoms:

$$CO_2 + OH^{-} \longrightarrow HCO_3{}^{-}$$

$$SO_3 + O^{2} \longrightarrow SO_4{}^{2-}$$

The strengths of Lewis acids and bases are discussed in terms of **hard** and **soft** categories. Familiarize yourself with this concept, so that you are able to classify various species as hard or soft. This method of classification will enable you to predict the relative extents of a variety of electron-sharing reactions.

In **displacement reactions**, one electron-pair donor replaces another (**base-displacement** reaction) or one electron-pair acceptor replaces another (**acid-displacement** reaction):

$$\begin{array}{ccc} A - B + \,:D & \longrightarrow & A - D + \,:B \\ \text{adduct} + \text{base} & \longrightarrow & \text{adduct} + \text{base} \end{array}$$

$$\begin{array}{ccc} A - B + C & \longrightarrow & C - B + A \\ \text{adduct} \quad \text{acid} & & \text{adduct} \quad \text{acid} \end{array}$$

TERMS

Some important new terms include the following:

Coordination number The number of bases bonded to the acid in an adduct. For example, the coordination number of aluminum in the adduct $Al(OH)_4{}^-$ is 4 and the coordination number of silver in $Ag(CN)_2{}^-$ is 2.

Amphoteric substance A substance that can act both as a Brønsted-Lowry base (a proton acceptor) and as a Lewis acid (an electron-pair acceptor). The term "amphoteric" should not be confused with "amphiprotic," which refers to a substance that can behave as a Brønsted-Lowry acid and base. Of particular interest are the amphoteric hydroxides (see Table 17.3).

Formation constant The equilibrium constant for a reaction in which an adduct is formed. For the reaction

$$Ag^+ + 2\,CN^- \rightleftharpoons Ag(CN)_2{}^-$$

the formation constant K_f is

$$\frac{[Ag(CN)_2{}^-]}{[Ag^+][CN^-]^2} = K_f$$

Instability constant The equilibrium constant for the reaction that represents the decomposition of an adduct into its acid and base. The instability constant for a given adduct is the reciprocal of the formation constant for that adduct.

Hard and soft acids and bases Categorizations that can be applied to Lewis acids and bases. **Hard acids** have small acceptor atoms of high positive charge, and **soft acids** have large acceptor atoms of low positive charge. Similarly, **hard bases** have highly electronegative and unpolarizable donor atoms, whereas the donor atoms of **soft bases** are less negative and more polarizable. In general, hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases. (For examples, see Table 17.6.)

PROBLEMS

1. The reaction of ammonium ion with hydroxide ion is usually thought of as a proton-transfer reaction. Can this reaction also be classified as an electron-sharing reaction?

2. Write an equation showing:
(a) $Al(H_2O)_6{}^{3+}$ acting as a Brønsted-Lowry acid
(b) Cd^{2+} acting as a Lewis acid
(c) $Al(OH)_3$ reacting as a Brønsted-Lowry base
(d) $Al(OH)_3$ reacting as a Lewis acid
(e) OH^- reacting as a Lewis base
(f) $Ag(NH_3)_2{}^+$ as an adduct

3. For each of the following adducts, give a possible preparation and predict the geometry:
(a) $SnCl_3{}^-$ (b) $SnCl_6{}^{2-}$ (c) $B(OH)_4{}^-$ (d) $AlF_4{}^-$

4. Why does Be^{2+} form the adduct $Be(OH_2)_4{}^{2+}$ whereas Al^{3+} forms $Al(OH_2)_6{}^{3+}$?

5. Write the electron-dot formulas, complete with formal charges, for $SnCl_5{}^-$ and $SnCl_6{}^{2-}$. Which would you predict to be more stable?

6. Rationalize the following observations:
(a) Silver chloride is significantly more soluble in 1 *M* $Hg(NO_3)_2$ than in pure water.
(b) Silver chloride is insoluble in H_2O but soluble in aqueous NH_3.
(c) Mg(OH)2 does not dissolve in 1 *M* NaOH, but $Al(OH)_3$ does.
(d) The solubilities of the IIB sulfides vary in the order $ZnS > CdS > HgS$.
(e) $B(OH)_3$ is a Lewis acid, while $Al(OH)_3$ is both a Lewis acid and a Brønsted-Lowry base.

7. Addition of concentrated HCl to a 1 *M* solution of $CuCl_2$ changes the color of the solution from blue to yellow-green. Addition of water to this solution changes the color back to the original blue. Similarly, addition of concentrated HCl to 1 *M* $CoCl_2$ changes the color of the solution from pink to deep blue, and addition of water to this solution changes it back to pink. Furnish an explanation.

8. The compound $B(OH)_3$ in water is known as boric acid and has an acid dissociation constant of 1.0×10^{-9}. However, the increase in hydrogen ion concentration that results from the dissolution of boric acid is not accomplished by proton transfer from the boric acid.
(a) Write a reaction for boric acid behaving as an acid in water.
(b) Calculate the pH of a 0.010 *M* solution of boric acid.

9. What single reagent can be used to separate the following solid compounds? Write an equation for each reaction.
(a) $Al(OH)_3$, $Bi(OH)_3$
(b) $AgCl$, $PbSO_4$
(c) $Ni(OH)_2$, $Al(OH)_3$
(d) $Zn(OH)_2$, $Cu(OH)_2$
(e) $Mg(NO_3)_2$, $SbCl_3$

10. Give a scheme that will separate the following aqueous cation mixtures:
(a) Ag^+, Al^{3+}, Fe^{3+}
(b) Cd^{2+}, Zn^{2+}, Bi^{3+}
(c) Ba^{2+}, Ag^+, Cr^{3+}

11. Provide a scheme for the separation of the ions in each of the following mixtures:
(a) Cr^{3+}, Fe^{3+}, Co^{2+}
(b) Sr^{2+}, Al^{3+}, Zn^{2+}
(c) Ag^+, Cu^{2+}, Fe^{3+}
(d) Cr^{3+}, Bi^{3+}, Ni^{2+}, Ag^+

12. Identify the following type of reaction:

$$(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4N^+\ I^-$$

Name the product as an ammonium ion. Should it be soluble in water?

13. Write equations for the reaction of Pb^{2+} and Hg^{2+} with iodide ion.

14. Determine the equilibrium constant for the reaction

$$PbI_2(s) + 2\,I^- \longrightarrow PbI_4^{2-}$$

15. A solution is 0.0010 *M* in cadmium chloride. How much cyanide ion must be added to reduce the concentration of cadmium ion to 1.0×10^{-8} *M*?

16. How many moles of sodium cyanide must be added to 100 mL of water so that the resulting solution will dissolve 0.10 mol of AgI?

17. Determine the nickel ion concentration, $[Ni^{2+}]$, in a solution prepared by dissolving 6.50 g of nickel(II) chloride in enough 5.0 *M* NH_3 to make 1.00 L of solution.

18. Will 100 mL of a 3.2 *M* solution of ammonia dissolve (a) 0.010 mol of silver chloride? (b) 0.010 mol of silver bromide?

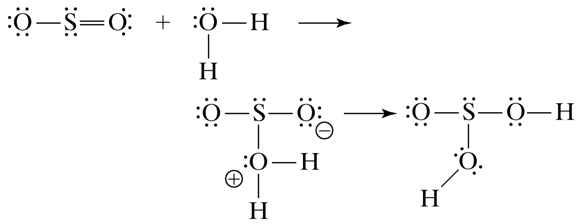
19. The solubility product constant for AgCl is 1.8×10^{-10}. The instability constant for $Ag(NH_3)_2^+$ is 6.2×10^{-8}. Find the equilibrium constant for the reaction:

$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

20. Present a concise discussion on each of the following topics:
(a) the mechanism of nucleophilic substitution reactions
(b) the hard and soft acid-base concept

21. Classify each of the following electron-sharing reactions as "addition," "base-displacement," or "acid-displacement."
(a) $SnCl_4 + 2\,Cl^- \rightleftharpoons SnCl_6^{2-}$
(b) $AgBr_4^{3-} + 4\,Cl^- \rightleftharpoons AgCl_4^{3-} + 4\,Br^-$
(c) $SO_3^{2-} + S \rightleftharpoons S_2O_3^{2-}$
(d) $Hg^{2+} + Zn(CN)_4^{2-} \rightleftharpoons Zn^{2+} + Hg(CN)_4^{2-}$

22. Write equations to explain the following facts:
(a) Aluminum hydroxide is amphoteric.
(b) A white precipitate forms when sodium chloride solution is slowly added to lead nitrate solution, but on continued addition of NaCl solution, the precipitate gradually dissolves.
(c) Although CF_4 does not undergo any reaction with fluoride ion, SiF_4 does.
(d) Sulfur dioxide reacts with water to form sulfurous acid.



23. Consider the reaction

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

According to the hard/soft acid-base model is the equilibrium constant for this reaction large or small?

24. Although zinc and cadmium are both in Group IIB, zinc hydroxide is amphoteric but cadmium hydroxide is not. Can this be rationalized with the hard/soft acid-base model?

25. According to the hard/soft acid-base model, which should be most insoluble—ZnS, CdS, or HgS?

26. Acid is often used to destroy ammonia complexes, e.g.,

$$Zn(NH_3)_4^{2+} + 4\,H^+ \longrightarrow Zn^{2+} + 4\,NH_4^+$$

Predict whether the equilibrium constant for this reaction is large or small?

27. Using the concept of hard and soft acids and bases, predict whether the following reactions have equilibrium constants greater than 1 or less than 1.
(a) $AgBr_4^{3-} + 4\,Cl^- \rightleftharpoons AgCl_4^{3-} + 4\,Br^-$
(b) $Cu^{2+} + Cd(NH_3)_4^{2+} \rightleftharpoons Cu(NH_3)_4^{2+} + Cd^{2+}$
(c) $Co^{3+} + Co(NH_3)_6^{2}+ \rightleftharpoons Co(NH_3)_6^{3+} + Co^{2+}$
(d) $Co(NH_3)_6^{3+} + 6\,PH_3 \rightleftharpoons Co(PH_3)_6^{3+} + 6\,NH_3$
(e) $HgO + S^{2-} \rightleftharpoons HgS + O^{2-}$

28. Predict whether the following reactions have equilibrium constants greater than or less than 1:
(a) $F_3BN(CH_3)_3 + P(CH_3)_3 \rightleftharpoons F_3BP(CH_3)_3 + N(CH_3)_3$
(b) $F_3BO(CH_3)_2 + N(CH_3)_3 \rightleftharpoons F_3BN(CH_3)_3 + O(CH_3)_2$
(c) $F_3BN(CH_3)_3 + B(CH_3)_3 \rightleftharpoons (CH_3)_3BN(CH_3)_3 + BF_3$
(d) $H_3O^+ + H_2S \rightleftharpoons H_3S^+ + H_2O$
(e) $H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O$
(f) $CdCl_4^{2-} + 4\,I^- \rightleftharpoons CdI_4^{2-} + 4\,Cl^-$
(g) $BF_4^- + 4\,I^- \rightleftharpoons BI_4^- + 4\,F^-$
(h) $Zn(OH)_4^{2-} + Cd^{2+} \rightleftharpoons Cd(OH)_4^{2-} + Zn^{2+}$

29. The lithium ion is smaller and therefore less polarizable than the cesium ion. Predict whether the equilibrium constant for the following reaction is greater than or less than 1. Estimate the equilibrium constant at 25 °C by calculating ΔH^0 from the data of Appendix 3.

$$LiF(s) + CsI(s) \rightleftharpoons LiI(s) + CsF(s)$$

30. Determine from the following data whether the trimethylcarbonium ion, $(CH_3)_3C^+$, is softer or harder than CH_3^+.

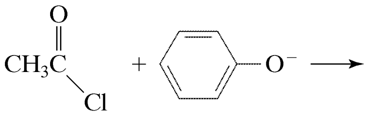
$$CH_3OH(g) + H_2S(g) \longrightarrow CH_3SH(g) + H_2O(g) \qquad \Delta H^0 = -42\ \text{kJ}$$

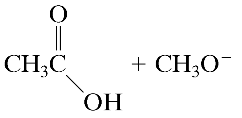
$$(CH_3)_3COH(g) + H_2S(g) \longrightarrow (CH_3)_3CSH(g) + H_2O(g) \qquad \Delta H^0 = -17\ \text{kJ}$$

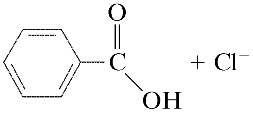
31. Hydrogen bonding can be visualized as a Lewis acid-base interaction between a covalently bonded proton (the acid) and a nonbonded pair of electrons (the base). Which kind of base would hydrogen-bond better—a hard or a soft base? Provide examples.

32. Predict whether the following common minerals are sulfides or oxides:
(a) chromite, a chromium(III) ore
(b) hematite, an iron(III) ore
(c) pyrolusite, a manganese(IV) ore
(d) sphalerite, a zinc(II) ore
(e) rutile, a titanium(IV) ore
(f) cinnabar, a mercury(II) ore

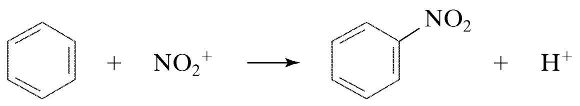
33. Supply products for the following reactions:
(a) $CH_3I + {}^-OCH_3 \rightarrow$
(b) $CH_3CH_2Br + {}^-NH_2 \rightarrow$

(c) 

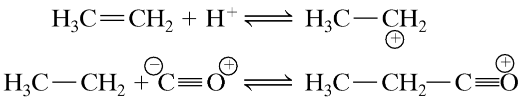
(d) 

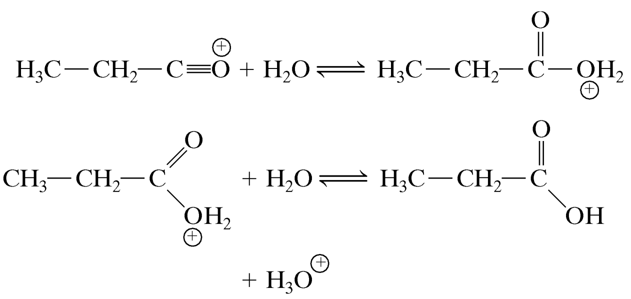
(e) 

34. Write an equation showing:
(a) $Pb(H_2O)_4{}^{2+}$ acting as a Brønsted-Lowry acid
(b) $Pb(H_2O)_4{}^{2+}$ as a reactant in a base-displacement reaction
(c) Zn^{2+} acting as a Lewis acid
(d) $Zn(OH)_2$ reacting as a Brønsted-Lowry base
(e) $Zn(OH)_2$ reacting as a Lewis acid
(f) NH_3 reacting as a Lewis base
(g) NH_3 as a reactant in a base-displacement reaction
(h) $Cd(NH_3)_4{}^{2+}$ as a reactant in an acid-displacement reaction
(i) CO_2 acting as a Lewis acid
(j) $H_2C{=}O$ acting as a Lewis acid
(k) SO_2 acting as a Lewis acid
(l) CH_3Br as a reactant in a base-displacement reaction
(m) $CH_3CO_2CH_3$ as a reactant in a base-displacement reaction
(n) benzene as a reactant in an acid-displacement reaction



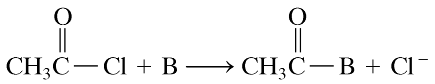
35. Decide which steps in the following sequence of reactions are Lowry-Brønsted acid-base reactions and which are Lewis acid-base reactions.





36. Distinguish carefully between:
(a) an addition reaction and a displacement reaction
(b) a base-displacement reaction and an acid-displacement reaction
(c) amphiprotic and amphoteric
(d) the reaction of $Al(OH)_3$ as an acid and its reaction as a base
(e) basicity and nucleophilicity
(f) a hard acid and a soft acid
(g) a nucleophile and an electrophile
(h) the S_N1 mechanism and the S_N2 mechanism

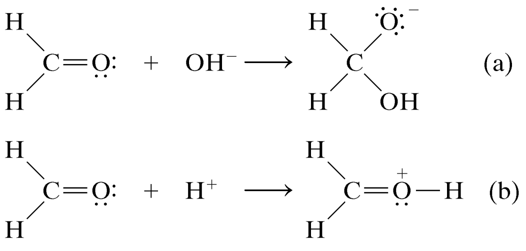
37. In the reaction



$$CH_3\overset{O}{\overset{\|}{C}}-Cl + B \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-B + Cl^-$$

which nucleophile in each of the following pairs is the stronger?
(a) F^-, I^-
(b) OH^-, SH^-
(c) $NH_2{}^-, PH_2{}^-$

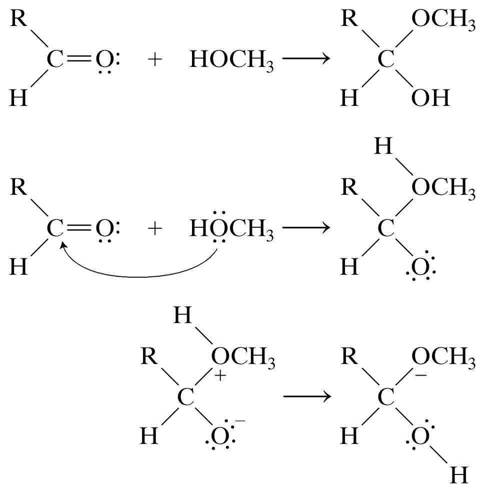
38. The compound $H_2C{=}O$ has both an electrophilic and a nucleophilic site.
(a) Identify these sites using an electron dot formula for $H_2C{=}O$.
(b) For the two reactions (a) and (b) below answer the following questions.



(1) Which reaction involves the electrophilic site of $H_2C{=}O$?
(2) Which involves nucleophilic attack on H^+?
(3) Which involves electrophilic attack of H^+?
(4) Which involves nucleophilic attack by OH^-?

39. Present a mechanism for the following reaction that includes nucleophilic attack by the oxygen of the alcohol on the carbon of the carbonyl.

See equation next page



40. For which reaction, A or B, are the following true?

$$\text{A} \quad CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

$$\text{B} \quad (CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$$

(a) The reaction is second order overall
(b) The reaction has a two-step mechanism
(c) The reaction proceeds through an intermediate with a positive charge
(d) The transition state of the rate-determining step contains both OH and Cl partially bonded to carbon
(e) The reaction has two transition states

41. Give a correctly labeled reaction profile for the reaction

$$(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$$

42. Give the structure and geometry of the intermediate in the reaction

$$(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$$

43. Fill in the blanks

(a) In the complex ion $Co(NH_3)_6^{2+}$, the coordination number of cobalt is _____________.
(b) The overall formation constant for $Ni(NH_3)_6^{2+}$ is 2.0×10^8. The instability constant for this ion is _____________.
(c) Hard acids prefer to bind to _____________ bases.
(d) In the reaction $BeF_2 + F^- \rightarrow BeF_3^-$, the Lewis acid is _____________ the base is ______, and BeF_3^- is called the _____________.
(e) The reaction $CH_3I + HS^- \rightarrow CH_3SH + I^-$ is an example of a _____________-displacement reaction.
(f) A substance that can accept either a proton or an electron pair is said to be _____________.
(g) In the reaction $Pb^{2+} + 4\ Cl^- \leftrightarrows PbCl_4^{2-}$, the nucleophile is _____________ and the electrophile is _____________.
(h) The acceptor atoms in soft acids are relatively _____________ in charge and _____________ in size.
(i) Acid-displacement reactions may also be called _____________ substitutions.
(j) Of the compounds CH_4, NH_3, and H_2O, the one that cannot act as a Lewis base is _____________.

18

Electron-Transfer Reactions

The preceding chapters have dealt with chemical reactions that involve exchange of ions, exchange of protons, and sharing of electrons. In this chapter a fourth type of reaction will be considered: those in which electrons are transferred from one reactant to another. Electron-transfer reactions are commonly referred to as **oxidation-reduction**, or **redox reactions**.

Originally, the term "oxidation" was applied to a reaction in which a substance combined with oxygen; for example, the oxidation of calcium to calcium oxide:

$$2\,\mathrm{Ca} + \mathrm{O_2} \longrightarrow 2\,\mathrm{CaO}$$

The reverse process—the loss of oxygen by a substance—was called reduction. Thus, for example, when mercuric oxide is heated, it decomposes to elemental mercury and oxygen. In this reaction, HgO is said to be reduced:

$$2\,\mathrm{HgO} \longrightarrow 2\,\mathrm{Hg} + \mathrm{O_2}$$

The meanings of the terms were later broadened to include the loss of hydrogen (oxidation) and the gain of hydrogen (reduction). Thus, in the hydrogenation of ethylene to ethane, the ethylene is reduced:

$$\mathrm{H_2C{=}CH_2} + \mathrm{H_2} \longrightarrow \mathrm{H_3C{-}CH_3}$$

The fundamental nature of the process by which calcium and oxygen combine implies that in order for a calcium atom to become a calcium ion, it must lose electrons, and in order for the atoms of the oxygen molecule to become oxide ions, they must gain electrons,

$$\mathrm{Ca} \longrightarrow \mathrm{Ca^{2+}} + 2\,e^-$$

$$\mathrm{O_2} + 4\,e^- \longrightarrow 2\,\mathrm{O^{2-}}$$

Similarly, in the reduction of HgO, mercury gains electrons and oxygen loses them:

$$\mathrm{Hg^{2+}} + 2\,e^- \longrightarrow \mathrm{Hg}$$

$$2\,\mathrm{O^{2-}} \longrightarrow \mathrm{O_2} + 4\,e^-$$

Numerous chemical reactions that do not involve hydrogen or oxygen occur by this same basic process: the transfer of electrons. For example, the simple reactions between iron and sulfur, and between sodium and chlorine, are precisely analogous to the oxidation of calcium:

$$\mathrm{Fe} + \mathrm{S} \longrightarrow \mathrm{FeS}$$

$$2\,\mathrm{Na} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{NaCl}$$

In the first reaction, iron loses two electrons to become the ferrous ion, $\mathrm{Fe^{2+}}$, and sulfur gains two electrons to become the sulfide ion, $\mathrm{S^{2-}}$. Similarly, in the second reaction, sodium loses an electron to become the sodium ion, Na^+, and a chlorine molecule gains two electrons to yield two chloride ions, Cl^-.

The fundamental aspect of these reactions that makes them different from the types of reactions described in previous chapters is not the gain or loss of oxygen or hydrogen, but rather the transfer of electrons.

Oxidation is the loss of electrons.

Reduction is the gain of electrons.

Because a substance can gain electrons only from another substance that loses electrons, the two processes occur simultaneously and the net number of electrons is conserved. The resulting overall transformation is therefore referred to as an oxidation-reduction reaction. The reactant that loses the electrons is said to be oxidized and is called the **reducing agent**, or **reductant**; the reactant that gains the electrons is said to be reduced and is called the **oxidizing agent**, or **oxidant**. Thus, in the reaction between sodium and chlorine in Figure 18.1, sodium is the reductant (it is oxidized) and chlorine is the oxidant (it is reduced).

18.1 OXIDATION NUMBERS

Oxidation-reduction processes can be described in terms of a system of useful, although artificial, positive and negative numbers called **oxidation numbers**, or **oxidation states**. An oxidation number is assigned to each atom in a compound to represent the electrical charge the atom would have if the electrons in the compound were assigned in a particular way. This number does not represent an actual charge on the atom and should not be confused with the ionic charge.

Oxidation numbers are assigned according to a set of arbitrary rules, as follows:

1. The oxidation number of the atoms in an elementary substance is zero.
2. The oxidation number of monatomic ions is the same as the ionic charge.
3. The oxidation number of hydrogen is $+1$, except in elemental hydrogen (in which it is zero) and in ionic hydrides such as NaH (in which it is -1).
4. The oxidation number of oxygen is -2, except in elemental oxygen (in which it is zero) and in peroxides such as H_2O_2 (in which it is -1).
5. Covalent binary compounds that contain neither hydrogen nor oxygen are treated as though they were ionic, using rule 2.
6. In a neutral compound, the sum of the oxidation numbers must equal zero; in a complex ion, the sum must equal the charge of the ion.

With few exceptions, these rules make it possible to assign oxidation numbers to all the atoms in any substance. The following examples illustrate the application of these rules. Nitrogen gas (N_2) is an elementary substance; the oxidation number of the nitrogen atoms in the molecule is zero (rule 1), which we indicate by writing

$$\overset{0}{N_2}$$

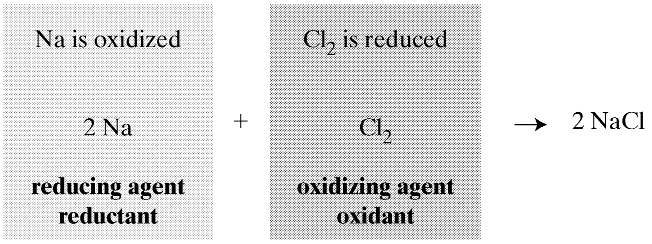


Figure 18.1 An electron transfer (redox) reaction.

The oxidation numbers for the ionic compound $CaCl_2$ are the same as the ionic charges (rule 2), that is, +2 for calcium and −1 for chlorine; hence we write

$$\overset{+2}{\mathrm{Ca}}\overset{-1}{\mathrm{Cl}_2}$$

Note that the sum of one calcium at +2 and two chlorines, each at −1 equals zero, in accordance with rule 6.

Consider now the oxidation numbers in $HClO_4$. One hydrogen atom with an oxidation number of +1 (rule 3) and four oxygen atoms with oxidation numbers of −2 (rule 4) equals −7. Because the sum of all the numbers must equal zero, we must assign an oxidation number of +7 to the Cl atom:

$$\overset{+1}{\mathrm{H}}\overset{+7}{\mathrm{Cl}}\overset{-2}{\mathrm{O}_4}.$$

As further illustrations, a number of formulas are listed in Figure 18.2, with oxidation numbers assigned in accordance with the rules described. The examples in the fourth column are illustrations of rule 5.

This system of oxidation numbers provides a method for keeping track of oxidation-reduction processes. First, it enables us to readily determine whether or not a given chemical reaction is a redox reaction; if it is, then the oxidation number of at least two different atoms must change—one must increase and the other decrease. Further, because oxidation is a loss of electrons, and electrons are negative, oxidation results in an increase in the oxidation number of an element. Reduction is the gain of electrons and is accompanied by a decrease in the oxidation number of an atom. Thus, the oxidant and reductant are easily identified.

Consider the reaction between phosphorus pentachloride and water:

$$\overset{+5}{\mathrm{P}}\overset{-1}{\mathrm{Cl}_5} + 4\,\overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}} \longrightarrow \overset{+1}{\mathrm{H}_3}\overset{+5}{\mathrm{P}}\overset{-2}{\mathrm{O}_4} + 5\,\overset{+1}{\mathrm{H}}\overset{-1}{\mathrm{Cl}}$$

Superficially, this process may appear to be a redox reaction, but assignment of oxidation numbers to reactants and products indicates that the reaction results in no change in any of these numbers, and therefore it is not an electron-transfer reaction. Similarly, we may conclude that the conversion of the chromate ion to dichromate in the presence of acid is also not an oxidation-reduction reaction because there is no change in oxidation numbers:

$$2\,\overset{+6}{\mathrm{Cr}}\overset{-2}{\mathrm{O}_4}{}^{2-} + 2\,\overset{+1}{\mathrm{H}}{}^{+} \longrightarrow \overset{+6}{\mathrm{Cr}_2}\overset{-2}{\mathrm{O}_7}{}^{2-} + \overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}$$

However, the reaction between copper metal and concentrated nitric acid is clearly a redox reaction, as shown by the changes in oxidation numbers:

$$\overset{0}{\mathrm{Cu}} + 4\,\overset{+1}{\mathrm{H}}\overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}_3} \longrightarrow \overset{+2}{\mathrm{Cu}}(\overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}_3})_2 + 2\,\overset{+4}{\mathrm{N}}\overset{-2}{\mathrm{O}_2} + 2\,\overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}$$

Furthermore, it is apparent that copper is the reducing agent (it is oxidized) and nitric acid is the oxidizing agent (it is reduced).

$\overset{+1}{\mathrm{N}_2}\overset{-2}{\mathrm{O}}$	$\overset{+1}{\mathrm{Na}_2}\overset{+4}{\mathrm{C}}\overset{-2}{\mathrm{O}_3}$	$\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}_3}$	$\overset{+4}{\mathrm{C}}\overset{-2}{\mathrm{S}_2}$
$(\overset{+5}{\mathrm{P}}\overset{-2}{\mathrm{O}_4})^{3-}$	$\overset{-2}{\mathrm{C}_2}\overset{+1}{\mathrm{H}_6}\overset{-2}{\mathrm{O}}$	$\overset{+1}{\mathrm{Na}_2}\overset{+2}{\mathrm{S}_2}\overset{-2}{\mathrm{O}_3}$	$\overset{+3}{\mathrm{B}}\overset{-1}{\mathrm{F}_3}$
$(\overset{+6}{\mathrm{U}}\overset{-2}{\mathrm{O}_2})^{2+}$	$(\overset{+3}{\mathrm{C}_2}\overset{-2}{\mathrm{O}_4})^{2-}$	$(\overset{+6}{\mathrm{Cr}_2}\overset{-2}{\mathrm{O}_7})^{2-}$	$\overset{+4}{\mathrm{C}}\overset{-1}{\mathrm{Cl}_4}$

Figure 18.2 Assignment of oxidation numbers.

Methodology 18.1

For the following reaction, provide oxidation numbers for each element and indicate which species is undergoing oxidation and which is being reduced.

$$3\,N_2H_4 + 4\,MnO_4^- \longrightarrow 3\,N_2 + 4\,MnO_2 + 4\,OH^- + 4\,H_2O$$

First, determine the oxidation number of each atom in N_2H_4.

> The compound is not an ionic hydride and therefore hydrogen must be assigned an oxidation number of +1. Since there are four hydrogens, the +4 (4 x +1) must be balanced by −4 divided over two nitrogens. Thus, each nitrogen is assigned an oxidation number of −2.

Next, determine the oxidation number of each element in every species.

$$3\,\overset{-2}{N}_2\overset{+1}{H}_4 + 4\,\overset{+7}{Mn}\overset{-2}{O}_4^- \longrightarrow 3\,\overset{0}{N}_2 + 4\,\overset{+4}{Mn}\overset{-2}{O}_2 + 4\,\overset{+4}{Mn}\overset{-2}{O}_2 + 4\,\overset{-2}{O}\overset{+1}{H}^- + 4\,\overset{+1}{H}_2\overset{-2}{O}$$

Finally, examine each of the elements on the left and right sides of the equation to see if a change in oxidation number has occurred.

> The nitrogen in N_2H_4 changes oxidation number, from −2 to 0, indicating a loss of 2 electrons per atom or 4 electrons per molecule. A loss of electrons is oxidation, so the N_2H_4 is being oxidized. The manganese in MnO_4^- changes from +7 to +4, indicating a gain of 3 electrons per atom. The MnO_4^- is being reduced.

Another practical use to which oxidation numbers can be put is in the balancing of equations. Whereas most equations depicting reactions of the types described in previous chapters are easily balanced by simple inspection, many redox reactions lead to equations with rather large coefficients, and balancing them by inspection may be both difficult and time consuming.

A case in point is the reaction between potassium permanganate and oxalic acid in sulfuric acid solution. The skeletal (unbalanced) equation is:

$$KMnO_4 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$$

Attempts to balance the equation by inspection quickly demonstrate that a balance is not readily achieved. When oxidation numbers are assigned to the atoms in the equation, we see that the oxidation number of manganese changes in the reaction from +7 to +2—a decrease of 5.

$$\overset{+7}{Mn} \xrightarrow{-5} \overset{+2}{Mn}$$

The oxidation number of carbon changes from +3 to +4, and because there are at least two carbon atoms on each side of the balanced equation (due to the formula $H_2C_2O_4$), this represents an increase of 2.

$$2\,\overset{+3}{C} \xrightarrow{+2} 2\,\overset{+4}{C}$$

In the overall reaction, the net change of oxidation numbers must be zero; that is, the total increase due to oxidation must be equal to the total decrease due to reduction. It is necessary therefore to multiply the manganese change by 2 and the carbon change by 5.

$$2(\overset{+7}{Mn} \xrightarrow{-5} \overset{+2}{Mn}) = 2\,\overset{+7}{Mn} \xrightarrow{-10} 2\,\overset{+2}{Mn}$$

$$5(2\,\overset{+3}{C} \xrightarrow{+2} 2\,\overset{+4}{C}) = 10\,\overset{+3}{C} \xrightarrow{+10} 10\,\overset{+4}{C}$$

With the assignment of the coefficients of Mn and C in the equation, the equation may be partially balanced as follows:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + H_2O$$

All that remains to be balanced are the H_2SO_4 and H_2O; these may easily be balanced by inspection. Three sulfates on the right require three on the left, so we place a 3 in front of H_2SO_4. This change gives a total of 16 hydrogen atoms on the left, and therefore we must place an 8 before H_2O. The equation is now completely balanced.

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O$$

Methodology 18.2

Balance the following reaction by using oxidation numbers.

$$K_2Cr_2O_7 + H^+ + Cu^o \longrightarrow Cr^{3+} + Cu^{2+} + H_2O + K^+$$

First, the species which gain and lose electrons must be determined.

Examination of the oxidation numbers shows that copper loses 2 electrons, while each chromium in the potassium dichromate (chromium has an oxidation number of +6 in the dichromate ion) gains 3 electrons, for a total gain of 6.

Now, balance the electrons.

The copper must be multiplied by 3 so that 6 electrons are lost by the copper, balancing the 6 that are gained by the chromium.

$$3(Cu^0 \longrightarrow Cu^{2+} + 2\,e^-)$$
$$2\,Cr^{6+} + 6\,e^- \longrightarrow 2\,Cr^{3+}$$

This sets the stoichiometric coefficients for the chromium and copper species in the reaction equation,

$$K_2Cr_2O_7 + H^+ + 3\,Cu^o \longrightarrow 2\,Cr^{3+} + 3\,Cu^{2+} + H_2O + K^+$$

The remainder of the reaction equation may be balanced by inspection.

There are two potassium ions on the left, so two are required on the right and we place a 2 before the K^+. In order to balance the seven oxygens in the dichromate on the left we multiply the H_2O on the right by 7. Now, with fourteen hydrogens on the right (two for each H_2O and we have 7 H_2Os), the H^+ on the left must be multiplied by 14. Thus, the balanced equation is

$$K_2Cr_2O_7 + 14\,H^+ + 3\,Cu^o \longrightarrow 2\,Cr^{3+} + 3\,Cu^{2+} + 7\,H_2O + 2\,K^+$$

18.2 HALF-REACTIONS

An oxidation-reduction reaction is really the sum of two separate processes—the oxidation (loss of electrons) and the reduction (gain of electrons). Aside from the fact that oxidation and reduction must occur simultaneously, the two processes are independent of each other. Therefore, it is convenient, and quite reasonable, to consider a redox reaction as consisting of two separate **half-reactions**—one involving electron loss, the other involving electron gain.

With this in mind, let us proceed to analyze the reaction represented by the following unbalanced molecular equation:

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + H_2O$$

Because this reaction occurs in aqueous solution, and because strong electrolytes are involved, the reaction is more appropriately represented by the use of ions,

$$K^+ + Cr_2O_7^{2-} + Fe^{2+} + SO_4^{2-} + H^+ \longrightarrow K^+ + SO_4^{2-} + Cr^{3+} + Fe^{3+} + H_2O$$

It is immediately apparent from this **ionic equation** that some of the substances present are not actually involved in the reaction at all; that is, they do not undergo any change whatsoever. This is true of potassium ion and sulfate ion, which may therefore be eliminated from the equation, to leave

$$\mathrm{Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O}$$

This equation, called the **net ionic equation**, is the best representation of the reaction that occurs, for it shows only those reactants that actually undergo transformation and those products that result from that transformation.

The net ionic equation is separated into two half-reactions. To achieve this, we choose any one of the reactants and consider what products must be derived from it. For example, $Cr_2O_7^{2-}$ obviously gives rise to Cr^{3+}; furthermore, one $Cr_2O_7^{2-}$ will yield two Cr^{3+},

$$\mathrm{Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+}} \tag{1}$$

The oxygen in the $C_2O_7^{2-}$ may be considered to be converted into water, because water is the only product that contains oxygen; one $Cr_2O_7^{2-}$ supplies enough oxygen for seven H_2O molecules. Therefore, equation (1) can be expanded to:

$$\mathrm{Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O} \tag{2}$$

But now the 14 hydrogen atoms in the water produced must be accounted for. Because the source of these is obviously H^+, equation (2) can be further expanded to:

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 7\,H_2O} \tag{3}$$

In equation (3) the numbers of each different atom are equal on both sides of the arrow, but the ionic charges are not; the net charge is +12 on the left and +6 on the right. This change in total ionic charge can be accounted for if six electrons are gained in the process. Adding this to equation (3) gives an equation that is balanced in all respects, and it represents the half-reaction describing the reduction of $Cr_2O_7^{2-}$ in acid solution,

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,}e^- \mathrm{\longrightarrow 2\,Cr^{3+} + 7\,H_2O} \tag{4}$$

The other half-reaction can be deduced by the same procedure. Ferrous ion gives rise to ferric ion, and the process involves the loss of one electron. Equation (5), then, is the oxidation half-reaction:

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} +}\, e^- \tag{5}$$

From equation (4), each mole of $Cr_2O_7^{2-}$ reduced requires six moles of electrons. Equation (5), on the other hand, shows that only one mole of electrons is liberated for each mole of Fe^{2+} oxidized. Six moles of Fe^{2+} must be oxidized, therefore, to provide enough electrons for the reduction of one mole of $Cr_2O_7^{2-}$. In other words, before the equations for the two half-reactions can be added together to give the equation for the overall reaction, the number of electrons lost must be made equal to the number gained. This condition can be met (in this instance) by multiplying equation (5) by the number 6. Finally, adding together the two statements yields the balanced net ionic equation for the redox reaction, equation (6).

$$\begin{array}{lr}
(4) & \mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,}e^- \mathrm{\longrightarrow 2\,Cr^{3+} + 7\,H_2O} \\
(5) & \mathrm{6\,Fe^{2+} \longrightarrow 6\,Fe^{3+} + 6\,}e^- \\
\cline{2-2}
(6) & \mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O}
\end{array}$$

Note that this procedure for analyzing an oxidation-reduction process results in a balanced net ionic equation. This alternate method of balancing redox equations is frequently called the **ion-electron method** to distinguish it from the **oxidation-state method** described earlier in this chapter. However, the ability to separate a redox reaction into its two half-reactions is of more importance than simply a means of balancing equations; it is essential to an understanding of the functioning of voltaic and electrolytic cells, which will be described later in this chapter.

As another illustration of the application of this procedure, consider the reaction of H_2SO_3 with $KMnO_4$ in acid solution. The unbalanced molecular equation is

$$H_2SO_3 + KMnO_4 + H_2SO_4 \longrightarrow MnSO_4 + K_2SO_4 + H_2O$$

Step 1. Write the unbalanced net ionic equation.

$$H_2SO_3 + MnO_4^- + H^+ \longrightarrow Mn^{2+} + SO_4^{2-} + H_2O$$

(Note that the weak electrolyte H_2SO_3 is written as a molecule and not as ions.)

Step 2. Deduce the oxidation half-reaction, using only H_2O and H^+ to balance the oxygen and hydrogen,

(a) $H_2SO_3 \rightarrow SO_4^{2-}$
(b) $H_2SO_3 + H_2O \rightarrow SO_4^{2-}$
(c) $H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4\,H^+$
(d) $H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4\,H^+ + 2\,e^-$

Step 3. Deduce the reduction half-reaction.

(a) $MnO_4^- \rightarrow Mn^{2+}$
(b) $MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$
(c) $MnO_4^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$
(d) $MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$

Step 4. Equalize the number of electrons lost and the number gained; that is, multiply the oxidation half-reaction by 5 and the reduction half-reaction by 2.

$$5\,H_2SO_3 + 5\,H_2O \longrightarrow 5\,SO_4^{2-} + 20\,H^+ + 10\,e^-$$

$$2\,MnO_4^- + 16\,H^+ + 10\,e^- \longrightarrow 2\,Mn^{2+} + 8\,H_2O$$

Step 5. Add the two half-reactions in Step 4 to obtain the balanced net ionic equation.

$$5\,H_2SO_3 + 2\,MnO_4^- \longrightarrow 5\,SO_4^{2-} + 2\,Mn^{2+} + 4\,H^+ + 3\,H_2O$$

We have seen in these two examples of reactions in acid solution that the half-reactions are derived by using H_2O and H^+ as needed in order to write balanced statements. However, not all redox reactions take place in acid solution. If the solution is basic, then the half-reactions must be developed with the proper use of H_2O and OH^-: for each oxygen atom that is needed, one H_2O is added to the side deficient in oxygen. Then, for each hydrogen atom that is needed, one H_2O is added to the side of the half-reaction deficient in H, and then the oxygens are re-balanced by adding one OH^- to the opposite side for each H_2O added in order to balance the hydrogen. The reaction of chromite ion with hypochlorite in alkaline solution serves to illustrate the procedure:

$$KCrO_2 + KClO + KOH \longrightarrow K_2CrO_4 + KCl + H_2O$$

Step 1. The unbalanced net ionic equation is

$$CrO_2^- + ClO^- + OH^- \longrightarrow CrO_4^{2-} + Cl^- + H_2O$$

Step 2. Deduce the oxidation half-reaction, using only OH^- and H_2O to balance the oxygen and hydrogen.

(a) $CrO_2^- \rightarrow CrO_4^{2-}$
(b) $CrO_2^- + 4\,OH^- \rightarrow CrO_4^{2-} + 2\,H_2O$
(c) $CrO_2^- + 4\,OH^- \rightarrow CrO_4^{2-} + 2\,H_2O + 3\,e^-$

Step 3. Deduce the reduction half-reaction.

(a) $ClO^- \rightarrow Cl^-$
(b) $ClO^- + H_2O \rightarrow Cl^- + 2\,OH^-$
(c) $ClO^- + H_2O + 2\,e^- \rightarrow Cl^- + 2\,OH^-$

Step 4. Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3.

$$2\,CrO_2^- + 8\,OH^- \longrightarrow 2\,CrO_4^{2-} + 4\,H_2O + 6\,e^-$$

$$3\,ClO^- + 3\,H_2O + 6\,e^- \longrightarrow 3\,Cl^- + 6\,OH^-$$

Step 5. Add the two half-reactions.

$$2\,CrO_2^- + 3\,ClO^- + 2\,OH^- \longrightarrow 2\,CrO_4^{2-} + 3\,Cl^- + H_2O$$

The proper use of H_2O and OH^- in dealing with reactions in basic solution is facilitated if one keeps in mind that two OH^- ions may be divided into one O atom and one H_2O molecule and that one H_2O molecule may be divided into one H atom and one OH^- ion. Thus, for each oxygen atom needed on one side of a half-reaction equation, two OH^- ions are added to that side and one H_2O is added to the other side. Similarly, for each H atom needed on a given side, one H_2O is added to that side and one OH^- is added to the other.

Methodology 18.3

Balance the following skeletal reaction, which occurs in basic solution:

$$MnO_4^- + N_2H_4 \longrightarrow MnO_2 + N_2$$

Write the unbalanced net ionic equation.

$$MnO_4^- + N_2H_4 \longrightarrow MnO_2 + N_2$$

Deduce the oxidation half-reaction.

(a) $N_2H_4 \rightarrow N_2$
(b) no oxygen atoms present
(c) $N_2H_4 + 4OH^- \rightarrow N_2 + 4\,H_2O$ (add 4 H_2O to right to balance H, then 4 OH^- to left to rebalance O)
(d) $N_2H_4 + 4\,OH^- \rightarrow N_2 + 4\,H_2O + 4\,e^-$ (balance charge by adding $4e^-$ to right)

Deduce the reduction half-reaction.

(a) $MnO_4^- \rightarrow MnO_2$
(b) $MnO_4^- \rightarrow MnO_2 + 2\,H_2O$
(c) $MnO_4^- + 4\,H_2O \rightarrow MnO_2 + 2\,H_2O + 4\,OH^-$ which reduces to
$MnO_4^- + 2\,H_2O \rightarrow MnO_2 + 4\,OH^-$
(d) $MnO_4^- + 2\,H_2O + 3\,e^- \rightarrow MnO_2 + 4\,OH^-$

Equalize the number of electrons lost and the number gained.

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 4.

$$3\,N_2H_4 + 12\,OH^- \longrightarrow 3\,N_2 + 12\,H_2O + 12\,e^-$$

$$4\,MnO_4^- + 8\,H_2O + 12\,e^- \longrightarrow 4\,MnO_2 + 16\,OH^-$$

Add the two half-reactions to obtain the balanced net ionic equation.

$$3\,N_2H_4 + 4\,MnO_4^- \longrightarrow 3\,N_2 + 4\,H_2O + 4\,MnO_2 + 4\,OH^-$$

Methodology 18.4

Balance the following skeletal reaction, which occurs in acidic solution.

$$I_2 + IO_3^- + Cl^- \longrightarrow ICl_2^-$$

Write the unbalanced net ionic equation.

$$I_2 + IO_3^- + Cl^- \longrightarrow ICl_2^-$$

Continued on the next page

Methodology 18.4 Continued

Deduce the oxidation half-reaction.

This is a somewhat more complex example in that the iodine undergoes both oxidation and reduction. The iodine in I_2 changes oxidation number from 0 to +1 in the ICl_2^- (loss of 1 e^- for each I, oxidation) while the iodine in IO_3^- changes from +5 to +1 in ICl_2^- (gain of 4 e^- for each I, reduction).

(a) $I_2 + 4\ Cl^- \rightarrow 2\ ICl_2^-$
(b) no oxygen atoms present
(c) no hydrogen atoms present
(d) $I_2 + 4\ Cl^- \rightarrow 2ICl_2^- + 2\ e^-$

Deduce the reduction half-reaction.

(a) $IO_3^- + 2\ Cl^- \rightarrow ICl_2^-$
(b) $IO_3^- + 2\ Cl^- \rightarrow ICl_2^- + 3\ H_2O$
(c) $IO_3^- + 2\ Cl^- + 6\ H^+ \rightarrow ICl_2^- + 3\ H_2O$
(d) $IO_3^- + 2\ Cl^- + 6\ H^+ + 4\ e^- \rightarrow ICl_2^- + 3\ H_2O$

Equalize the number of electrons lost and the number gained.

Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 1.

$$2\ I_2 + 8\ Cl^- \longrightarrow 4\ ICl_2^- + 4\ e^-$$

$$IO_3^- + 2\ Cl^- + 6\ H^+ + 4\ e^- \longrightarrow ICl_2^- + 3\ H_2O$$

Add the two half-reactions to obtain the balanced net ionic equation.

$$IO_3^- + 6\ H^+ + 2\ I_2 + 10\ Cl^- \longrightarrow 5\ ICl_2^- + 3\ H_2O$$

18.3 REDOX COUPLES

It should be noted that all half-reactions are reversible, and the direction* in which a given half-reaction goes depends upon whether it is reacting with a stronger or a weaker oxidizing agent. Consider, for example, the half-reaction

$$Cu^{2+} + 2\ e^- \longrightarrow Cu$$

If zinc metal is placed in a solution of Cu^{2+}, the reaction that occurs is

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Since Zn^{2+} is a weaker oxidizing agent than Cu^{2+}, the Cu^{2+} is reduced and the half-reaction occurs in the direction $Cu^{2+} + 2\ e^- \rightarrow Cu$. On the other hand, if copper metal is placed in a solution of Ag^+, the reaction is

$$2\ Ag^+ + Cu \longrightarrow 2\ Ag + Cu^{2+}$$

Silver ion is a stronger oxidizing agent (more likely to be reduced) than Cu^{2+}, and therefore Cu is oxidized; the half-reaction for the change in copper occurs in the direction $Cu \rightarrow Cu^{2+} + 2\ e^-$.

It is convenient, therefore, to speak of the participants in these reversible half-reactions as redox couples—a couple consisting of an oxidized form and the corresponding reduced form. Three redox couples have just been illustrated: Cu^{2+}/Cu, Ag^+/Ag, and Zn^{2+}/Zn. Note that redox couples are somewhat analogous to conjugate acids and bases (Chapter 16).

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* Notice that the prediction of the direction or extent of an electron-transfer reaction is exactly analogous to the predictions of extent of proton-transfer reactions. For those reactions, the reaction goes from stronger acid to weaker acid.

18.4 VOLTAIC CELLS

That a redox reaction is indeed an electron-transfer process and may be treated as the sum of two separate half-reactions may be demonstrated by a rather simple experiment.

Two aqueous solutions are prepared: one contains $K_2Cr_2O_7$ and H_2SO_4 and the other contains KI. The first is orange, due to $Cr_2O_7^{2-}$, and the other is colorless. Some of the solution containing the $K_2Cr_2O_7$ is poured slowly into a sample of the KI solution. As the pouring is continued, the mixture does not take on the orange color of the $Cr_2O_7^{2-}$, but instead becomes green. In other words, a visible reaction occurs on mixing the two solutions. Relatively simple chemical tests show that the green color is due to the presence of Cr^{3+} and that the mixture also contains I_2. The reaction that occurred must have been an oxidation-reduction reaction: the $Cr_2O_7^{2-}$ was reduced to Cr^{3+} and the I^- was oxidized to I_2. The equations for the two half-reactions and the overall reaction are

$$
\begin{array}{r}
Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \\
3(2\,I^- \longrightarrow I_2 + 2\,e^-) \\
\hline
Cr_2O_7^{2-} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O
\end{array}
$$

Now suppose that the two solutions, unmixed, are poured into separate beakers and the beakers are placed side by side. Some metallic conductor that will not react with either of the solutions (for instance, a piece of platinum rod) is suspended in each solution, and the two metals are connected by wires through a voltmeter. Finally, a U-tube is filled with a solution of some electrolyte (such as dilute K_2SO_4) that will not react with either of the solutions in the beakers, the ends are plugged loosely with glass wool, and the U-tube is inverted so that one arm is dipping into each of the two solutions. The complete apparatus is shown below. As soon as the U-tube is immersed in the solutions, a voltage and a current can be measured on the meter (Figure 18.3).

If the current flow is allowed to continue without any stirring of the two solutions, the yellow-brown color of iodine appears after a short time around the platinum rod in the right beaker and a change from the orange of $Cr_2O_7^{2-}$ to the green of Cr^{3+} occurs around the platinum in the left beaker.

Clearly, the same reaction occurs in this apparatus as that which occurs when the two solutions are mixed together. However, in this apparatus the electron transfer takes place externally through the connecting wire. In the beaker on the right, I^- is oxidized to I_2, with electrons being transferred to the platinum rod:

$$2\,I^- \longrightarrow I_2 + 2\,e^-$$

The electrons move through the wire and voltmeter to the platinum rod on the left, where they are consumed in the reduction of dichromate ions:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

This external flow of electrons constitutes an electric current, which is observed on the meter.

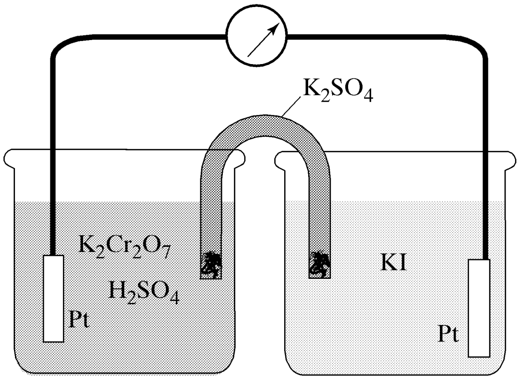

Figure 18.3 A voltaic cell.

Note that the color changes (and therefore the reactions) occurred at the surfaces of the metal rods and not at the ends of the U-tube. Yet the U-tube is apparently essential, because the voltmeter indicated no current flow without it. Suppose that in the apparatus shown in Figure 18.3, the U-tube is not in place. In the right-hand beaker some iodide ions contact the platinum, transfer electrons to it, and are thus oxidized to iodine. The process leaves an excess of potassium ions, which gives the solution a positive charge and prevents the further release of electrons to the platinum. The reduction that occurs in the left beaker leaves an excess of negative ions (sulfate), which gives the solution a negative charge that repels electrons and prevents their transfer from the platinum into the solution. In short, without the U-tube, the two reactions would still occur, but to such a slight extent that no measurable current would flow. With the U-tube in place, however, excess sulfate ions on the left can move into it, and on the right sulfate ions move out of it into the solution to balance the charge of the excess potassium ions. Thus, the U-tube provides a pathway for ion flow between the two solutions and prevents the buildup of an ionic charge in either one. This equalization of ionic charge can also be accomplished by the flow of potassium ions into the right-hand side of the U-tube and out of the left-hand side. In an actual operating cell, both sulfate and potassium ions migrate.

This apparatus, in which an electric current is produced from a spontaneous oxidation-reduction reaction, is called a **galvanic** or **voltaic cell**. The platinum rods are called **electrodes**, and the U-tube with its electrolytic solution is called a **salt bridge**. Each solution, together with its electrode, is referred to as a **half-cell**. In the half-cell where oxidation occurs, the solution gives up electrons to the electrode. These electrons then continue to flow away from the electrode to make room for additional electrons from the solution. Therefore, that electrode is designated as the negative electrode. In the other half-cell, the reduction process takes electrons from the electrode, making that electrode the positive one. Electrons flow into this electrode to replenish those lost to the solution. Electrons flow externally from the negative to the positive electrode. (Thus, in Figure 18.3, the electrode on the right is negative, the one on the left is positive, and electrons flow through the voltmeter from right to left.) The terms **anode** and **cathode** are also used to distinguish between the two electrodes. By definition, an anode is any electrode at which oxidation occurs, and a cathode is any electrode at which reduction occurs. Therefore, in a voltaic cell, the positive electrode may be called the cathode and the negative electrode may be called the anode.

The specific reaction used in the experiment just described was chosen simply because the color changes that occur make the reaction visible. The experiment is merely an example of a general phenomenon; that is, any redox reaction can be made the basis of a voltaic cell by placing the ingredients of each half-reaction in a separate half-cell and providing suitable electrodes and a suitable salt bridge.

As a further illustration, consider the construction of a voltaic cell based on the reaction of CrO_2^- and ClO^- in basic solution. The two half-reactions and the balanced overall reaction are:

$$\text{Oxidation:} \quad CrO_2^- + 4\,OH^- \longrightarrow CrO_4^{2-} + 2\,H_2O + 3\,e^-$$

$$\text{Reduction:} \quad ClO^- + H_2O + 2\,e^- \longrightarrow Cl^- + 2\,OH^-$$

$$\text{Overall:} \quad 2\,CrO_2^- + 3\,ClO^- + 2\,OH^- \longrightarrow 2\,CrO_4^{2-} + 3\,Cl^- + H_2O$$

In the construction of a voltaic cell from this reaction, one half-cell must contain the materials involved in the oxidation half-reaction, and the other must contain the materials of the reduction half-reaction. Therefore, in one beaker we place an aqueous solution containing CrO_2^-, CrO_4^{2-}, and OH^-. (Note that CrO_4^{2-} is not a reactant, but that it will be formed as soon as any current is drawn from the cell, so that whether or not we place any CrO_4^{2-} in the solution at the start, it will in fact be present as soon as the cell has begun to function.) The other beaker holds an aqueous solution of ClO^-, Cl^-, and OH^-. Platinum serves as the electrodes, and a solution of Na_2SO_4 or NaOH is a satisfactory salt bridge. The assembled cell is shown in Figure 18.4.

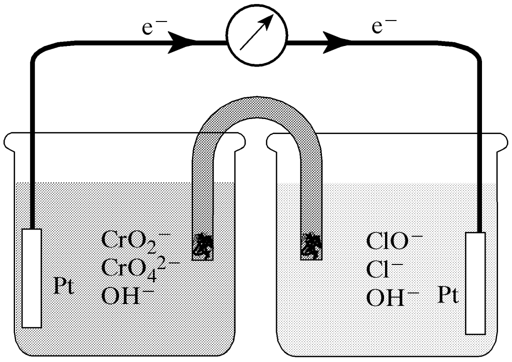

Figure 18.4 A CrO_2^-—ClO^- voltaic cell.

Because oxidation occurs in the left-hand half-cell, electrons are released to that electrode, move through the wire from left to right, and are consumed in the reduction reaction at the right-hand electrode. Therefore, the electrode on the left is the anode (negative) and the one on the right is the cathode (positive).

In both the examples cited, all the substances involved in the reactions—reactants and products—are in solution, and the electrodes are inert (that is, they do not enter into the reaction itself but serve only as a means of conducting electrons). In redox reactions in which a metal is involved as reactant or product, a piece of that metal may serve as an electrode. Consider, for example, the reaction that occurs when a strip of zinc metal is placed in an aqueous solution of copper(II) sulfate. The zinc dissolves because zinc atoms in the metal are oxidized to ions, and copper metal is formed because copper ions are reduced to copper atoms,

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

A voltaic cell based on this reaction can be constructed so that one half-cell consists of a zinc rod submerged in a solution containing zinc ions and the other half-cell consists of a copper rod submerged in a solution of copper ions. As current is drawn from the cell, zinc is oxidized ($Zn \rightarrow Zn^{2+} + 2\,e^-$) and copper ions are reduced ($Cu^{2+} + 2\,e^- \rightarrow Cu$). Therefore, the zinc electrode is the anode and the copper electrode is the cathode, and electrons flow externally from zinc to copper. This cell is shown in Figure 18.5.

A conventional shorthand notation for the description of voltaic cells employs a vertical line that separates the electrode from the solutes of the half-cell and a double vertical line that represents the salt bridge. The anode (the one at which oxidation occurs) is written on the left and the cathode on the right. This notation is illustrated in Figure 18.6 for the first of the three cells described above.

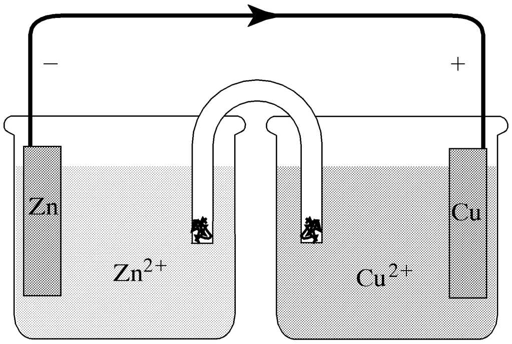

Figure 18.5 A copper-zinc voltaic cell.

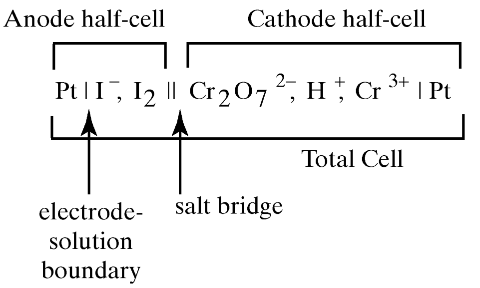

Figure 18.6 Shorthand notation for a voltaic cell.

Electromotive Force

Any voltaic cell capable of producing an electric current may be thought of as possessing a "driving force" behind the flow of electrons; that is, a force that tends to push the electrons through the external circuit from the negative to the positive electrode. This driving force is called the **electromotive force** (emf) and is commonly expressed in units of *volts* (V). The emf of a cell may be measured simply by attaching a voltmeter across the two electrodes. (It should be noted, however, that an ordinary voltmeter draws current from the cell, and therefore the emf will change slightly as a result of the measurement process. For very careful emf measurements, potentiometers are used.) Because the emf of a cell is expressed as electrical potential and is easily measured by a voltmeter, it is often referred to as a cell potential or cell voltage and given the abbreviation E_{cell}. Regardless of the terminology, because the emf or cell potential is a measure of the driving force behind the flow of electrons, it is also a measure of the tendency of the cell reaction to occur. The higher the voltage, the greater the tendency of the redox reaction in question to occur.

Electrode Potentials

In order to obtain a clearer understanding of the electromotive force and its relationship to a cell reaction, it is necessary to consider the processes occurring at the individual electrodes.

Consider any half-cell, separate and unconnected to anything else; that is, an electrode submerged in a solution containing all the substances involved in a half-reaction. For example, it might be platinum in a solution of $Cr_2O_7^{2-}$, Cr^{3+}, and H^+; it might be platinum in a solution containing I_2 and I^-; or it might be copper in a Cu^{2+} solution.

The solutes in the solution have a certain tendency to remove electrons from the metal electrode and thereby leave it with less than its normal complement of electrons. This makes the electrode positive with respect to the solution; that is, a potential is developed between the electrode and the solution. This potential is called the **electrode potential** (E); because its magnitude is a measure of the tendency of the solute system to gain electrons (that is, the tendency for reduction to occur), it may also be called a **reduction potential**. It follows, then, that the larger the electrode potential, the more readily reduction occurs and the stronger an oxidant is for a given system.

If two half-cells with different electrode potentials are connected by a salt bridge and an external circuit so as to produce a voltaic cell, reduction will take place at the electrode with the higher electrode potential and oxidation will occur at the electrode of lower electrode potential. The cell potential is simply the difference between the two electrode potentials. Furthermore, since the E_{cell} value must be positive, it is equal to the electrode potential at the positive electrode (the cathode) minus the electrode potential at the negative electrode (the anode). Because reduction always occurs at the cathode in a spontaneous cell reaction, the E_{cell} can also be expressed as $E_{(\text{red.})} - E_{(\text{oxid.})}$,

$$E_{\text{cell}} = E_{(+)} - E_{(-)} = E_{(\text{cathode})} - E_{(\text{anode})} = E_{(\text{red.})} - E_{(\text{oxid.})}$$

The magnitude of a single electrode potential depends on several factors: (1) the particular redox system in question, (2) the temperature, and (3) the relative concentrations of the substances involved in the half-reaction. The relationship between the electrode potential and these factors is expressed by the **Nernst equation** (developed by Walther Nernst in 1889), which is derived from thermodynamic considerations.*

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\mathrm{red}]^b}{[\mathrm{ox}]^a}$$

where E is the electrode potential under nonstandard conditions; E° is the standard electrode potential, a constant characteristic of the particular half-reaction; R is the ideal gas constant (8.314 J/mol-K); T is the absolute temperature; n is the number of moles of electrons lost or gained in the half-reaction equation; F is the Faraday constant (written as 96.48 kJ/V); and $\ln \frac{[\mathrm{red}]^b}{[\mathrm{ox}]^a}$ is the natural logarithm of the molar-concentration ratio of the reduced form to that of the oxidized form, each raised to the power of their stoichiometric coefficients (i.e., the reaction quotient, Q, for the half-reaction when written as a reduction).

The Nernst equation may be restated in a simplified, more easily used form. Since R and F are constants, they may be combined. Further, if we assume some definite temperature, say 25 °C, then T may also be combined with the constant. Finally, we convert to logarithms to the base 10 by multiplying by 2.303. At 25 °C, the equation becomes

$$E = E^\circ - \frac{0.059}{n} \log \frac{[\mathrm{red}]^b}{[\mathrm{ox}]^a}$$

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* The work required to move an electron with a charge q across a potential E, is given by

$$(1) \qquad \text{Work} = qE$$

The total charge transferred in a redox reaction is equal to the number of moles of electrons transferred (n) multiplied by the charge on one mole, which is the Faraday constant (F), 96,500 coulombs/mole.

$$(2) \qquad q_{\text{total}} = nF$$

The total work performed in a redox reaction is then obtained from

$$(3) \qquad \text{Work} = nFE$$

In order to change the free energy (ΔG) of a system, work is required. Therefore, work is also related to free energy (see Chapter 14),

$$(4) \qquad \text{Work} = -\Delta G$$

By combining equations (3) and (4), a relationship between ΔG and electrode potential may be obtained,

$$(5) \qquad \Delta G = -nFE\text{; or, at standard conditions, } \Delta G^\circ = -nFE^\circ$$

While ΔG° is the change in free energy for a reaction when all products and reactants are in their standard states, the difference in free energy between products and reactants at any given point during the progression of a reaction (nonstandard states) is given by the expression

$$(6) \qquad \Delta G = \Delta G^\circ + \mathrm{RT} \ln Q$$

where Q is the reaction quotient and R is a constant (8.31 J/mol-K). Substituting the relationships in equation (5) into equation (6) we obtain,

$$(7) \qquad -nFE = -nFE^\circ + RT \ln Q$$

which, upon rearrangement, provides

$$(8) \qquad E = E^\circ - \frac{RT}{nF} \ln Q$$

For the generalized half-reaction

$$a_{(\mathrm{ox})} + n\,e^- \longrightarrow b_{(\mathrm{red})}$$

(the oxidized form plus n electrons yields the reduced form), the reaction quotient (Q) $= \frac{[\mathrm{red}]^b}{[\mathrm{ox}]^a}$. Equation (8) then becomes the Nernst expression.

Of course, the value of the combined constant has a slightly different value at other temperatures.

Some illustrations of the form of the Nernst equation for actual half-reactions follow.

1. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

$$E = E^\circ - \frac{0.059}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

2. $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$

$$E = E^\circ - \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

(Note that $[H_2O]$ does not appear in the Nernst equation, because it is a constant.)

3. $Zn^{2+} + 2\,e^- \rightarrow Zn$

$$E = E^\circ - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

(Note that [Zn] does not appear. Recall the discussion of heterogeneous equilibria in Chapter 13.)

4. $CrO_4^{2-} + 2\,H_2O + 3\,e^- \rightarrow CrO_2^- + 4\,OH^-$

$$E = E^\circ - \frac{0.059}{3}\log\frac{[CrO_2^-][OH^-]^4}{[CrO_4^2]}$$

Standard Electrode Potentials

As previously mentioned, a particular **standard electrode potential** (E°) is associated with each different redox couple (analogous to a standard free energy ΔG°). If the values of these constants for specific couples are known, they can be used in the Nernst equation to predict the magnitude of electrode potentials for different solutions and to calculate the E_{cell} value of various voltaic cells. Furthermore, the E° values themselves are measures of the relative strengths of oxidizing agents; that is, the stronger the oxidizing agent, the more readily it is reduced, and the larger is the value of the standard electrode potential.

Let us begin our study of the evaluation of standard electrode potentials by returning to the generalized statement of the Nernst equation:

$$E = E^\circ - \frac{0.059}{n}\log\frac{[\text{red}]^b}{[\text{ox}]^a}$$

If the concentrations of reduced and oxidized forms are chosen so that the ratio in the logarithmic term is equal to 1, then $\log 1 = 0$ and E will equal E°. If both [red] and [ox] have a value of 1, then the ratio will equal 1 regardless of the values of the exponents a and b.

To illustrate with a specific example, let us examine the half-reaction

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

The Nernst equation for the electrode potential for this system is

$$E = E^\circ - \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

Suppose we prepare a solution in which $[Cr_2O_7^{2-}]$, $[Cr^{3+}]$, and $[H^+]$ are 1 M each, and we immerse a platinum foil in that solution. Because

$$\frac{(1)}{(1)(1)^{14}} = 1 \qquad \text{and} \qquad \log 1 = 0$$

we obtain $E = E°$. In other words, the electrode potential developed at the platinum rod will be the standard electrode potential, $E°$, for the $Cr_2O_7^{2-}/Cr^{3+}$ couple. Therefore, if we can in some way measure the electrode potential, E, of this solution, we will have evaluated the constant $E°$ for the system.

Unfortunately, it is not possible to measure a single electrode potential directly, because there is no complete circuit and no current flow. We can only measure the difference between two electrode potentials, which is accomplished by connecting them to form a cell and measuring the E_{cell} of that cell: $E_{cell} = E_{(+)} - E_{(-)}$.

By way of illustration, let us return to a consideration of the simple cell described in Figure 18.6. The electrode potentials are

$$E_{(+)} = E^{\circ}_{(+)} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$E_{(-)} = E^{\circ}_{(-)} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]}$$

If $[Cu^{2+}] = 1\ M$ and $[Zn^{2+}] = 1\ M$, then

$$E_{(+)} = E^{\circ}_{(+)} \qquad \text{and} \qquad E_{(-)} = E^{\circ}_{(-)}$$

Finally, we have

$$E_{cell} = E^{\circ}_{(+)} - E^{\circ}_{(-)}$$

Thus, if we construct the cell in question so that one solution is 1 M in Zn^{2+} and the other is 1 M in Cu^{2+}, the measured cell potential will be the difference between the $E°$ value for the Cu^{2+}/Cu couple and the $E°$ value for the Zn^{2+}/Zn couple. When we actually measure the E_{cell} of this cell, which may be depicted as

$$Zn|Zn^{2+}(1\ M)\|Cu^{2+}(1\ M)|Cu$$

we get a value of 1.10 V. Therefore:

$$E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn} = 1.10\text{ V}$$

Recognizing, then, that we cannot measure the absolute values of standard electrode potentials but only differences between them, we find it expedient to develop a system of *relative* standard electrode potentials. Thus, if we choose some particular redox couple to serve as a reference couple and assign it some arbitrary $E°$ value, we can measure the $E°$ values of other redox couples relative to the value assigned the reference couple.

The redox couple that has been chosen to serve as the basis of this relative system is represented by the half-reaction

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

and the $E°$ value assigned to it is 0.00 V. A half-cell for measuring the potential of this H^+/H_2 couple consists of a platinum rod dipping into a solution of acid, with the platinum enclosed inside a tube that permits hydrogen gas to be bubbled over the electrode (Figure 18.7). If the hydrogen is admitted at a pressure of exactly 1 atm, then the electrode potential is given by the expression

$$E = E^{\circ} - \frac{0.059}{2} \log \frac{1}{[H^+]^2}$$

Further, if the concentration of H^+ in the solution is exactly 1 M, then the potential at the electrode is the standard potential for the H^+/H_2 couple ($E = E°$), which has been assigned a value of 0.00 V.

The standard electrode potential for any redox couple can be measured by constructing a half-cell, connecting it with the standard hydrogen electrode, and measuring the potential of the cell thus produced. The $E°$ value for the Zn^{2+}/Zn couple can be mea-

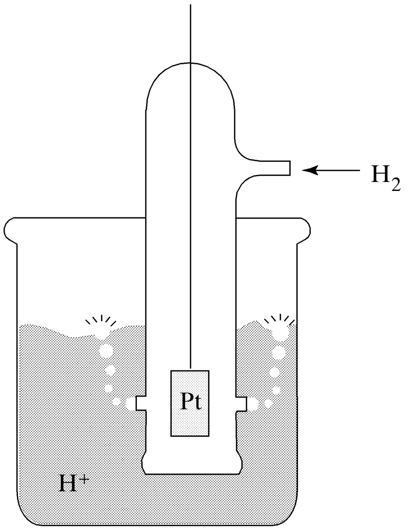

Figure 18.7 Determination of the standard electrode potential for the H$^+$/H$_2$ couple.

sured as follows. A rod of zinc metal is placed into a 1 *M* solution of Zn^{2+}. The metal is connected to the wire of a standard hydrogen electrode, and the two solutions are connected by a suitable salt bridge. When the E_{cell} of this cell is measured, it is found that the hydrogen electrode is positive, the zinc electrode is negative, and the E_{cell} is 0.76 V.

$$E_{\text{cell}} = E_{(+)} - E_{(-)} = E_{(\text{red.})} - E_{(\text{oxid.})} = E^{\circ}_{\text{H}^+/\text{H}_2} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = 0.76 \text{ V}$$

Because $E^{\circ}_{\text{H}^+/\text{H}_2}$ has been assigned a value of 0.00, we have

$$0.00 - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = 0.76 \text{ V}$$
$$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

Therefore, the standard electrode potential for the half-reaction

$$\text{Zn}^{2+} + 2\,e^- \longrightarrow \text{Zn}$$

is −0.76 V relative* to the standard hydrogen electrode.

Returning to our zinc-copper cell, for which the E_{cell} was found to be 1.10 V, it is now obvious that the E° value for the Cu^{2+}/Cu couple is 0.34 V.

$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - (0.76) = 1.10 \text{ V}$$
$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 1.10 - 0.76 = 0.34$$

By the use of procedures similar to the one just described, the standard electrode potentials of a large variety of redox couples have been measured. A few of these are given in Table 18.1; a larger list is found in Appendix 5.

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* Note that as current is drawn from the cell, the half-reactions and overall reaction that occur are

$$\begin{array}{ll} (+) & 2\,\text{H}^+ + 2\,e^- \longrightarrow \text{H}_2 \\ \underline{(-)} & \underline{\qquad \text{Zn} \longrightarrow \text{Zn}^{2+} + 2\,e^-} \\ & \text{Zn} + 2\,\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2 \end{array}$$

Thus, the cell could properly be designated as

$$\underset{\text{(anode)}}{\text{Zn}\,|\,\text{Zn}^{2+}(1\,M)}\,\|\,\underset{\text{(cathode)}}{\text{H}^+(1\,M),\ \text{H}_2(1\text{ atm})\,|\,\text{Pt}}$$

TABLE 18.1 Some Standard Electrode Potentials (25 °C)

HALF-REACTION	E^0(V)	HALF-REACTION	E^0(V)
$F_2 + 2\,e^- \rightarrow 2\,F^-$	+2.87	$Sn^{2+} + 2\,e^- \rightarrow Sn$	−0.14
$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	+1.51	$Ni^{2+} + 2\,e^- \rightarrow Ni$	−0.25
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	+1.36	$Fe^{2+} + 2\,e^- \rightarrow Fe$	−0.44
$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$	+1.33	$Zn^{2+} + 2\,e^- \rightarrow Zn$	−0.76
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	+1.06	$Al^{3+} + 3\,e^- \rightarrow Al$	−1.66
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Mg^{2+} + 2\,e^- \rightarrow Mg$	−2.36
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$Na^+ + e^- \rightarrow Na$	−2.71
$I_2 + 2\,e^- \rightarrow 2\,I^-$	+0.54	$Ba^{2+} + 2\,e^- \rightarrow Ba$	−2.91
$Cu^{2+} + 2\,e^- \rightarrow Cu$	+0.34	$K^+ + e^- \rightarrow K$	−2.93
$2\,H^+ + 2\,e^- \rightarrow H_2$	0.00	$Li^+ + e^- \rightarrow Li$	−3.05
$Pb^{2+} + 2\,e^- \rightarrow Pb$	−0.13		

Check Point 18.1

Calculate the standard potential for the following cell,

$$Ag\,|\,Ag^+\,\|\,MnO_4^-, Mn^{2+}, H^+\,|\,Pt$$

Solution:

0.71 V

◇ ◇ ◇ ◇ ◇

18.5 STRENGTHS OF OXIDIZING AGENTS AND THE SPONTANEITY OF REACTIONS

Because the magnitude of $E°$ is a measure of the relative tendency for reduction to occur, the relative strengths of oxidizing and reducing agents are predictable from the $E°$ values. In Table 18.1, the substances on the left of the arrows are the oxidized forms; therefore, they are the potential oxidizing agents. Because the half-reactions are listed in order of decreasing $E°$, it follows that any oxidizing agent is stronger than any that is listed below it in the table. Accordingly, F_2 is the strongest oxidant listed and the most likely to undergo reduction, MnO_4^- in acid solution is the next strongest, and so on, with Li^+ being the weakest. On the other hand, the substances to the right of the double arrows are reducing agents; therefore the order of relative strength as reductants is inverted. That is, if F_2 has a very high tendency to be reduced to F^-, then F^- must have a very low tendency to be oxidized to F_2. Hence, F^- is the weakest reducing agent in the table, while Li is the strongest, K the second strongest, and so forth.

In many cases a species' relative strength as a reducing or oxidizing agent can be explained from considerations of electronic structure. The alkali metals are all relatively strong reducing agents, meaning they are likely to give up an electron and be oxidized. If we think about the electron configurations of these elements, all have one electron in excess of a noble-gas configuration located in an *s* orbital.* We should not be surprised, then, that these elements have a relatively large propensity to lose an electron to form a +1 ion and acquire a noble-gas configuration. The weakest reducing agent in the table is F^-. The fluoride ion has a complete octet and would not be expected to undergo oxidation to lose an electron and its noble-gas configuration. Fluorine, on the other hand, may be expected to gain electrons to form the fluoride ion, and the species with the highest

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* For example,

$$\text{Li: } 1s^22s^1 \quad \text{Na: } 1s^22s^22p^63s^1$$

reduction potential is indeed F_2. The redox behavior of other species may be explained in a similar manner. However, it is important to remember that these are generalizations with many exceptions and that not all redox behavior can be explained in such a simple manner.

Also note that each half-reaction in Table 18.1 and Appendix 6 is balanced, which provides a simplified method for balancing redox reactions. In this method, the two half-reactions involved in the redox process are chosen and written in the direction in which they occur (as a reduction or oxidation). The electrons transferred are balanced by multiplying one or both of the reactions by the appropriate coefficient. The two half-reactions are then added to give the overall reaction. This method is illustrated in Problem 18.1.

Problem 18.1

Balance the following skeletal reaction, which occurs in acidic solution, using appropriate half-reactions from Appendix 6.

$$\mathrm{MnO_4^{-} + 2\,S_2O_3^{2-} \longrightarrow Mn^{2+} + S_4O_6^{2-}}$$

Solution:

First, identify the two half-reactions,

Oxidation half-reaction: $\mathrm{2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,e^{-}}$

Reduction half-reaction: $\mathrm{MnO_4^{-} + 8\,H^{+} + 5\,e^{-} \longrightarrow Mn^{2+} + 4\,H_2O}$

Now balance electrons by multiplying the oxidation half-reaction by 5 and the reduction half-reaction by 2, and then add to give overall balanced reaction.

$$\begin{array}{r}
\mathrm{10\,S_2O_3^{2-} \longrightarrow 5\,S_4O_6^{2-} + 10\,e^{-}} \\
\mathrm{2\,MnO_4^{-} + 16\,H^{+} + 10\,e^{-} \longrightarrow 2\,Mn^{2+} + 8\,H_2O} \\
\hline
\mathrm{2\,MnO_4^{-} + 16\,H^{+} + 10\,S_2O_3^{2-} \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,S_4O_6^{2-}}
\end{array}$$

A logical extension of this relationship between the values of E° and the relative strengths of oxidizing and reducing agents is the prediction of whether or not a particular redox reaction will occur spontaneously. It follows from the foregoing discussion that any oxidant in the table will oxidize (be reduced by) any reductant that lies below it. For example, Pb^{2+} is more easily reduced (a stronger oxidizing agent) than Zn^{2+} and therefore Pb^{2+} will oxidize zinc metal. Or, we might ask if an acidic permanganate solution will oxidize chloride ion to chlorine. In other words, will the following reaction occur spontaneously?

$$\mathrm{2\,MnO_4^{-} + 16\,H^{+} + 10\,Cl^{-} \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,Cl_2}$$

Note that this equation is generated by adding the proper half-reactions and balancing the number of electrons,

$$\begin{array}{r}
\mathrm{2(MnO_4^{-} + 8\,H^{+} + 5\,e^{-} \longrightarrow Mn^{2+} + 4\,H_2O)} \\
\mathrm{5(2\,Cl^{-} \longrightarrow Cl_2 + 2\,e^{-})} \\
\hline
\mathrm{2\,MnO_4^{-} + 16\,H^{+} + 10\,Cl^{-} \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,Cl_2}
\end{array}$$

Table 18.1 tells us that the E° for the reduction of MnO_4^{-} is 1.51 V, whereas the E° for the reduction of Cl_2 is only 1.36 V. Acidic permanganate is therefore a stronger oxidizing agent than Cl_2; thus MnO_4^{-} will be reduced and Cl^{-} will be oxidized, and the reaction in question is spontaneous.

The spontaneity of this reaction may also be ascertained from the voltaic cell based on the reaction. Will a cell constructed from the two half-cells in question actually generate a flow of current that will cause the electrode of the MnO_4^{-} half-cell to be positive and the electrode of the Cl_2/Cl^- half-cell to be negative? In other words, will the cell designated as

$$\mathrm{Pt}\,|\,\mathrm{Cl^-}(1\ M), \mathrm{Cl_2}(1\ \mathrm{atm})\,\|\,\mathrm{MnO_4^-}\ (1\ M), \mathrm{H^+}(1\ M), \mathrm{Mn^{2+}}(1\ M)\,|\,\mathrm{Pt}$$

have an E_{cell} that is positive?

$$E_{\text{cell}} = E_{(+)} - E_{(-)} = 1.51 - 1.36 = +\,0.15\ \mathrm{V}$$

The calculated E_{cell} is positive; therefore the cell will function as written and the reaction is spontaneous.

Let us now consider the spontaneity of the reaction between acidic dichromate and chloride. Will an acidic dichromate solution oxidize chloride to chlorine? We can write an equation for the reaction by combining the proper half-reactions:

$$\begin{array}{r}
\mathrm{Cr_2O_7^{2-}} + 14\,\mathrm{H^+} + 6\,e^- \longrightarrow 2\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O} \\
3(2\,\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2\,e^-) \\
\hline
\mathrm{Cr_2O_7^{2-}} + 14\,\mathrm{H^+} + 6\,\mathrm{Cl^-} \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O} + 3\,\mathrm{Cl_2}
\end{array}$$

Referring to Table 18.1, we find that Cl_2 is a stronger oxidizing agent than $Cr_2O_7^{2-}$; therefore, $Cr_2O_7^{2-}$ will not oxidize Cl^-, and the reaction written is not spontaneous. In fact, the reverse of the reaction will occur spontaneously.

Investigation of this reaction in terms of the cell produced from it:

$$\mathrm{Pt}\,|\,\mathrm{Cl^-}(1\ M), \mathrm{Cl_2}(1\ \mathrm{atm})\,\|\,\mathrm{Cr_2O_7^{2-}}\ (1\ M), \mathrm{H^+}\ (1\ M), \mathrm{Cr^{3+}}\ (1\ M)\,|\,\mathrm{Pt}$$

leads to the conclusion that this cell would not function as written, because the calculated E_{cell} is negative.

$$E_{\text{cell}} = E_{(+)} - E_{(-)} = 1.33 - 1.36 = -0.03\ \mathrm{V}$$

It must be emphasized that because these predictions of spontaneity are based on the use of standard electrode potentials, we are merely predicting whether or not a particular reaction will occur spontaneously at 25 °C when all substances involved in the reaction are in the standard state (concentration of 1 *M* for solutions and a partial pressure of 1 atm for gases). Thus, for example, in our prediction that the reaction between acidic dichromate and chloride ion is not spontaneous, we have not concluded that it is impossible to bring about this reaction. Actually, $Cr_2O_7^{2-}$ can be made to oxidize Cl^- by proper selection of conditions, such as by lowering the partial pressure of Cl_2, removing Cr^{3+} as it forms, or using a very high concentration of $Cr_2O_7^{2-}$. In fact, any change of conditions that will raise the electrode potential of the $Cr_2O_7^{2-}/Cr^{3+}$ couple above the potential of the Cl_2/Cl^- couple will cause the reaction to occur. Furthermore, it should be noted that these predictions are based only on thermodynamic considerations, not on the kinetics of the reactions. A prediction of spontaneity indicates only that the reaction is thermodynamically favored; it indicates nothing about the rate of the reaction.

18.6 STANDARD ELECTRODE POTENTIALS AND THE EQUILIBRIUM CONSTANT

In making predictions concerning the spontaneity of redox reactions from values of E°, what we are really doing is making a qualitative statement about the equilibrium position of the reaction. If we predict that a given reaction is spontaneous, we are saying that the equilibrium position lies in favor of the products; conversely, for a nonspontaneous reaction, the equilibrium position favors the reactants.

We can also relate the standard electrode potentials of the redox couples involved in a reaction to the equilibrium position of that reaction quantitatively; that is, the equilibrium constant for a redox reaction can be expressed as a function of E° values. Let us illustrate this relationship with the reaction between acid dichromate and ferrous ion, for which the balanced equation is

$$\mathrm{Cr_2O_7^{2-}} + 14\,\mathrm{H^+} + 6\,\mathrm{Fe^{2+}} \longrightarrow 2\,\mathrm{Cr^{3+}} + 6\,\mathrm{Fe^{3+}} + 7\,\mathrm{H_2O}$$

The reduction half-reaction is

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

and the oxidation half-reaction is

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

The driving force behind this reaction is the difference between the two electrode potentials:

$$E_{\text{cell}} = E_{\text{Cr}} - E_{\text{Fe}}$$

These two potentials as expressed by the Nernst equation are

$$E_{\text{Cr}} = E^\circ_{\text{Cr}} - \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$E_{\text{Fe}} = E^\circ_{\text{Fe}} - 0.059\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

As the reaction proceeds, $[Cr_2O_7^{2-}]$ and $[H^+]$ decrease, while $[Cr^{3+}]$ increases, making the logarithmic term in the Nernst equation increase; therefore E_{Cr} becomes smaller. Similarly, because $[Fe^{2+}]$ is decreasing and $[Fe^{3+}]$ is increasing, the ratio decreases; thus, E_{Fe} becomes larger. If E_{Cr} is decreasing and E_{Fe} is increasing, these two values must eventually become equal, and the driving force of the reaction (the E_{cell}) becomes zero.

$$E_{\text{cell}} = E_{\text{Cr}} - E_{\text{Fe}} = 0$$

At this point the system is in equilibrium, because the driving force is the same in both the forward and reverse directions.

Note that this same line of reasoning explains why the E_{cell} value of a voltaic cell gradually decreases as current is drawn from it until it eventually reaches zero (equilibrium is reached).

In view of the above discussion, at equilibrium the following relationship holds:

$$E_{\text{Cr}} = E_{\text{Fe}}$$

Therefore:

$$(1)\qquad E^\circ_{\text{Cr}} - \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}} = E^\circ_{\text{Fe}} - 0.059\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Rearranging terms, equation (1) becomes

$$(2)\qquad E^\circ_{\text{Cr}} - E^\circ_{\text{Fe}} = \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}} = -0.059\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Now, since

$$0.059\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{0.059}{6}\log\frac{[Fe^{2+}]^6}{[Fe^{3+}]^6}$$

we may rewrite equation (2) as follows:

$$(3)\qquad E^\circ_{\text{Cr}} - E^\circ_{\text{Fe}} = \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}} = -\frac{0.059}{6}\log\frac{[Fe^{2+}]^6}{[Fe^{3+}]^6}$$

Combining terms in equation (3) gives

$$(4)\qquad E^\circ_{\text{Cr}} - E^\circ_{\text{Fe}} = \frac{0.059}{6}\log\frac{[Cr^{3+}]^2[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}[Fe^{2+}]^6}$$

But for the reaction in question, we have

$$K = \frac{[Cr^{3+}]^2[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}[Fe^{2+}]^6}$$

Therefore, equation (4) becomes

$$(5) \qquad E^\circ_{\mathrm{Cr}} - E^\circ_{\mathrm{Fe}} = \frac{0.059}{6} \log K$$

and rearrangement gives

$$\log K = \frac{6[E^\circ_{\mathrm{Cr}} - E^\circ_{\mathrm{Fe}}]}{0.059}$$

We have thus derived an expression for the value of the equilibrium constant at 25 °C as a function of the values of the E°s for each half-reaction.

By following the same derivation procedure for any redox reaction, one can show that the general expression for the relationship at 25 °C is

$$\log K = \frac{n[E^\circ_{\mathrm{red}} - E^\circ_{\mathrm{ox}}]}{0.059}$$

where $E^\circ{}_{\mathrm{red}}$ is the standard electrode potential of the couple being reduced in the reaction, $E^\circ{}_{\mathrm{ox}}$ is the standard electrode potential of the couple being oxidized, and n is the number of moles of electrons transferred in the overall balanced reaction. Using this formula to calculate the equilibrium constant for the reaction between MnO_4^- and Cl^-, which we have predicted to be spontaneous, we get

$$\log K = \frac{10(1.51 - 1.36)}{0.059} = \frac{10(0.15)}{0.059} = 25.4$$

$$K = 10^{25.4} = 2.5 \times 10^{25}$$

Applying the calculation to the nonspontaneous reaction between $Cr_2O_7^{2-}$ and Cl^- gives

$$\log K = \frac{6(1.33 - 1.36)}{0.059} = \frac{6(-0.03)}{0.059} = -3.0$$

$$K = 1 \times 10^{-3}$$

Note that the relative magnitudes of these two equilibrium constants agree with our predictions about the spontaneity* of the two reactions.

The relationship between standard electrode potentials and the equilibrium constant also enables us to relate standard electrode potentials to the standard free-energy change of the reaction in question. The factor 0.059 in our simplified form of the Nernst equation is the result of combining several constants and assuming the temperature to be 25 °C:

$$(1) \qquad 0.059 = \frac{2.303\, RT}{F}$$

Thus, the more general form of the relationship between log K and the standard cell potential is

$$(2) \qquad \log K = \frac{n(E^\circ_{\mathrm{red}} - E^\circ_{\mathrm{ox}})F}{2.303\, RT}$$

The relationship between log K and ΔG° given in Chapter 14,

$$(3) \qquad \Delta G^\circ = -2.303\, RT \log K$$

allows us to express ΔG° in terms of the standard cell potentials (substituting the value for log K given in equation (2) into equation (3),

$$\Delta G^\circ = \frac{-2.303\, RTnF(E^\circ_{\mathrm{red}} - E^\circ_{\mathrm{ox}})}{2.303\, RT}$$

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* Notice that this term refers to the extent of the reaction, not the rate of the reaction.

Therefore:

$$\Delta G^\circ = -n\,F(E^\circ_{\text{red}} - E^\circ_{\text{ox}}) \tag{4}$$

This relationship[†] may also be expressed as

$$\Delta G^\circ = -n\,F\,E^\circ_{\text{cell}}$$

where E°_{cell} is the emf of a cell in which the two electrode potentials are the *standard* electrode potentials for the two half-reactions in question.

Thus, we can calculate the value of ΔG° for any oxidation-reduction reaction if we know the appropriate E° values and the number of moles of electrons (n) transferred in the balanced redox reaction equation.

Problem 18.2

Calculate the standard free-energy change for the reaction

$$2\,MnO_4^- + 5\,H_2SO_3 \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 4\,H^+ + 3\,H_2O$$

Solution:

The two half-reactions and their standard electrode potentials are

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O \qquad E^\circ = 1.51\text{ V}$$
$$SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow H_2SO_3 + H_2O \qquad E^\circ = 0.17\text{ V}$$

The number of electrons transferred is 10. Substituting the appropriate values into the expression

$$\Delta G^\circ = -nF\,E^\circ_{\text{cell}}$$

gives

$$\Delta G^\circ = -10\,(96.48\text{ kJ/V})\,(1.51\text{ V} - 0.17\text{ V})$$
$$\Delta G^\circ = -1.29 \times 10^3\text{ kJ}$$

18.7 CONCENTRATION CELLS

Previously, we saw that the magnitude of a single electrode potential depended upon a number of factors, including the specific redox reaction in question, the temperature, and the concentrations of the substances involved in the half-reactions. A qualitative indication of the effect of concentration on electrode potential may be obtained by applying Le Châtelier's principle to the electrode reaction in question. For example, let us qualitatively consider the effect of the Ag^+ concentration on the reduction potential for the Ag^+/Ag couple. The reduction half-reaction is written as

$$Ag^+ + e^- \longrightarrow Ag^\circ \qquad E^\circ = 0.80\text{ V}$$

If the concentration of the reactant Ag^+ is decreased, we would expect the extent of the reaction to decrease also. A decrease in the extent of the reaction would indicate less propensity to react and, therefore, a lower electrode potential. Solutions of Ag^+ that are less than 1.0 M (standard conditions) would provide electrode potentials of less than 0.80 V. If the silver ion concentration is increased above 1.0 M, we would expect the extent of the reaction to increase, and hence the electrode potential will also increase. If we alter the concentration of the products, we can also influence the extent of the reaction and the magnitude of the electrode potential. A concentration of products greater than 1.0 M will cause the extent of the reaction to shift toward the reactants, decreasing the

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[†] Note that this relationship was developed previously in this chapter from thermodynamic considerations involving work.

electrode potential, while a concentration of products less than 1.0 *M* will cause the reaction to shift toward the products and increase the electrode potential. The concentration dependencies are quantitatively described by the Nernst equation, and this equation may be used to calculate specific electrode potentials under non-standard conditions. Calculations of this type are illustrated in Methodology 18.5 and Problem 18.3.

Methodology 18.5

Apply Le Châtelier's principle to predict if the electrode potential for an electrode prepared by immersing a strip of Cd metal in a solution that is 0.01 *M* in Cd^{2+} at 25 °C would be greater or less than the E° value, and then calculate the electrode potential under these nonstandard conditions and compare to your prediction.

First, write the equation for the reduction half-reaction and look up (Appendix 6) the standard electrode potential for that half-reaction,

$$Cd^{2+} + 2\,e^- \longrightarrow Cd^\circ \qquad E^\circ = 20.40\ \mathrm{V}$$

Apply Le Châtelier's principle to make a prediction.

> The Cd^{2+} concentration in this electrode is less than 1.0 M and the Cd^{2+} is a reactant. Therefore, if the reactant concentration goes down, the extent of the reaction will decrease and we would predict the electrode potential to decrease as well. The E value under these conditions should be less than E°.

To calculate the electrode potential, first write the appropriate Nernst expression,

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Cd^\circ]}{[Cd^{2+}]}$$

Substitute the appropriate values into the Nernst expression,

$$E = -0.40\ \mathrm{V} - \frac{0.059}{2}\log\frac{[1]}{[0.01]}$$

$$E = -0.46\ \mathrm{V}$$

Compare the calculated value with your prediction.

> |The predicted E value for this electrode would be less than E° and we can see that the calculated E value of -0.46 V is less than the E° value of -0.40 V, so our prediction matches our calculation.

Problem 18.3

Provide the half-cell potential for the following half-reaction:

$$\|Cr_2O_7^{2-}\ (0.002\ M),\ Cr^{3+}\ (0.005\ M),\ H^+\ (1.0\ M)|Pt$$

Solution:

The half-reaction involved in the half-cell is

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \qquad E^\circ = 1.33\ \mathrm{V}$$

The Nernst expression is

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]^2[H^+]^{14}}$$

Substituting appropriate values in the Nernst expression gives

$$E = 1.33\ \mathrm{V} - \frac{0.059}{6}\log\frac{[0.005]^2}{[0.002][1.00]^{14}}$$

$$E = 1.32\ \mathrm{V}$$

Because each electrode potential is dependent upon the concentrations of species involved in the redox couple, the overall potential of a voltaic cell also shows a dependence on the concentration of the species involved in the cell reaction. The cell potential (or emf) under nonstandard conditions may be calculated from the electrode potential for each half-reaction, followed by using the equation

$$E_{\text{cell}} = E_c - E_a = E_{\text{red}} - E_{\text{ox}} = E_{(+)} - E_{(-)}$$

Alternatively, a Nernst equation for the entire reaction may be derived and employed. This equation is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q \qquad \text{or} \qquad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log Q \ \text{ at } 25\ ^\circ\text{C}$$

where E°_{cell} is the standard cell potential and Q is the reaction quotient* for the overall cell reaction. If a voltaic cell is prepared with nonstandard concentrations, these concentrations must be included in the cell notation. These calculations are illustrated in Methodology 18.6 and Problem 18.4.

Methodology 18.6

Calculate the potential of the voltaic cell in which the anode is a piece of copper immersed in a solution of 0.50 M Cu^{2+} and the cathode is a 0.10 M solution of Ag^+ with a silver metal electrode.

Write the equation for each half-reaction (as reductions).

Anode (oxidation): $Cu^{2+} + 2\,e^- \longrightarrow Cu^\circ$

Cathode (reduction): $Ag^+ + e^- \longrightarrow Ag^\circ$

Calculate the nonstandard electrode potential for each half-reaction.

The electrode potential for the copper half-reaction is

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Cu^\circ]}{[Cu^{2+}]}$$

$$E = 0.34\text{ V} - \frac{0.059}{2}\log\frac{[1]}{[0.50]}$$

$$E = 0.33\text{ V}$$

The electrode potential for the silver half-reaction is

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Ag^\circ]}{[Ag^+]}$$

$$E = 0.80\text{ V} - \frac{0.059}{1}\log\frac{[1]}{[0.10]}$$

$$E = 0.74\text{ V}$$

Calculate the overall cell potential.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{red}} - E_{\text{ox}} = E_{(+)} - E_{(-)} = 0.74\text{ V} - 0.33\text{ V} = 0.41\text{ V}$$

Continued on the next page

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* Remember, the reaction quotient is an expression of the same form as K, only for conditions other than equilibrium. It is equal to the concentration of each product raised to the power of its stoichiometric coefficient divided by the concentration of each reactant raised to the power of its stoichiometric coefficient.

Methodology 18.6 Continued

Alternatively, the Nernst expression for the overall cell reaction may be employed:

Overall reaction: $Cu^\circ + 2\,Ag^+ \longrightarrow Cu^{2+} + 2\,Ag^\circ$

$$E^\circ_{cell} = 0.80\ V - 0.34\ V = 0.46\ V$$

Nernst expression: $$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Cu^{2+}][Ag^\circ]}{[Cu^\circ][Ag^+]^2}$$

$$E_{cell} = 0.46\ V - \frac{0.059}{2}\log\frac{[0.50][1]}{[1][0.10]^2}$$

$$E_{cell} = 0.41\ V$$

Problem 18.4

Calculate the cell potential for the following reaction:

$$Pt|U^{3+}\ (1.0 \times 10^{-4}\ M),\ U^{4+}\ (0.10\ M)||MnO_4^-\ (0.050\ M),\ Mn^{2+}\ (1.5\ M),\ H^+\ (0.10\ M)|Pt$$

Solution:

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_c = E^\circ_{Mn}\frac{0.059}{n}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$E_c = 1.51\ V - \frac{0.059}{5}\log\frac{[1.5]}{[0.05][0.10]^8}$$

$$E_c = 1.40\ V$$

$$E_a = E^\circ_U - \frac{0.059}{n}\log\frac{[U^{3+}]}{[U^{4+}]}$$

$$E_a = -0.61V - \frac{0.059}{1}\log\frac{[1.0 \times 10^{-4}]}{[0.10]}$$

$$E_a = -0.43\ V$$

$$E_{cell} = 1.40\ V - (-0.43\ V) = 1.83\ V$$

All of the voltaic cells used as illustrations in the preceding discussions have consisted of half-cells involving two different redox couples. Because electrode potentials depend not only on the specific couple involved, but also on the concentrations of the electrolytes, it is possible to construct a voltaic cell in which the two half-cells involve the same redox couple, if the concentrations are different. A cell of this type, called a **concentration cell**, is illustrated by the following simple example, illustrated in Figure 18.8.

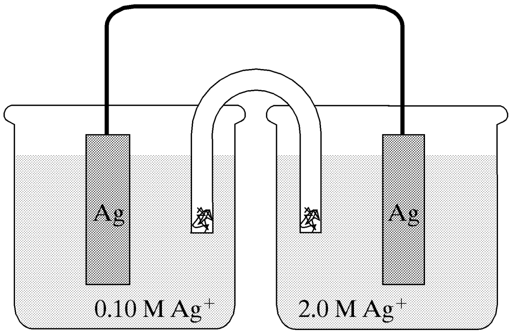

Figure 18.8 A concentration cell.

A piece of silver metal dipping into a 0.10 *M* $AgNO_3$ solution serves as one half-cell, and another piece of silver metal dipping into a 2.0 *M* $AgNO_3$ solution (see below) serves as the other half-cell. In both half-cells, the redox couple is

$$Ag^+ + e^- \longrightarrow Ag$$

The electrode potential on the left may be calculated from the Nernst equation,

$$E = E^\circ - 0.059 \log \frac{1}{[Ag^+]} = 0.80 - 0.059 \log \frac{1}{0.1}$$

$$E = 0.80 - 0.059(1) = 0.74 \text{ V}$$

The same procedure is followed to calculate the electrode potential on the right,

$$E = E^\circ - 0.059 \log \frac{1}{[Ag^+]} = 0.80 - 0.059 \log \frac{1}{2.0}$$

$$E = 0.80 - (-0.02) = 0.82 \text{ V}$$

Since the electrode on the right of this concentration cell has the larger electrode potential, it is positive, and the left-hand electrode is negative. The E_{cell} value is $0.82 - 0.74 = 0.08$ V. When current is drawn from the cell, the electrode reactions are

$$\text{Right:} \quad Ag^+ + e^- \longrightarrow Ag$$

$$\text{Left:} \quad Ag \longrightarrow Ag^+ + e^-$$

This cell may be represented by the notation

$$Ag\,|\,Ag^+(0.10\ M)\,\|\,Ag^+(2.0\ M)\,|\,Ag$$

18.8 SOME VOLTAIC CELLS OF PRACTICAL USEFULNESS

Although voltaic cells can be constructed from a large variety of redox reactions, most of them are not useful as sources of direct current. For instance, cells involving gases in their reactions may be impractical in the matter of space requirements and convenience; cells requiring platinum or other precious metals for electrodes are too expensive; and for many cells, the cell voltage produced is too small for practical applications. A number of cells, however, have practical applications and are produced commercially. One of the most common is the **lead storage cell**, in which the anode is lead and the cathode is a grid of lead packed with lead dioxide. These "plates" are immersed in an aqueous solution of sulfuric acid (see Figure 18.9). When current is drawn from the cell, the electrode reactions are

$$\text{(cathode)} \quad PbO_2(s) + SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O$$

$$\text{(anode)} \quad Pb(s) + SO_4^{2-} \longrightarrow PbSO_4(s) + 2\,e^-$$

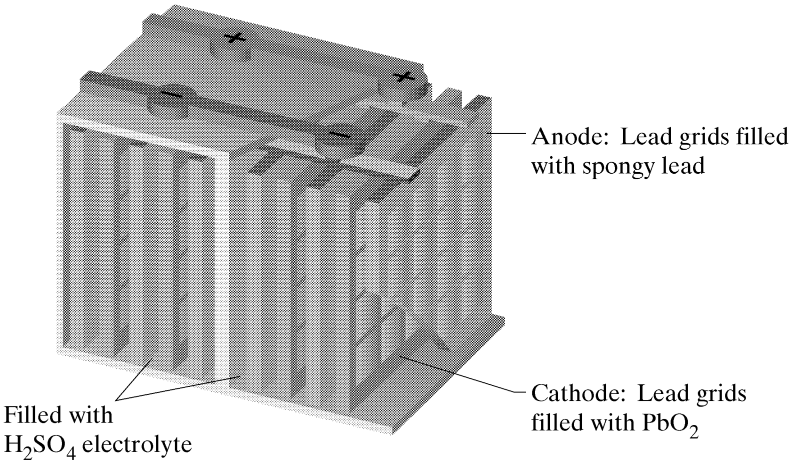

Figure 18.9 A lead storage cell.

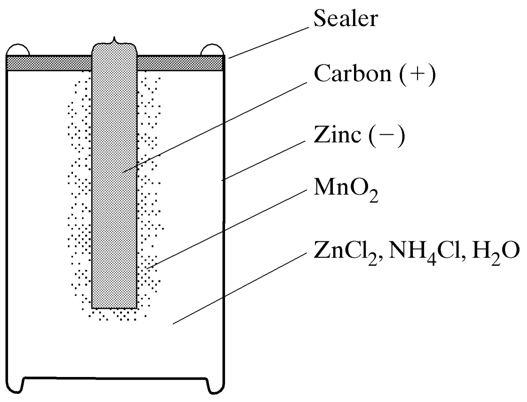

Figure 18.10 The dry cell.

The overall reaction involves the conversion of both Pb and PbO_2 into $PbSO_4$, and sulfuric acid is consumed in the process:

$$Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{2-} \longrightarrow 2\,PbSO_4 + 2\,H_2O$$

The state of "charge" of the cell can be determined by measuring the amount of H_2SO_4 remaining: this is most conveniently done by measuring the density of the electrolyte. The cell can be "recharged" by applying an external source of current in a direction opposite to the current produced by the cell, which causes the reverse of these electrode reactions to take place.

The cell potential of the lead storage cell is approximately 2 V. In its most commonly used form, three or six of these cells are joined in series to produce the common 6-volt motorcycle or 12-volt automobile battery.

Another type of storage cell that is commercially available is the **nickel-cadmium alkaline cell**. The active electrode substances are Cd and NiO(OH), and the electrolyte is a solution of KOH. When current is drawn from the cell, the electrode reactions are

$$\text{(cathode)} \quad NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$$

$$\text{(anode)} \quad Cd + 2\,OH^- \longrightarrow Cd(OH)_2 + 2\,e^-$$

This cell has a potential of about 1.4 V and is rechargeable, which means that the reaction is reversible. A battery of Ni-Cd cells has a longer life and requires less maintenance than a lead storage battery.

Another cell in common use is the **dry cell**. This cell usually consists of a zinc container filled with a paste of ammonium chloride, zinc chloride, water, and an inert filler. Imbedded in the center of this paste mixture is a carbon rod surrounded by manganese dioxide (Figure 18.10). The zinc container is the negative electrode (anode), and the carbon rod is the positive electrode (cathode). The maximum cell potential of the dry cell is approximately 1.5 V. The electrode reactions are complex but are usually represented as:

$$(-)\ Zn \longrightarrow Zn^{2+} + 2\,e^-$$

$$(+)\ 2\,NH_4^+ + 2\,MnO_2 + 2\,e^- \longrightarrow Mn_2O_3 + 2\,NH_3 + H_2O$$

A similar type of dry cell also employs a carbon rod and zinc container as electrodes, but has an electrolyte consisting of a mixture of HgO and KOH. The potential of this cell is about 1.35 V, and the electrode reactions are

$$(-)\ Zn + 2\,OH^- \longrightarrow Zn(OH)_2 + 2\,e^-$$

$$(+)\ HgO + H_2O + 2\,e^- \longrightarrow Hg + 2\,OH^-$$

18.9 FUEL CELLS

Since combustion of natural fuels (coal, oil, gas) is an oxidation-reduction process in which the fuel is oxidized and oxygen is reduced, it is theoretically possible to construct a cell to produce electric current directly from fuel combustion. Sir William Robert Grove produced the first such cell in 1839, using hydrogen as the fuel, oxygen as the oxidant, and sulfuric acid as the electrolyte, with an overall cell reaction of

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

In the conventional use of fuel to produce electricity, the heat energy released from the combustion is used to convert water into steam, and the steam is used to drive a turbine, which drives a generator. There is a considerable loss of energy in this process; maximum efficiency is only about 40%. Direct production of electricity from the oxidation of the fuel in a cell should yield a much higher efficiency, potentially over 80%. Consequently, a great deal of effort in recent years has gone into the development of practical cells based on fuel combustion. These cells, in which the reactants are supplied continuously and the products are removed continuously, are called **fuel cells**. With reactants and products being continuously added and removed, these cells are much different than batteries, which have the reactants as an integral part of the cell. Therefore, because nothing is added or removed from the fuel cell itself, they have long lifetimes and do not "run down." Fuel cells serve only as a direct converter of chemical energy to electrical energy.

In theory, any hydrocarbon may be used as a fuel. Unfortunately, the combustion of most fuels requires high temperatures, which introduce practical problems in the operation of such cells; e.g., corrosion of the container and electrodes, and reduced efficiency because of the need to continuously supply thermal energy to the cell. The heat required for combustion generally increases with the molecular size of the hydrocarbon and only methanol, methane, and most often and most effectively, hydrogen, have been employed as practical fuels. Several types of fuel cells employ hydrogen as the fuel, distinguished only by the electrolyte that supports the redox reaction.

An alkaline fuel cell (AFC) using hydrogen as fuel is illustrated schematically in Figure 18.11. In this cell, pure hydrogen and oxygen are bubbled through electrodes of porous, compressed carbon in which finely divided catalysts have been incorporated, although a variety of other electrode compositions, using nickel and noble metals such as platinum and gold, have also been employed. The electrodes are immersed in a concentrated solution of NaOH or KOH and the cell is operated at a temperature of approximately 250 °C. The operational temperature of this cell is limited by the vapor pressure of water from the aqueous electrolyte solutions. The hydrogen and oxygen are consumed

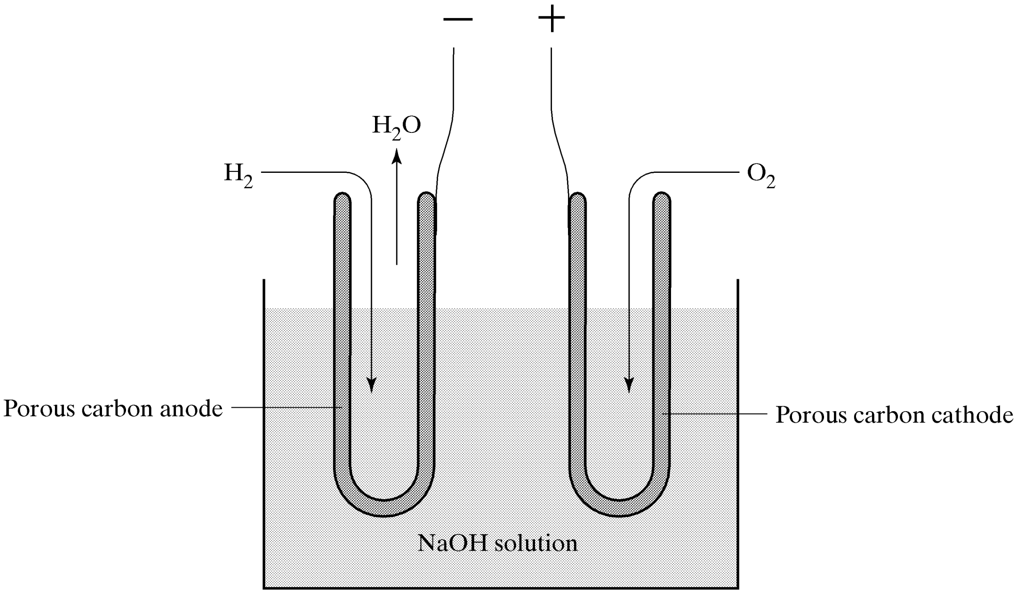

Figure 18.11 An alkaline fuel cell.

in the reaction, and the water that is formed is removed by evaporation. The reactions that occur are:

$$\begin{array}{rcr} \text{Anode:} & H_2 + 2\,OH^- \longrightarrow 2\,H_2O + 2\,e^- & E^\circ = -0.83\text{ V} \\ \text{Cathode:} & O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^- & E^\circ = 0.40\text{ V} \\ \text{Overall:} & 2\,H_2 + O_2 \longrightarrow 2\,H_2O & E^\circ_{rx} = 1.23\text{ V} \end{array}$$

Although the theoretical potential developed in such a cell is 1.23 V, the experimental output is somewhat less, on the order of 0.8 V, due to several factors, including losses due to cell resistance and activation energies. Many cells can be linked in series to develop large voltages and act as a power supply. Due to their high energy-to-weight ratio and their power generation with no production of harmful products, useful AFCs were first extensively developed and employed for spacecraft power in the Gemini and Apollo space missions, and a new generation of AFCs currently power the Space Shuttle orbiters. As a side benefit to power generation, the water produced by the fuel cell is used as drinking water by the shuttle's crew. The major practical problem with terrestrial use of an AFC is the cell's susceptibility to poisoning by CO_2 (carbon dioxide is commonly found in most sources of hydrogen and oxygen unless the gases are highly purified), which reacts with the electrolyte to form carbonate salts. For the space flights, cost was a secondary consideration and ultra-pure gases could be employed regardless of cost. For practical and economical use, however, this is not possible and AFCs have found limited application. Consequently, fuel cell designs with other electrolytes, such as phosphoric acid, molten carbonate salts, polymers, and solid oxides are being developed.

Attractive characteristics of fuel cells include their energy efficiency, low production of pollutants, their clean, quiet, and safe operation without a great deal of supervision, and the fact that no substantial source of water is required for power generation, which allows power sources to be placed wherever needed. Relatively small fuel cells have provided electrical power for buildings in remote settings where electric service was unavailable, and they have been used in demonstration studies to power buildings such as schools and hospitals. Urban Southern California, with its poor air quality driving the search for alternative, cleaner forms of power generation, has been the site of several of these demonstration systems. Multi-megawatt electric power stations have also been built for demonstration in both the United States and Japan. The clean burning nature of fuel cells makes them particularly attractive for vehicular power, especially in areas of high pollution. Ballard Power Systems of Vancouver, British Columbia, has a 20-passenger bus in service that operates on a compressed hydrogen fuel cell and pilot studies on a variety of vehicle types are in progress in the United States.

Currently, many technical challenges remain to be solved before fuel cells find widespread commercial application. The primary drawbacks are cost and cell lifetime. Over the operating lifetime of a cell, fuel cell power is still substantially more expensive than other sources, although technological improvements are continually reducing the costs. Additionally, the most efficient fuel cells employ hydrogen, which has no large-scale natural source. Hydrogen is normally obtained by the cracking of petroleum, which generates CO_2 and other pollutants at the H_2 production site, or by electrochemical dissociation of water, which is costly in both money and energy. In transportation applications, safe and practical storage of the H_2 is a serious problem, as is the current lack of a H_2 distribution network, which limits fuel access and hence the useful range of a fuel-cell vehicle.

Extensive research to overcome these problems is ongoing. New fuel cell designs and materials are lowering the production costs and increasing cell lifetimes. In particular, development of better electrochemical catalysts that lower the activation energies in the cell reactions will improve the energy conversion efficiency and possibly allow low-temperature use of methanol as a fuel. Methanol is more widely available and much easier to store, alleviating several problems associated with transportation applications.

In 1990, the United States Department of Energy spent in excess of \$40 million on research and development of fuel cells, while Japan and Europe spent in excess of \$100 million. Many private companies and industrial consortia also continue to develop and refine applications of fuel cells. As fuel cell technology matures, the cost of the cell can be expected to decrease while their performance increases. Eventually, power generation by fuel cell technology will likely be competitive with fossil fuels, especially given the environmental costs associated with the burning of fossil fuels, and fuel cells may become a viable energy alternative for the 21st century.

18.10 ELECTROLYTIC CELLS

In Chapter 11 we established that substances can be classified as electrolytes and nonelectrolytes. For example, molten ionic compounds (salts) and aqueous solutions of electrolytes (acid, bases, and salts) conduct electric current. This conduction, called **electrolytic conduction** to distinguish it from **metallic conduction**, is the result of oxidation-reduction processes.

Perhaps the simplest example of this process is the conduction in a molten salt of monatomic ions, such as sodium chloride. Consider sodium chloride that is kept at a temperature above its melting point, so that it remains in the liquid state. Two inert electrodes are placed in the melt, and a direct-current source (for instance, a battery of voltaic cells) is connected across the electrodes (see Figure 18.12).

Sodium ions, which are positive, are attracted to the negative electrode, and the negative chloride ions are attracted to the positive electrode. But this migration of ions does not in itself account for the completion of the electrical circuit. At the negative electrode, sodium ions accept electrons from the electrode and are reduced to sodium atoms. Simultaneously, chloride ions give up electrons to the positive electrode and are oxidized to elemental diatomic chlorine. The overall process taking place, then, is an oxidation-reduction reaction, consisting of two half-reactions: reduction at the negative electrode and oxidation at the positive electrode.

$$\begin{array}{r} (-)\ \mathrm{Na}^+ + e^- \longrightarrow \mathrm{Na} \qquad\qquad \\ (+)\ 2\,\mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2 + 2\,e^- \\ \hline 2\,\mathrm{Na}^+ + 2\,\mathrm{Cl}^- \longrightarrow 2\,\mathrm{Na} + \mathrm{Cl}_2 \end{array}$$

The apparatus described is called an **electrolytic cell**, and the complete process that takes place is called **electrolysis**. The material being electrolyzed (in this case, molten NaCl) is referred to as the **electrolyte**. During electrolysis, reduction occurs at the negative electrode, which may therefore be called the cathode; the positive electrode, then, is the anode, since oxidation occurs there. (Note the difference in these designations between an electrolytic cell and a voltaic cell. Recall that in a voltaic cell, the anode is the negative electrode and the cathode is the positive one.)

It should be noted that electrons do not flow through the electrolyte. They are generated by the direct-current source and move through the connecting wire into the cathode, where they are consumed by the reduction process. Other electrons are generated at the anode by the oxidation process and move from there to the source through the wire. The difference between an electrolytic cell and a voltaic cell should now be apparent. In a

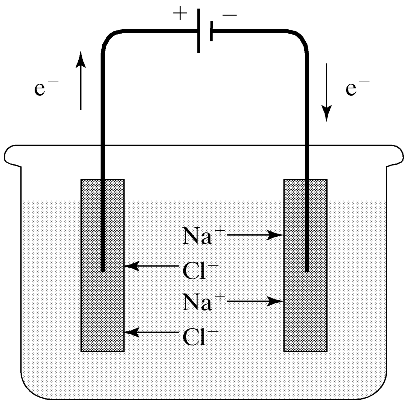

Figure 18.12 Schematic of the electrolysis of molten NaCl.

voltaic cell an oxidation-reduction reaction occurs spontaneously to produce an electric current, whereas in an electrolytic cell, an electric current is used to force a nonspontaneous reaction to take place.

Electrolysis of Aqueous Solutions

The discussion of electrolysis of molten NaCl also applies in general to the electrolysis of aqueous solutions of electrolytes. The latter are somewhat more complicated, however, because of the presence of water.

Let us consider the electrolysis of a dilute solution of NaCl. The electrolytic cell is the same as that shown above, except that a dilute aqueous NaCl solution replaces the molten NaCl. At the cathode, two different reductions are possible: reduction of Na^+ or reduction of water molecules,

$$\begin{aligned} Na^+ + e^- &\longrightarrow Na & E^\circ &= -2.71\ V \\ 2\,H_2O + 2\,e^- &\longrightarrow H_2 + 2\,OH^- & E^\circ &= -0.83\ V \end{aligned}$$

Comparison of the standard electrode potentials of the two redox couples in question indicates that water is much more readily reduced than sodium ion; therefore the product at the cathode is hydrogen gas, not sodium metal.

Similarly, at the anode, two oxidations are possible: oxidation of Cl^- or oxidation of H_2O,

$$\begin{aligned} 2\,Cl^- &\longrightarrow Cl_2 + 2\,e^- & E^\circ &= -1.36\ V \\ 2\,H_2O &\longrightarrow O_2 + 4\,H^+ + 4\,e^- & E^\circ &= -1.23\ V \end{aligned}$$

(Note that the E° values given here are standard *oxidation* potentials, which are the negative of the reduction potential. This is simply a matter of convenience, because we are comparing oxidation processes.) The E° values favor oxidation of H_2O rather than Cl^-, but since they differ so little, the oxidation that will actually occur depends on the relative concentrations. Only if the solution of NaCl is dilute will O_2 be the anode product; more concentrated solutions will give only Cl_2. Thus, the electrode reactions and overall reaction for the electrolysis of aqueous NaCl solution may be summarized as follows:

Very dilute solution

$$\begin{array}{lrcl} \text{Cathode} & 2\,H_2O + 2\,e^- & \longrightarrow & H_2 + 2\,OH^- \\ \text{Anode} & 2\,H_2O & \longrightarrow & O_2 + 4\,H^+ + 4\,e^- \\ \hline \text{Overall} & 6\,H_2O & \longrightarrow & 2\,H_2 + O_2 + 4\,H^+ + 4\,OH^- \end{array}$$

More concentrated solution

$$\begin{array}{lrcl} \text{Cathode} & 2\,H_2O + 2\,e^- & \longrightarrow & H_2 + 2\,OH^- \\ \text{Anode} & 2\,Cl^- & \longrightarrow & Cl_2 + 2\,e^- \\ \hline \text{Overall} & 2\,H_2O + 2\,Cl^- & \longrightarrow & H_2 + Cl_2 + 2\,OH^- \end{array}$$

As a further illustration of this "competition" of electrode reactions, let us examine the electrolysis of an aqueous copper(II) sulfate solution using inert electrodes. At the cathode, the two possible reductions are

$$\begin{aligned} Cu^{2+} + 2\,e^- &\longrightarrow Cu & E^\circ &= +0.34\ V \\ 2\,H_2O + 2\,e^- &\longrightarrow H_2 + 2\,OH^- & E^\circ &= -0.83\ V \end{aligned}$$

It is obvious that the reduction of Cu^{2+} is favored and will take place rather than the reduction of water.

At the anode, the two possible oxidations and their standard oxidation potentials are

$$\begin{aligned} 2\,SO_4^{2-} &\longrightarrow S_2O_8^{2-} + 2\,e^- & E^\circ &= -2.01\ V \\ 2\,H_2O &\longrightarrow O_2 + 4\,H^+ + 4\,e^- & E^\circ &= -1.23\ V \end{aligned}$$

Therefore, water will be oxidized rather than SO_4^{2-}, and the reactions that actually occur, therefore, are

$$\begin{array}{ll} \text{Cathode} & Cu^{2+} + 2\,e^- \longrightarrow Cu \\ \text{Anode} & 2\,H_2O \longrightarrow O_2 + 4\,H^+ + 2\,e^- \\ \hline \text{Overall} & 2\,Cu^{2+} + 2\,H_2O \longrightarrow 2\,Cu + O_2 + 4\,H^+ \end{array}$$

This same kind of “competition” may exist between several ions if more than one electrolyte is present in solution. For example, we may raise the question: In the electrolysis of a solution containing both Cu^{2+} and Ag^+, what will the cathode reaction be? Looking at the standard electrode potentials for the three “competing” reductions:

$$\begin{array}{rl} Cu^{2+} + 2\,e^- \longrightarrow Cu & E^\circ = +0.34\text{ V} \\ Ag^+ + e^- \longrightarrow Ag & E^\circ = +0.80\text{ V} \\ 2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^- & E^\circ = -0.83\text{ V} \end{array}$$

we must conclude that the reduction of Ag^+ will take place preferentially. It must be kept in mind that this prediction is based on the assumption that Ag^+ and Cu^{2+} are present in equimolar* concentrations.

Thus, the products of an electrolysis depend not only on what electrolytes are present but also on the concentrations in which they are present. Given the exact concentrations of all species present in a solution to be electrolyzed, we can use standard electrode potentials and the Nernst equation to predict accurately what the electrode reactions will be.

However, for the electrolysis of a single-electrolyte solution at moderate concentrations, we can use the following simple rules to make qualitative predictions about the electrode reactions:

Cathode reactions

1. If the electrolyte is an acid, then the reaction is

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

2. If the electrolyte is a base or a salt (e.g., NaOH, $AgNO_3$) and

(a) if the cation is that of a very active metal (Na^+, Ba^{2+}, Mg^{2+}, etc.)—that is, has a very low E°—then the reaction is:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$$

(b) if the cation is that of a less reactive metal (Cu^{2+}, Ag^+, Cd^{2+}, etc.)—that is, has a moderate to high E°—then the reaction is

$$M^{n+} + n\,e^- \longrightarrow M$$

Anode reactions

1. If the electrolyte is a base (e.g., NaOH, KOH), the reaction is

$$4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^-$$

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* The concentration dependence on the potential at which a metal ion is reduced can be quantified by use of the Nernst expression. For example, the electrode potential at which a 10^{-9} *M* solution of Ag^+ can undergo reduction would be,

$$E - E^\circ_{Ag} - \frac{0.059}{1}\log\frac{1}{[Ag^+]} = 0.80\text{ V} - 0.059\log 10^9 = 0.27\text{ V}$$

The electrode potential at which a 10.0 *M* solution of Cu^{2+} would be reduced is,

$$E = E^\circ_{Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]} = 0.34\text{ V} - 0.0295\log 0.1 = 0.37\text{ V}$$

Thus, if we had a solution very concentrated in Cu^{2+} and extremely dilute in Ag^+, copper may, in fact, plate out before silver.

2. If the electrolyte is an acid or a salt and
   (a) if the anion is a monatomic ion with a relatively high standard oxidation potential (Br^-, I^-, etc.), then the reaction is, for example:

$$2\,Br^- \longrightarrow Br_2 + 2\,e^-$$

   (b) if the anion is a complex ion with the central atom in its maximum oxidation state (NO_3^-, SO_4^{2-}, ClO_4^-, etc.), then the reaction is

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$$

Electrolysis with Active Electrodes

All of the electrolytic cells discussed thus far have utilized *inert* electrodes—electrodes that do not themselves enter into the reaction but serve only as conductors of electrons, or at most, surfaces on which other metals plate out. If electrolyses are carried out using electrodes of less inert metals, the electrodes themselves may undergo reactions.

In the preceding section the electrolysis of a $CuSO_4$ solution with inert electrodes (Pt) was discussed, the reactions being

$$\begin{array}{lr} \text{Cathode} & Cu^{2+} + 2\,e^- \longrightarrow Cu \\ \text{Anode} & 2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- \end{array}$$

Suppose a similar electrolysis is carried out with copper electrodes. The cathode reaction is the same as with the inert electrode; that is, copper metal is plated out. However, at the anode an additional reaction is now possible. The "competing" oxidations and their standard oxidation potentials are

$$\begin{array}{rl} 2\,SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^- & E^\circ = -2.01 \\ 2H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- & E^\circ = -1.23 \\ Cu \longrightarrow Cu^{2+} + 2\,e^- & E^\circ = -0.34 \end{array}$$

Clearly, the tendency for the copper electrode to be oxidized to Cu^{2+} is greater than the tendency for either of the other possible oxidations to occur.

Accordingly, in the electrolysis of $CuSO_4$ solution between copper electrodes, the reactions are

$$\begin{array}{lr} \text{Cathode} & Cu^{2-} + 2\,e^- \longrightarrow Cu \\ \text{Anode} & Cu \longrightarrow Cu^{2-} + 2\,e^- \\ \hline \text{Overall} & Cu^{2+} + Cu \longrightarrow Cu + Cu^{2+} \end{array}$$

Note that there is no net chemical reaction. In the overall process, copper is simply removed from the anode and plated onto the cathode. The concentration of $CuSO_4$ in the solution does not change.

Electrolysis with active electrodes has a number of practical applications, one of which is **electroplating**. Suppose that we wish to plate a covering of silver onto some metallic object. This may be done electrolytically by making the object to be plated the cathode, using a bar of silver as the anode, and using a solution containing Ag^+ as the electrolyte. Silver is removed from the anode by oxidation and plated onto the cathode by reduction.

Another application of active electrode electrolysis, **electrorefining**, may be illustrated with the process used to obtain very pure copper. Copper metal produced from its ores contains small amounts of other metals, such as Zn, Fe, Ag, and Au, as impurities. When extremely pure copper is required, these impurities may be removed by employing a bar of the impure copper as the anode in an electrolytic cell. A thin sheet of pure copper serves as the cathode, and a solution of $CuSO_4$ is used as the electrolyte. As electrolysis proceeds, copper is oxidized and goes into solution from the anode along with other, more active metals—that is, zinc, iron, and other metals with high oxidation potentials. Because the less active metals, such as silver and gold, have low oxidation potentials, they are not oxidized; as the impure copper electrode is eroded away, these metals fall to the bottom of the cell and are later recovered from the "anode mud." Copper plates out at the cathode in pure form, and the other metal ions (such as Zn^{2+} and Fe^{2+}) remain in solution.

Faraday's Laws

Up to this point, our discussion has been concerned only with the *qualitative* aspects of electrolysis. We have considered what will happen under certain conditions—what the electrode reactions will be—not the extent to which they will occur. Let us now examine the *quantitative* aspect of electrolysis—the relationship between the amount of substance reacting at an electrode and the quantity of electricity used.

The basic unit of quantity of electricity (or charge) generally used in chemistry is the **coulomb** (C). Passage of one coulomb of electricity through a circuit is equivalent to passage of 6.2418×10^{18} electrons. The rate of flow of electricity (the quantity per unit of time), called the **current**, is measured in units called **amperes** (A), with one ampere being defined as one coulomb per second. Thus, the quantity of electricity flowing through a circuit in a given time can be calculated from the current in amperes,

$$\text{Coulombs} = \text{Amperes} \times \text{Seconds}$$

In 1833, the English chemist Michael Faraday described the relationship between the quantity of electricity and the amount of substances reacting at the electrodes during electrolysis. He summarized his observations in two statements. The first of these, referred to as **Faraday's first law**, states that:

The weight of a chemical substance liberated at an electrode is directly proportional to the quantity of electricity passed through the cell.

This is simply to say that if *one* gram of copper is produced in the electrolysis of a $CuSO_4$ solution by the passage of n coulombs, then $2n$ coulombs will produce *two* grams of copper.

Faraday's second law states that:

The weights of different substances produced by the passage of a given quantity of electricity are proportional to the equivalent* weights of those substances.

The importance of this statement may be illustrated as follows. Suppose we carry out an electrolysis of molten NaCl by passing n coulombs of electricity through the cell, and we determine accurately the weights of Na and Cl_2 produced. We then carry out an electrolysis of a $CuSO_4$ solution, passing exactly the same quantity (n coulombs) through that cell, and determine the weights of Cu and O_2 produced. We will find that the weights of

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* The **equivalent weight** of a substance in an oxidation-reduction reaction is the weight of that substance consumed or produced by the transfer of one mole of electrons (6.022×10^{23} electrons). Thus, the equivalent weight of sodium is the same as its atomic weight, because one mole is oxidized or reduced by one mole of electrons,

$$Na^+ + e^- \longrightarrow Na$$

The equivalent weight of copper, on the other hand, is one-half its atomic weight, since two moles of electrons are required to oxidize or reduce one mole of copper,

$$Cu^2 + 2\ e^- \longrightarrow Cu$$

Because the production of one mole of O_2 (32 g) by oxidation of water requires the loss of four moles of electrons,

$$2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4\ e^-$$

the equivalent weight of O_2 is one-fourth its formula weight, or 8 g.

Na, Cl_2, Cu, and O_2 produced are in the same ratio to one another as are the equivalent weights of the four substances.

It follows from Faraday's Laws that there is some definite quantity of electricity that will cause the oxidation or reduction of one equivalent weight of any substance. That quantity of electricity, equal to 6.022×10^{23} electrons or 1 mole of electrons, is called one Faraday and has been shown to be equal to approximately 96,500 C. The number of moles of electrons transferred in a redox reaction may be related to the number of moles of product produced or reactant consumed through the number of electrons involved in the process. For example, the transfer of 1 mole of electrons (96,500 C) will cause the reduction of 1 mol of Na^+ because each sodium ion requires one electron to be reduced to Na°. Therefore, 96,500 C will consume 1 mol of Na^+ and generate 1 mol (23 g) of Na°. In the case of Cu^{2+}, one mole of electrons will produce 0.5 mol of Cu° metal because each Cu^{2+} requires two electrons for reduction.

Faraday's Laws enable one to make valuable predictions relating current, time, and quantity of products produced in electrolyses, as summed up below.

$$\text{current} \times \text{time} = \text{charge (Coulombs)}$$

$$\frac{\text{charge (Coulombs)}}{\text{1 Faraday (96,500 C/mol } e^-)} = \text{moles } e^-$$

$$\frac{\text{moles } e^-}{n \text{ value for redox species}} = \text{moles species generated or reacted}$$

For example, let us calculate the weight of nickel produced from a solution of $Ni(NO_3)_2$ electrolyzed between platinum electrodes using a current of 5.0 A for 30 min. First, the quantity of electricity passed through the cell must be found,

$$5.0\text{ A} \times 30\text{ min} \times 60\text{ s/min} = 9.0 \times 10^3\text{ A-s} = 9.0 \times 10^3\text{ C}$$

Now, the reduction half-reaction is written to determine the number of moles of electrons per mole of nickel involved in the electrodeposition process,

$$Ni^{2+} + 2\,e^- \longrightarrow Ni \qquad (2\,e^- \text{ per mole Ni})$$

Finally, we can solve for grams of Ni produced:

$$\frac{9.0 \times 10^3\text{ C}}{96{,}500\text{ C/mol } e^-} \times \frac{1\text{ mol Ni}}{2\text{ mol } e^-} \times 58.69\text{ g/mol Ni} = 2.7\text{ g Ni}$$

Methodology 18.7

In the electrolysis of a sulfuric acid solution using a current of 3.50 A, how long will it take to liberate 5.00 g of oxygen at the anode?

Determine the anode reaction that provides the number of moles of electrons required for each mole of O_2 liberated,

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$$

Calculate the number of moles of O_2 liberated.

$$\frac{5.00\text{ g}}{32.0\text{ g/mol}} = 0.156\text{ mol } O_2$$

How many moles of electrons are required to liberate 0.156 mol of O_2?

$$0.156\text{ mol } O_2 \times \frac{4\,e^-}{\text{mol } O_2} = 0.624\text{ mol } e^-$$

What quantity of electricity carries a mole of electrons?

One mole of electrons is 96,500 C.

Continued on the next page

Methodology 18.7 Continued

What quantity of electricity will provide 0.624 mol of electrons?

$$0.624 \text{ mol } e^- \times \frac{96500 \text{ C}}{\text{mol } e^-} = 6.02 \times 10^4 \text{ C}$$

If the current is 3.5 A, how many Coulombs per second are passing through the cell?

$$3.5 \text{ A} = 3.5 \text{ C/s}$$

How many minutes will be required for a current of 3.5 A to produce 6.02 × 10^4 C?

$$\frac{6.02 \times 10^4 \text{ C}}{3.5 \text{ C/s}} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.9 \times 10^2 \text{ min}$$

Problem 18.5

What current will be required to produce 1.0 g of Na in 10.0 min by the electrolysis of molten NaCl?

Solution:

$$\frac{1.0 \text{ g}}{23.0 \text{ g/mol Na}} \times \frac{1 \text{ mol Na}}{1 \text{ mol } e^-} \times \frac{96500 \text{ C}}{\text{mol } e^-} \times \frac{1}{10 \text{ min} \times 60 \text{ s/min}} = 7.0 \text{ C/s}$$

$$= 7.0 \text{ A}$$

CHAPTER SUMMARY

In your study of electron-transfer reactions you need to learn the terminology used in connection with these reactions and to acquire several skills related to redox equations. One of these skills involves the system of oxidation numbers. You should memorize the rules by which oxidation numbers are assigned, and then learn to apply these rules (a) to assign oxidation numbers to the elements in compounds and ions, (b) to identify the oxidizing and reducing agents in redox reactions, and (c) to balance redox equations by the **oxidation-state method**.

Given the equation for any aqueous redox reaction, you should be able to arrive at the correct equations for the half-reactions. Once you have learned the procedure, you must continue to practice until you have mastered it. This skill is essential not only to balance equations by the **ion-electron method**, but also to understand the electrochemical phenomena that are examined in this chapter.

Electron-transfer reactions are the basis of the operation of **electrochemical** cells, of which there are two distinct types: **voltaic** (or **galvanic**) **cells** and **electrolytic cells**. In a voltaic cell, a spontaneous oxidation-reduction reaction takes place and causes the transfer of electrons from the reductant to the oxidant, producing an external electric current. Thus, chemical energy is converted into electrical energy. To thoroughly understand how a voltaic cell works, you will need to learn about **electromotive force**, **electrode potential**, **standard electrode potential**, and the **Nernst equation**, as well as the relationships among these concepts. You should be able to (a) devise and diagram a voltaic cell based on any given redox reaction, including the polarity of the cell and the direction of electron flow, (b) predict the electrode reactions that occur in any given voltaic cell, (c) use the Nernst equation to calculate the electrode potentials, and (d) calculate the electromotive force (emf) or E_{cell} value of voltaic cells.

The concept of the **standard electrode potential**, ***E*°**, is particularly important. You should understand how $E°$ values are measured and be able to use them to (a) determine the relative strengths of oxidizing and reducing agents, (b) predict whether given redox reactions are spontaneous, and (c) calculate equilibrium constants for redox reactions.

An **electrolytic cell** is an electrochemical cell in which an electric current is used to cause an oxidation-reduction reaction. Here, electrical energy is converted into chemical energy (the opposite of the process that occurs in a voltaic cell). You should master the terminology used in the study of electrolytic cells and learn to predict which electrode reactions will occur with various electrolytes. You should also be able to perform a variety of calculations based on Faraday's Laws and your knowledge of electrical units.

TERMS

Some of the important terms used in this chapter are as follows:

Oxidation A loss of electrons; also, an increase in oxidation number.

Reduction A gain of electrons; a decrease in oxidation number.

Oxidant (oxidizing agent) The reactant that is reduced (that gains electrons) in a redox reaction.

Reductant (reducing agent) The reactant that is oxidized (that loses electrons) in a redox reaction.

Oxidation number (oxidation state) A number assigned to each atom in a compound to represent the electrical charge that the atom would have if the electrons in the compound were distributed in a particular way. Oxidation numbers are assigned according to a set of arbitrary rules; in many cases, such a number does not represent an actual charge on the atom.

Oxidation-state method A procedure in which changes in oxidation numbers are used to balance redox equations.

Ion-electron method A method in which redox equations are balanced by writing the half-reactions.

Voltaic (galvanic) cell An electrochemical cell in which an electric current is produced from a spontaneous redox reaction. The voltaic cell consists of two **half-cells** and a **salt bridge**. Each half-cell contains the ingredients of one of the half-reactions and an **electrode**.

Anode Any electrode at which oxidation occurs. In a voltaic cell the anode is the negative electrode; in an electrolytic cell it is the positive electrode.

Cathode Any electrode at which reduction occurs. In a voltaic cell the cathode is the positive electrode; in an electrolytic cell it is the negative electrode.

Electromotive force, emf A measure of the driving force behind the flow of electrons from a voltaic cell. The electromotive force is the difference between the two electrode potentials, expressed in volts. It is also referred to as the cell potential.

Electrode potential, E A potential that develops between an electrode and a solution containing a redox couple. The magnitude of the electrode potential is a measure of the tendency of the solutes to gain electrons; therefore, the electrode potential can also be called a **reduction potential**. (A measure of the tendency for the solutes to *lose* electrons—that is, for oxidation to occur—is called the **oxidation potential**. The oxidation potential of any given half-cell is numerically equal to the electrode potential, but of opposite sign.)

Nernst equation An equation that describes the electrode potential for a given half-reaction at a specific set of conditions. For the hypothetical half-reaction

$$\mathrm{a\,(ox)} + ne^- \longrightarrow \mathrm{b(red)}$$

the Nernst equation defines the electrode potential E as

$$E = E^\circ - \frac{RT}{nF}\ln\frac{[\mathrm{red}]^b}{[\mathrm{ox}]^a}$$

Standard electrode potential, E° A constant characteristic of a particular half-reaction; the electrode potential of a redox couple when the concentrations of all constituents are 1 *M*. (The **standard oxidation potential** of a redox couple is numerically equal to the standard electrode potential, but of opposite sign.)

Concentration cell A voltaic cell in which the two half-cells contain the same redox couple but in different concentrations.

Fuel cell A voltaic cell in which the reactants are supplied continuously and the products are removed continuously.

Electrolytic cell An electrochemical cell in which an electric current is used to cause oxidation and reduction processes to occur at the electrodes.

Electrolysis The process that occurs in an operating electrolytic cell: reduction occurs at the cathode, oxidation at the anode.

Faraday's Laws Two laws relating the quantity of electricity to the quantity of the substances reacting at the electrodes during electrolysis. The first law states that the weight of a chemical substance liberated at an electrode is directly proportional to the amount of current passed through the cell. The second law states that the weights of different substances produced by the passage of a given quantity of electricity are proportional to the equivalent weights of those substances.

Equivalent weight In an oxidation-reduction reaction, the equivalent weight of a substance is that weight (in grams) that loses or gains one mole of electrons.

PROBLEMS

1. What is the oxidation number of sulfur in each of the following compounds?
(a) ZnS (b) $K_2S_2O_8$
(c) SO_2 (d) $KHSO_3$
(e) H_2SO5 (f) S_2O_7
(g) $Na_2S_2O_3$ (h) $H_2S_2O_7$

2. Assign oxidation numbers to all the atoms in each of the following compounds:
(a) $AgNO_3$ (b) CsF (c) SO_3
(d) C_2H_6 (e) SO_4^{2-} (f) $C_2H_3O_2^-$
(g) $Mg_2P_2O_7$ (h) As_4 (i) $KBrO_3$
(j) Hg_2Cl_2 (k) $Cr(OH)_3$ (l) CaH_2
(m) UO_2^{2+} (n) $HAsO_2$ (o) $Na_2S_2O_3$
(p) $S_2O_8^{2-}$ (q) $Ce(NO_3)_3$ (r) Sb_2S_3

3. Identify the oxidant and the reductant in each of the following reactions:
(a) $CO_3^{2-} + SO_2 + S \rightarrow S_2O_3^{2-} + CO_2$
(b) $2\,NH_3 + 3\,CuO \rightarrow N_2 + 3\,Cu + 3\,H_2O$
(c) $2\,OH^- + 2\,NO_2 \rightarrow NO_3^- + NO_2^- + H_2O$
(d) $Hg_2^{2+} + S^{2-} \rightarrow Hg + HgS$
(e) $Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \rightarrow 3\,CaSiO_3 + 2\,P + 5\,CO$

4. Use oxidation numbers to find the oxidant and the reductant in the following reaction equations:
(a) $3\,\underline{CuS} + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 3\,\underline{S} + 4\,H_2O$
(b) $K_2Cr_2O_7 + 14\,HCl + 2\,SnCl_2 \rightarrow 2\,CrCl_3 + 3\,SnCl_4 + 2\,KCl + 7\,H_2O$
(c) $2\,CuSO_4 + 4\,KI \rightarrow 2\,\underline{CuI} + I_2 + 2\,K_2SO_4$
(d) $2\,KOH + Cl_2 \rightarrow KCl + KClO + H_2O$
(e) $\underline{AgCl} + 2\,NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
(f) $\underline{BaSO_4} + 4\,C \rightarrow \underline{BaS} + 4\,CO$
(g) $\underline{3\,KClO_3} + 3\,H_2SO_4 \rightarrow 3\,KHSO_4 + HClO_4 + 2\,ClO_2 + H_2O$

5. For each of the following unbalanced "molecular" equations, write the half-reactions and the balanced net ionic equation.
(a) $C_3H_6O + K_2Cr_2O_7 + HCl \rightarrow CO_2 + CrCl_3 + H_2O + KCl$
(b) $KIO_3 + KI + HNO_3 \rightarrow KNO_3 + I_2 + H_2O$
(c) $Ca(OH)_2 + Br_2 \rightarrow CaBr_2 + Ca(BrO_3)_2$
(d) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$
(e) $\underline{FeS_2} + HNO_3 \rightarrow Fe_2(SO_4)_3 + H_2SO_4 + NO_2 + H_2O$

6. Complete and balance the following equations for reactions that take place in acidic solution:
(a) $C_2H_4 + MnO_4^- \rightarrow Mn^{2+} + CO_2$
(b) $ClO_3^- + HNO_2 \rightarrow Cl^- + NO_3^-$

7. Complete and balance the following equations for reactions that take place in basic solution:
(a) $Zn + NO_3^- \rightarrow Zn(OH)_4^{2-} + NH_3$
(b) $CrO_4^{2-} + S^{2-} \rightarrow + S$

8. Balance the following equations which show the starting materials and the reaction products. It is not necessary to supply any additional reactants or products.
(a) $KNO_3 \rightarrow KNO_2 + O_2$
(b) $Na + H_2O \rightarrow NaOH + H_2$
(c) $Fe + H_2O \rightarrow Fe_3O_4 + H_2$
(d) $C_2H_5OH + O_2 \rightarrow CO_2 + H_2O$
(e) $Fe_3O_4 + H_2 \rightarrow Fe + H_2O$
(f) $CO_2 + NaOH \rightarrow NaHCO_3$
(g) $MnO_2 + HCl \rightarrow H_2O + MnCl_2 + Cl_2$

(h) $Zn + KOH \rightarrow K_2ZnO_2 + H_2$
(i) $Cu + H_2SO_4 \rightarrow H_2O + SO_2 + CuSO_4$
(j) $Al(NO_3)_3 + NH_3 + H_2O \rightarrow Al(OH)_3 + NH_4NO_3$
(k) $Al(NO_3)_3 + NaOH \rightarrow NaAlO_2 + NaNO_3 + H_2O$

9. For each of the following unbalanced "molecular" equations, write (1) the oxidation half-reaction, (2) the reduction half-reaction, and (3) the balanced net ionic equation:
(a) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$
(b) $Ce(SO_4)_2 + FeSO_4 \rightarrow Ce_2(SO_4)_3 + Fe_2(SO_4)_3$
(c) $FeSO_4 + HNO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO + H_2O$
(d) $\underline{Ag_2S} + HNO_3 \rightarrow AgNO_3 + NO + S + H_2O$
(e) $K_2Cr_2O_7 + H_2S + HCl \rightarrow CrCl_3 + S + KCl + H_2O$
(f) $NaOH + Cl_2 \rightarrow NaCl + NaClO_3 + H_2O$
(g) $\underline{Fe(OH)_2} + Na_2O_2 + H_2O \rightarrow \underline{Fe(OH)_3} + NaOH$
(h) $\underline{Bi_2S_3} + HNO_3 \rightarrow Bi(NO_3)_3 + S + NO + H_2O$
(i) $H_3AsO_4 + Zn + HNO_3 \rightarrow AsH_3 + Zn(NO_3)_2 + H_2O$
(j) $\underline{CrI_3} + NaOH + Cl_2 \rightarrow Na_2CrO_4 + NaIO_4 + NaCl + H_2O$

10. The following unbalanced skeletal ionic equations represent reactions taking place in acid solution. Convert them to balanced ionic equations, introducing H^+ and H_2O as necessary.
(a) $Fe^{2+} + NO_3^- \rightarrow Fe^{3+} + NO$
(b) $Cr^{3+} + ClO_3^- \rightarrow Cr_2O_7^{2-} + ClO_2$
(c) $MnO_4^- + H_2O_2 \rightarrow Mn^{2+} + O_2$
(d) $IO_3^- + I^- \rightarrow I_2$
(e) $Fe^{3+} + SO_3^{2-} \rightarrow Fe^{2+} + SO_4^{2-}$
(f) $\underline{Sb_2S_3} + NO_3^- \rightarrow \underline{Sb_2O_5} + S + NO$
(g) $\underline{As_2S_3} + NO_3^- \rightarrow SO_4^{2-} + H_3AsO_4 + NO$

11. The following unbalanced skeletal equations represent reactions taking place in basic solution. Convert them to balanced ionic equations, introducing OH^- and H_2O as necessary:
(a) $Cl_2 \rightarrow Cl^- + ClO^-$
(b) $\underline{Co(OH)_2} + O_2 \rightarrow \underline{Co(OH)_3}$
(c) $Al \rightarrow Al(OH)_4^- + H_2$
(d) $MnO_4^- + S_2^- \rightarrow \underline{MnS} + S$
(e) $NO_2^- + Al \rightarrow NH_3 + AlO_2^-$

12. For the reaction below answer the following questions:

$$HNO_3(aq) + Na_2Cr_2O_7(aq) + NaCl(aq) \longrightarrow Cr(NO_3)_3(aq) + Cl_2(g) + H_2O(l) + NaNO_3(aq)$$

(a) Provide the balanced net ionic equation for this reaction.
(b) What are the spectator ions, if any?
(c) If 575 mL of 6.00 *M* HNO_3 and 136 g $Na_2Cr_2O_7$ are reacted with an excess of NaCl, what is the limiting reagent for the reaction?
(d) What volume (L) of $Cl_2(g)$ will be produced at 745 torr and 45.0 °C, assuming the same quantities of each reactant as listed in part (c) and assuming the reaction has an 80.0 percent yield?

13. Consider the following reaction:

$$HCl(aq) + KMnO_4(aq) + H_2O_2(l) \longrightarrow MnCl_2(aq) + O_2(g) + H_2O(g) + KCl(aq)$$

(a) Provide the balanced reaction equation for the reaction.
(b) Provide the balanced net ionic equation for the reaction.
(c) Given 100.0 mL of 6.0 *M* HCl, 36.0 g $KMnO_4$, and an excess of H_2O_2, determine the number of liters of oxygen gas produced at 25.0 °C and 1.00 atm.

14. A lead storage battery, such as the one which runs your automobile, discharges according to the following reaction: solid lead metal reacts with solid lead (IV) oxide and aqueous sulfuric acid to make solid lead (II) sulfate and water.
(a) Write a complete balanced chemical equation for this reaction which includes the physical states of each species in parentheses (*s, l, g,* or *aq*).
(b) If the battery contains 5.30 L of 15.5 *M* sulfuric acid, what volume of concentrated (18.0 *M*) sulfuric acid must be added to water to just fill the battery compartments with 15.5 *M* sulfuric acid?

15. A test for the presence of ozone in air involves bubbling the air sample through an acidified solution of Mn^{2+}. If ozone is present, a purple color due to MnO_4^- is observed. Write a balanced ionic equation for the reaction.

16. When H_2S is bubbled into a basic solution of CrO_4^{2-}, a precipitate of $Cr(OH)_3$ is formed. Write a balanced equation for the reaction.

17. Aqueous hydrazine (N_2H_4) is a strong enough reducing agent in basic solution to convert oxygen gas into hydrogen peroxide (H_2O_2); nitrogen gas is also formed in the reaction. Write a balanced equation for the reaction.

18. Give the conventional shorthand notation for the voltaic cell constructed from each of the following reactions:
(a) $H_2O_2 + 2\,H^+ + 2\,Br^- \rightarrow 2\,H_2O + Br_2$
(b) $Cd + Pb^{2+} \rightarrow Pb + Cd^{2+}$
(c) $Cu + 2\,Fe^{3+} \rightarrow Cu^{2+} + 2\,Fe^{2+}$
(d) $Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$
(e) $Hg + 2\,Ce^{4+} \rightarrow Hg^{2+} + 2\,Ce^{3+}$
(f) $ClO_3^- + 6\,H^+ + 6\,I^- \rightarrow Cl^- + 3\,I_2 + 3\,H_2O$

19. Give the shorthand notation for the voltaic cell constructed from each of the following pairs of half-cells. Write the electrode reactions and the overall reaction that occurs when the cell is producing current. Solution concentrations are 1.00 *M* unless otherwise noted.

Half-cell A	Half-cell B
(a) $Ni\,\vert\,Ni^{2+}$	$Cd\,\vert\,Cd^{2+}$
(b) $Cu\,\vert\,Cu^{2+}$	$Pt\,\vert\,NO_3^-, H^+, NO$
(c) $Pt\,\vert\,Fe^{3+}, Fe^{2+}$	$Pt\,\vert\,I^-, I_2$
(d) $Co\,\vert\,Co^{2+}$	$Co\,\vert\,Co^{2+}$(0.01 *M*)
(e) $Pt\,\vert\,H_3PO_4, H^+, H_3PO_3$	$Pt\,\vert\,ClO_3^-, H^+, Cl^-$

20. Order the following from least to most likely to be reduced:

$Li^+, Ni^{2+}, Co^{3+}, Sn^{2+}$

21. Order the following from least to most likely to be oxidized:

$Ca^0, Cu^0, Fe^{2+}, Sn^{2+}$

22. Determine if the following will react spontaneously (no calculations should be necessary) and write a balanced equa-

tion for the most likely reaction that does occur between the two species.
(a) K^+ with Na^+ (b) NO_3^- with Bi (c) Ni^{2+} with V^{3+}

23. (a) Will Ag° react spontaneously with Fe^{3+}? Why or why not?
(b) Write a balanced reaction equation for the preferential reaction that occurs in the following mixture:

$$Co^{3+}, Ag^+, Cu^\circ, Al^\circ$$

24. Calculate the standard cell potential for each of the following voltaic cells:
(a) $Pt \mid Cr^{2+}, Cr^{3+} \parallel Cu^{2+} \mid Cu$
(b) $Fe \mid Fe^{2+} \parallel Br_2, Br^- \mid Pt$
(c) $Ag \mid Ag^+ \parallel Cr_2O_7^{2-}, H^+, Cr^{3+} \mid Pt$
(d) $Co \mid Co^{2+} \parallel Co^{3+}, Co^{2+} \mid Pt$

25. The following chemicals are available for the construction of electrochemical cells: Cu°, $CuCl_2$, I_2, NaI, $NaMnO_4$, $MnCl_2$, and Pt°.
(a) Design a cell for the electrolysis of an aqueous $CuCl_2$ solution. Label all parts and indicate what reactions *could* occur and what reactions actually do occur at each electrode. Write the overall reaction.
(b) What reaction would take place if the electrolysis were carried out with copper electrodes?
(c) What reaction would occur if a mixture of $CuCl_2$ and NaI (aqueous solution) were electrolyzed in the cell above?
(d) Design a galvanic cell using any of the above chemicals. Label all parts and indicate which reactions will occur.
(e) What is the emf of your cell when the concentration of all species is 1 *M*?
(f) Which of the above chemicals would produce the cell with the highest emf?

26. Using the half-reactions in Table 18.1, write balanced equations for five reactions that will occur spontaneously and for five reactions that will *not* occur spontaneously.

27. After a solution of tin(II) chloride in dilute HCl has been prepared, solid tin metal is added to prevent the tin(II) from being oxidized by the air to tin(IV). Explain.

28. Is iron(III) ion reduced to iron(II) ion by iron metal?

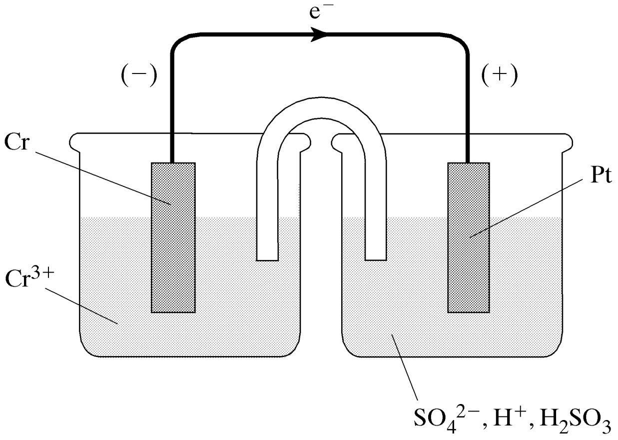
29. Account for the following observations: A sample of pure solid barium sulfite dissolves in hydrochloric acid. However, when the resulting solution is allowed to stand for a period of time, a white precipitate slowly forms.

30. You are given aqueous solutions of $AgNO_3$, $Cu(NO_3)_2$, $Mg(NO_3)_2$, $Fe(NO_3)_3$, $Zn(NO_3)_2$, and $Ni(NO_3)_2$. You also have available the free metal of each of the six cations. Using only these materials, suggest a chemical method for arranging the metals in order of increasing reducing power.

31. In preparing an acidic solution of potassium permanganate, would you use sulfuric acid or hydrochloric acid? Explain your choice.

32. Galvanized iron has a coating of zinc metal to protect the iron from rusting. Explain how this works.

33. Answer the following questions based on the electrochemical cell constructed as shown below at 25 °C,



(a) With the switch open, what value would the voltmeter read if connected to measure a spontaneous reaction?
(b) If the switch if closed and the reaction is allowed to proceed to equilibrium, what reading would you ultimately obtain on the voltmeter and why?
(c) What would happen if we tried to run the reaction without the salt bridge?
(d) What would you predict would happen to the mass of the copper electrode as the reaction proceeded in a spontaneous direction?
(e) Indicate which electrode is the anode and cathode for the spontaneous reaction.

34. (a) Can Cl_2 oxidize Br^-?
(b) Verify that Hg_2^{2+} will oxidize Sn^{+2}.
(c) Explain the difference between the *E*°'s for the reactions:

$$Ag^+ + e^- \longrightarrow Ag^\circ \qquad E^\circ = 0.80$$
$$AgCl + e^- \longrightarrow Ag^\circ + Cl^- \qquad E^\circ = 0.22$$

35. Given that

$$Hg^{2+} + 2\,e^- \longrightarrow Hg^\circ \qquad E^\circ = +0.85\text{ V}$$
$$Hg_2^{2+} + 2\,e^- \longrightarrow 2\,Hg^\circ \qquad E^\circ = +0.79\text{ V}$$

calculate the equilibrium constant and standard free-energy change, ΔG°, for the disproportionation reaction at 25 °C.

$$Hg_2^{2+} \longrightarrow Hg^{2+} + Hg^\circ$$

If the standard free energy of formation, ΔG_f°, of Hg_2^{2+} is 155 kJ/mol, what is $\Delta G_f^\circ(Hg^{2+})$?

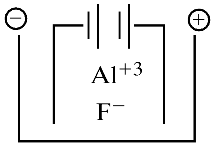
36. It is sometimes necessary to compute *E*° for a given half-reaction from other half-reactions of known *E*°. For example, the standard electrode potential for the oxidation of titanium metal to Ti^{+3} can be obtained from the following half-reactions:

$$Ti^{2+} + 2\,e^- \longrightarrow Ti^\circ \qquad E^\circ = -1.63\text{ V}$$
$$Ti^{3+} + e^- \longrightarrow Ti^{2+} \qquad E^\circ = -0.37\text{ V}$$

Calculate *E*° for $Ti^\circ \rightarrow Ti^\circ + 3\,e^-$

37. Choose from among the following materials to create a cell that will produce a voltage of at least 2.20 V. Diagram the cell, giving the polarity of the electrodes and their names, the direction of electron flow, and the exact contents of each beaker.

Cu, $CuCl_2$, I_2, KI, $SnCl_2$, Sn, Zn, Al, NaCl,
water, copper wire



Calculate the standard electromotive force of this cell and the free-energy change at 25 °C for the overall reaction that occurs in the cell.

38. Calculate the equilibrium constant for each of the following reactions:
(a) $Cr_2O_7^{2-} + 6\ Br^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ Br_2 + 7\ H_2O$
(b) $Cl_2 + 2\ Ag \rightarrow 2\ \underline{AgCl}$
(c) $2\ Cr^{3+} + 3\ Fe \rightarrow 2\ Cr + 3\ Fe^{2+}$

39. Calculate the equilibrium constant for each of the reactions in Problem 18.

40. Calculate the cell or solution potentials for the following:
(a) $E°$ for the balanced reaction of VO_2^+ reacting with zinc metal.
(b) the reduction potential for the half-cell: Cu/Cu^{2+} (0.10 *M*)
(c) *E* for the following cell:
$Pt|Fe^{3+}$ (0.010 *M*), Fe^{2+} (0.0010 *M*)$\|Ag^+$ (0.035 *M*)$|Ag$
(d) *E* for the following cell:
$Pt|TiO^{2+}$ (0.20 *M*), Ti^{3+} (0.010 *M*), H^+(0.0020 *M*)$\|$
Cl^-(0.20 *M*), AgCl(satd.)/Ag°
(e) *E* vs. S.H.E. (standard hydrogen electrode) for the solution that results when 150 ml of 0.10 *M* Co^{3+} are mixed with 50 ml of 0.10 *M* V^{2+}. (Hint: Consider whether or not any reactions that may be considered to go to completion are present and determine what species remain in solution at the conclusion of the reaction. The redox couple that is defined, i.e., the concentrations of both the oxidized and reduced forms are known, will determine the potential of the solution.)

41. Consider the following electrochemical cell.

$Ni|Ni^{2+}$ (1.0 *M*), 25 °C$\|Fe^{3+}$ (1.0 *M*)
Fe^{2+} (0.10 *M*), 0 °C$|$ Pt

(a) Give the half-reaction that occurs at the anode.
(b) Give the half-reaction that occurs at the cathode.
(c) Determine the EMF for the voltaic cell.
(d) What is the EMF for the same cell if a gold electrode is used in place of the platinum electrode?

Some potentially useful reduction potentials:

$Au^{3+} + 3\ e^- \longrightarrow Au\ +1.50\ V$
$Pt^{2+} + 2\ e^- \longrightarrow Pt\ +1.20\ V$
$Fe^{3+} + 1\ e^- \longrightarrow Fe^{2+}\ +0.77\ V$
$Ni^{2+} + 2\ e^- \longrightarrow Ni\ -0.25\ V$
$Fe^{2+} + 2\ e^- \longrightarrow Fe\ -0.44\ V$

42. Consider the hypothetical electrochemical cell at 25 °C.

$Mg|Mg^{2+}$ (1.0 *M*)$\|Cu^{2+}$ (1.0 *M*)$|Cu$

(a) Give the half-reaction that occurs at the cathode.
(b) Determine the potential for this cell in volts.
(c) Calculate the equilibrium constant, *K*, for the reaction: $Mg^{2+} + Cu \leftrightarrows Mg + Cu^{2+}$

43. Balance the following reaction using the half-reaction method and determine if the reaction is spontaneous under standard conditions.

$Cr^{3+}(aq) + Br^2(aq) \longrightarrow Cr_2O_7^{2-}(aq) + Br^-(aq)$ (in acidic solution)

44. The potential for the cell below is 0.00 V. What is the standard reduction potential for Be^{2+}?

$Be|Be^{2+}$ (0.020 *M*)$\|Th^{4+}$ (1.0 *M*)$|Th$

45. For the cell $Al|Al^{3+}$ (1.0 M)$\|Pb^{2+}$ (1.0 M)$|Pb$
(a) Give the half-reaction that occurs at the cathode.
(b) Determine the potential for this cell in volts.
(c) Calculate the equilibrium constant, *K*, for the reaction: $Pb^{2+} + Al \leftrightarrows Pb + Al^{3+}$.

46. Balance the following reaction using the half-reaction method *and* determine if the reaction is spontaneous under standard conditions.

$Cr_2O_7^{2-}(aq) + Mo \longrightarrow Cr^{3+}(aq) + Mo^{3+}(aq)$(in acidic solution)

47. The potential for the cell below is 0.00 V. What is the concentration of Zr^{4+}?

$Ti|Ti^{2+}$ (1.00 *M*)$\|Zr^{4+}$ (? *M*)$|Zr$

48. Indicate whether each of the following half-cells behaves as the anode or cathode when coupled with a standard hydrogen electrode in a galvanic cell, and calculate the potential of the cell.
(a) Pb/Pb^{2+} (2.0×10^{-4} *M*)
(b) Ag°/AgBr (satd.), KBr ($1.0 = 10^{-4}$ *M*)
(c) Pt/MnO_4^-(0.10 *M*), Mn^{2+} (0.15 *M*) at a pH = 2

49. Using the appropriate K_{sp} value, calculate the $E°$ value for the half-reaction,

$PbCl_2(s) + 2\ e^- \longrightarrow Pb° + Cl^-(aq)$

50. Calculate the equilibrium constant for the reaction represented by each of the equations written in answer to Problem 26.

51. For each of the following;
(a) balance the redox reaction
(b) indicate the oxidation and reduction half-reactions
(c) calculate the $E°$ value for the reaction
(d) calculate the equilibrium constant for the reaction at 25 °C
1. $Cu(OH)_2 + ClO_3^- \rightarrow ClO_4^- + Cu°$ (basic solution)

2. $Cu + HNO_3 \rightarrow Cu^{2+} + NO_2$ (acidic solution)
3. $S_2O_3^{2-} + I_2 \rightarrow I^- + S_4O_6^{2-}$ (acidic solution)

52. Calculate the solubility product constant for $Mg(OH)_2$.

$$\underline{Mg(OH)_2} + 2\,e^- \longrightarrow \underline{Mg} + 2\,OH^- \qquad E^\circ = -2.67$$

53. Calculate the formation constant for $Ag(NH_3)_2^+$.

54. The following electrochemical cell is constructed using a weak acid, HA.

$$\text{Pt, } H_2\ (1.00\ \text{atm})\,|\,\text{HA}\ (0.010\ M),\ \text{NaA}\ (0.040\ M)\,\|\,AgNO_3\ (1.00\ M)\,|\,Ag^\circ$$

The cell is observed to develop a potential of 0.45 volts at 25 °C. Calculate the K_a value for the weak acid at 25 °C.

55. The following simple electrochemical cell is to be used as a battery.

$$Al\,|\,Al^{3+}\ (1.00\ \text{L of } 1.00\ M)\,\|\,Ag^+\ (1.00\ \text{L of } 1.00\ M)\,\|\,Ag^\circ$$

(a) Write the chemical reaction that supplies the voltage and determine the initial voltage of the battery at 25 °C?
(b) If the battery is used to power a small radio that draws 10.0 mA of current, how many moles of electrons must have been transferred if the radio is played for 1000 hours?
(c) How many moles of Al° and Ag^+ must have reacted to supply this many electrons, and what are the concentrations of Al^{3+} and Ag^+ after the radio has played 1000 hours?
(d) What is the battery's voltage after playing the radio 1000 hours?
(e) At this rate of decrease in voltage, how long will the battery last before it goes "dead" where dead is defined as a battery that has less than 0.90% of its original voltage capability.

56. A cell consisting of a S.H.E. reference electrode and a silver wire is dipped into a solution containing silver ions, providing a potential of 0.48 V. What is the concentration of Ag^+ in the cell solution?

57. Using electrochemical reactions, calculate the K_{sp} for AgI, and calculate the ΔG° value for the dissolution reaction at 25 °C.

58. (a) Using electrochemical tables, calculate the K_f of $Ag(CN)_2^-$.
(b) In the $Ag(CN)_2^-$ complex, which ion acts as the Lewis acid and which as the Lewis base?

59. The solubility product constant for $PbSO_4$ is 1.6×10^{-8}. The standard electrode potential for $Pb^{2+} + 2\,e^- \rightarrow Pb$ is -0.126 V. Use these data to calculate the standard electrode potential for

$$\underline{PbSO_4} + 2\,e^- \longrightarrow Pb + SO_4^{2-}$$

60. For the following reaction, the E° value at standard conditions is 1.10 V:

$$Zn + 2\,VO^{2+} + 4\,H^+ \longrightarrow 2\,V^{3+} + 2\,H_2O + Zn^{2+}$$

(a) Calculate the equilibrium constant for the reaction.
(b) Calculate the value of E° for the half reaction

$$VO^{2+} + 2\,H^+ + e^- \longrightarrow V^{3+} + H_2O$$

(c) How would increasing the pH of the reaction mixture affect the E value for the reaction? Explain.

61. A voltaic cell is to be constructed, based on the following redox couples:

$$Cr^{3+} + 3\,e^- \longrightarrow Cr \qquad E^\circ = -0.744\ \text{V}$$

$$SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow H_2SO_3 + H_2O \qquad E^\circ = 0.172\ \text{V}$$

(a) Sketch the cell, showing all the materials used. Indicate the polarity of the cell and the direction of electron flow.
(b) Write the balanced equation for the overall reaction that occurs when the cell is producing electric current.
(c) Compute the standard potential of the cell.

62. Calculate the standard free-energy change for each of the following reactions:
(a) $Cl_2 + 2\,Br^- \rightarrow 2\,Cl^- + Br_2$
(b) $3\,S_2O_8^{2-} + 2\,\underline{MnO_2} + 4\,H_2O \rightarrow 6\,SO_4^{2-} + 2\,MnO_4^- + 8\,H^+$
(c) $6\,HNO_2 + Cl^- \rightarrow ClO_3^- + 6\,NO + 3\,H_2O$

63. Write equations for the anode reaction, the cathode reaction, and the overall reaction for the electrolysis of each of the following aqueous solutions with inert electrodes.
(a) Li_2SO_4 (b) $Sn(NO_3)_2$ (c) NiI_2 (d) $Ba(OH)_2$

64. In the electrolysis of an aqueous solution of each of the following compounds, using platinum electrodes, write an equation for the anode reaction, the cathode reaction, and the overall reaction.
(a) H_3PO_4 (b) $NaC_2H_3O_2$ (c) $CdSO_4$
(d) KOH (e) $CuBr_2$ (f) $Mg(ClO_4)_2$
(g) CaI_2 (h) $Hg(NO_3)_2$

65. What weight of chromium will be plated from a solution of $Cr(NO_3)_3$ by a current of 6.0 A in 2.0 hr?

66. How long will it take to liberate exactly 1.0 L of O_2 (measured at STP) by electrolysis of a sulfuric acid solution using a current of 2.5 A?

67. What is the current required to liberate 1 mol of H_2 from an acid solution in 30 min?

68. A certain alloy of silver and zinc is 70.91% silver. If a 1.203-g sample of the alloy is dissolved, and the solution is electrolyzed between platinum electrodes, how many coulombs are required to completely plate out the metals?

69. An object is to be gold-plated by electrolysis, using a solution of $AuCl_3$ as the electrolyte. How long will it take to plate 100 mg of gold, if the average current used is 7.50 A?

70. What weight of Co^{3+} will be reduced electrolytically to Co^{2+} by a current of 10.0 A flowing for 20.0 min?

71. In the electrolysis of a saturated solution of $KHSO_4$ using platinum electrodes and a high current, a gas is evolved at the cathode and a white solid precipitates in the vicinity of the anode. Analysis of the dried solid gave results of

28.77% K, 23.65% S, and 47.58% O; the formula weight is 270.

(a) What is the formula of the white solid?
(b) Write equations for the electrode reactions occurring during the electrolysis.

72. You "grind away" on the starter of your car for 2 min before it starts on a cold day in early January. If the lead storage battery in your car furnishes 125 A, approximately how much lead would have been converted to lead sulfate at the anode?

73. A bronze alloy that contains Cu, Zn, and Sn is dissolved in nitric acid to give $\underline{SnO_2}$, Cu^{2+}, Zn^{2+}, and NO(g).

(a) Write the balanced equation for the reaction of tin with nitric acid.

(b) A 1.0000-g sample of the alloy yielded 0.0127 g of SnO_2, and the copper ion was plated out of solution by passing a current of 1.00 A through the solution for 0.591 hr. Calculate the percentage composition of the alloy.

74. In order to standardize a solution of potassium permanganate, a chemistry student titrated two samples of sodium oxalate, each of which was dissolved in 100 mL of a dilute sulfuric acid solution. The data are given below:

	Sample 1	Sample 2
grams of pure $Na_2C_2O_4$	1.5703	1.4823
volume of $KMnO_4$	43.25 mL	41.24 mL

Calculate the average molarity of the $KMnO_4$ solution.

75. Calculate the time needed to deposit 0.500 g of Tl^{3+} as the neutral metal on a cathode if the current is maintained at a constant 1.20 A.

76. A 12.34-g mineral sample with an unknown concentration of silver was analyzed by dissolving the sample and reducing the silver ion onto a platinum electrode. The electrode gained 0.5671 g during the process. What is the weight percent silver in the sample?

77. A mineral ore sample is obtained that contains manganese (Mn) at a level of 14.56 % by weight. A sample weighing 4.1277 g is dissolved in 150.0 mL of a nitric acid/water solution, which generates the Mn^{2+} ion. This ion will be completely reduced to the metal on a platinum electrode in an electrodeposition experiment.

(a) If the Pt electrode weighs 23.4612 g before the experiment, what will its weight be after the complete reduction of the Mn^{2+}?
(b) What is the theoretical potential (vs. S.H.E.) required to be applied in order to begin the plating reaction?
(c) If the reduction process took 35 minutes to complete, what was the average current for the reduction reaction?

78. If an aqueous solution of $Ni(NO_3)_2$ is electrolyzed between platinum electrodes using a current of 4.84 A for 375 minutes, what mass of $Ni_{(s)}$ will be deposited on the cathode?

79. For the electrolysis of an aqueous solution of $CuBr_2$ determine what product will be formed at the cathode and how many amperes of current would be required in order to obtain 1.0 g of the product within 2.0 hr.

80. Diagram an electrolytic cell for the electrolysis of molten AlF_3. Show clearly what will be formed at the cathode and determine how many grams of this material would be formed by using a current of 1 A for 10 hr.

81. How much current must be supplied to completely plate out the nickel in 100 mL of a 0.30 M $Ni(NO_3)_2$ solution in 15 min?

82. Aluminum can be produced by electrolysis of molten Al_2O_3 using a carbon anode. The reactions that occur are given below.

$$C + 2\,O^{2-} \longrightarrow CO_2 + 4\,e^-$$

$$Al^{3+} + 3\,e^- \longrightarrow Al$$

(a) Label the anode and cathode reactions.
(b) How long will it take to generate the aluminum necessary for a case of soda cans if each can uses 5.00 g of aluminum and the current through the cell is maintained at 50.00 A with a cell efficiency of 90%?

83. A solution contains 0.15 M Co^{2+} and 0.075 M Cd^{2+}. An electrolysis experiment is set up.

(a) Which metal will plate out first?
(b) At approximately what voltage will this occur? (vs. S.H.E.)
(c) What is the cathode potential necessary to lower the Co^{2+} concentration to 1×10^{-5} M, thereby effectively separating the two metal ions?

84. You are given a mixture of 0.15 M $Ni(NO_3)_2$ and $Al(NO_3)_3$ in 1.0 L of water and told to plate the metal ions as the neutral metal on a platinum electrode. In order to accomplish this procedure, answers to the following questions are necessary. All potential values should be relative to the S.H.E. which will serve as the oxidation half-reaction in this problem.

(a) Which ion will be electrodeposited *second* and at what potential will this occur?
(b) What is the concentration of the first plated ion when the second begins to plate?
(c) If we want to remove all of the nickel by electrodeposition, what current flow would be necessary to plate all of the nickel in 10 min?

85. Fill in the blanks

1. Oxidation may be defined as a ___________ of electrons, or as an increase in ___________.

2. A substance that becomes oxidized in a chemical reaction is called the ___________ agent.

3. The oxidation state of a monatomic ion is the same as the ion's ___________.

4. In a voltaic cell from which current is being drawn, ___________ occurs at the positive electrode and ___________ occurs at the negative electrode.

5. The salt bridge in a galvanic cell permits the flow of ___________.

6. The positive electrode of a voltaic cell is called the ___________, but the positive electrode of an electrolytic cell is called the ___________.

7. The difference between the two electrode potentials in a voltaic cell is called the ___________ of the cell.

8. Standard electrode potentials ($E°$) are measured relative to the standard ___________ electrode.

9. The oxidation number of sulfur in $H_2S_2O_4$ is ___________.

10. The higher a redox couple's standard electrode potential, the more readily ___________ occurs.

11. When current is drawn from a lead storage battery, ___________ is oxidized and ___________ is reduced.

12. The oxidation number of carbon in CH_2O is ___________.

13. In the electrolysis of a KOH solution, ___________ is produced at the anode and ___________ is produced at the cathode.

14. In the electrolysis of a solution containing equimolar concentrations of Hg^{2+} and Cd^{2+}, ___________ will be plated out preferentially.

15. A current of 1 amp is the passage of one ___________ of electricity per second.

86. Multiple-choice questions

1. If the standard electrode potential of a given redox couple is +1.00 V, then the standard oxidation potential for that couple is:
   (a) +1.00 V (b) −1.00 V
   (c) 0.00 V (d) 0.059 V

2. The larger the $E°$ of a redox reaction:
   (a) the faster the reaction rate
   (b) the slower the reaction rate
   (c) the larger the equilibrium constant
   (d) the smaller the equilibrium constant

3. As current is drawn from the cell:

   $$Pt\,|\,Fe^{2+}, Fe^{3+}\,\|\,MnO_4^-, Mn^{2+}, H^+\,|\,Pt$$

   there is an increase in the concentration of:
   (a) Fe^{2+} (b) MnO_4^- (c) Mn^{2+} (d) H^+

4. The oxidation number of sulfur in the tetrathionate ion $S_4O_6^{2-}$ is:
   (a) +2 (b) +2.5 (c) +3 (d) +4

5. In plating chromium metal from a solution of $Cr_2(SO_4)_3$, the equivalent weight of Cr is:
   (a) 104 (b) 52 (c) 26 (d) 17.3

6. Which of the following is the strongest oxidizing agent?
   (a) Ni^{2+} (b) Ni (c) Al^{3+} (d) Al

7. If 1 mol each of NaCl and KBr are melted together and the molten mixture is subjected to electrolysis, the first products formed at the electrodes are:
   (a) Na and Cl_2 (b) K and Br_2
   (c) Na and Br_2 (d) K and Cl_2

8. In the electrolysis of a concentrated aqueous solution of NaCl between platinum electrodes, Cl_2 is liberated at the anode and:
   (a) Na is liberated at the cathode
   (b) O_2 is liberated at the cathode
   (c) the cathode gradually dissolves
   (d) the solution gradually becomes more basic

9. When a redox reaction is at equilibrium:
   (a) the $E°$ values of the two half-reactions are equal
   (b) the E value is zero
   (c) the products are at higher concentration than the reactants
   (d) the oxidant and the reductant are present in equal concentrations

10. If the electrolysis of a $AgNO_3$ solution with inert electrodes is continued until 1 mol of Ag is plated out at the cathode, then the amount of gaseous product produced at the anode is:
    (a) $\frac{1}{4}$ mol (b) $\frac{1}{2}$ mol (c) 2 mol (d) 4 mol

Answers to Selected Problems

CHAPTER 1

1. a. $1.3 \times 10^{-3}\text{ cm} \times \dfrac{1.00\text{ m}}{100\text{ cm}} \times \dfrac{10^{9}\text{ nm}}{1.00\text{ m}} = 1.3 \times 10^{4}\text{ nm}$

b. $1.00\text{ ton} \times \dfrac{2000\text{ lb}}{1\text{ ton}} \times \dfrac{453.6\text{ g}}{1.0\text{ lb}} \times \dfrac{1.0\text{ kg}}{1000\text{ g}} = 907\text{ kg}$

c. $1.56 \times 10^{12}\text{ kJ} \times \dfrac{1000\text{ J}}{1\text{ kJ}} \times \dfrac{1\text{ GJ}}{10^{9}\text{ J}} = 1.56 \times 10^{6}\text{ GJ}$

d. $1.8 \times 10^{-8}\text{ cm} \times \dfrac{1.00\text{ m}}{100\text{ cm}} \times \dfrac{10^{12}\text{ pm}}{1.00\text{ m}} = 1.8 \times 10^{2}\text{ pm}$

3. a. $1.0\text{ oz} \times \dfrac{1\text{ g}}{0.035\text{ oz}} \times \dfrac{15.4\text{ grains}}{1\text{ g}} = 4.4 \times 10^{2}\text{ grains}$

b. $1.0\text{ lb} \times \dfrac{453.6\text{ g}}{1\text{ lb}} \times \dfrac{0.035\text{ oz}}{1\text{ g}} = 16\text{ oz}$

c. $1\text{ grain} \times \dfrac{1\text{ g}}{15.4\text{ grains}} = 0.0649\text{ g}$

d. $1\text{ grain} \times \dfrac{1\text{ g}}{15.4\text{ grains}} \times \dfrac{1\text{ lb}}{453.6\text{ g}} = 1.43 \times 10^{-4}\text{ lb}$

4. $\dfrac{68\text{ mi}}{1\text{ h}} \times \dfrac{5280\text{ ft}}{1\text{ mi}} \times \dfrac{12\text{ in}}{1\text{ ft}} \times \dfrac{1\text{ m}}{39/37\text{ in}} \times \dfrac{1\text{ hr}}{3600\text{ s}} = 30\text{ m/s}$

5. $\left(8\text{ in} \times \dfrac{1\text{ m}}{39.97\text{ in}}\right)\left(11\text{ in} \times \dfrac{1\text{ m}}{39.97\text{ in}}\right) = 5.68 \times 10^{-2}\text{ m}^2$

6. $93 \times 10^{6}\text{ miles} \times \dfrac{1609\text{ m}}{\text{mile}} = 1.5 \times 10^{11}\text{ m}$

$\dfrac{1.5 \times 10^{11}\text{ m}}{3 \times 10^{8}\text{ m/sec}} = 500\text{ sec} = 8.3\text{ min}$

7. $\left(3.25\text{ in.} \times 2.54\,\dfrac{\text{cm}}{\text{in}}\right)^{3} = 563\text{ cm}^3$

$563\text{ cm}^3 \times \dfrac{1\text{ L}}{1000\text{ cm}^3} = 0.563\text{ L}$

8. $\dfrac{2 \times 9.1095 \times 10^{-28}\text{ g} + 2 \times 1.67265 \times 10^{-24}\text{ g} + 2 \times 1.67495 \times 10^{-24}\text{ g}}{4\pi(50.04 \times 10^{-12}\text{ m})^{3}/3} =$
$1.276 \times 10^{7}\text{ g/m}^3$

9. $7.0\text{ lb} \times \dfrac{453.6\text{ g}}{1\text{ lb}} \times \dfrac{1\text{ mL}}{1.02\text{ g}} \times \dfrac{1\text{ L}}{1000\text{ mL}} = 3.1\text{ L}$

10. $\dfrac{355\text{ mL}}{1\text{ min}} \times \dfrac{60\text{ min}}{\text{hr}} \times \dfrac{1.0\text{ L}}{1000\text{ mL}} = 21.3\text{ L/hr}$

11. $\dfrac{4.50\text{ g}}{\text{marble}} \times \dfrac{1.00\text{ lb}}{453.6\text{ g}} \times \dfrac{500\text{ marbles}}{\text{bag}} = 4.96\text{ lb/bag}$

12. $3.80 \times 10^{3}\text{ kcal} \times \dfrac{10^{3}\text{ cal}}{1\text{ kcal}} \times \dfrac{4.184\text{ J}}{1\text{ cal}} = 1.59 \times 10^{7}\text{ J}$

13. $100\text{ g} \times \dfrac{100\text{ mL}}{13.6\text{ g}} = 7.35\text{ mL of Hg}$

$100.00\text{ mL} - 7.35\text{ mL} = 92.65\text{ mL of water}$

14. (a) $1\text{ ft} \times \dfrac{12\text{ in}}{1\text{ ft}} \times \dfrac{2.54\text{ cm}}{1\text{ in}} \times \dfrac{10\text{ mm}}{1\text{ cm}} \times \dfrac{1\text{ dime}}{1\text{ nm}} =$
305 dimes

(b) $305\text{ dimes} \times 2.5\text{ g/dime} \times \dfrac{1\text{ lb}}{453.6\text{ g}} = 1.7\text{ lb}$

15. a. $2.0\text{ mol of atoms} \times \dfrac{6.022 \times 10^{23}\text{ atoms}}{1\text{ mol}} \times 256 \times 10^{-12}\text{ m/atom} = 3.1 \times 10^{14}\text{ m}$

b. $\dfrac{3.67 \times 10^{9}\text{ mi} \times 1.609\text{ km/mi} \times 1000\text{ m/km}}{3.1 \times 10^{14}\text{ m}} = 0.019$

The distance between the sun and Pluto is only 1.9% the length of the chain of 2.0 mol of copper atoms.

c. $\dfrac{3.1\ 3\ 10^{14}\text{ m}}{3.00 \times 10^{8}\text{ m/s}}\ 5\ 1.0\ 3\ 10^{6}\ s$ or approximately 12 days

16. $1\text{ g} \times \dfrac{1\text{ lb}}{453.6\text{ g}} \times \dfrac{16\text{ oz}}{1\text{ lb}} \times \dfrac{\$300}{1\text{ oz}} = \$10.58$

17. weight of nugget = 12.2345 − 10.6482 = 1.5863 g
Using a density of 1.000 g/mL for water (the density of water actually depends upon the temperature, and is 1.0000 g/mL at 4° C.)

volume of flask = (21.6235 − 10.6482) g\1g/mL = 10.9753 mL

volume of water $= \dfrac{(22.8947 - 12.2345)\text{ g}}{1\text{ g/mL}} = 0.3151\text{ mL}$

volume of nugget = 10.9753 mL − 10.6602 mL = 0.3151 mL

density of nugget $= \dfrac{1.5863\text{ g}}{0.3151\text{ mL}} = 5.034\text{ g/mL}$

18. $\frac{1.23\text{ kg}}{1\text{ L}} = 1.23\text{ kg/L} = 1/23\text{ g/mL}$

19. $\frac{1\text{ lb} \times 453.6\text{ g/lb}}{8.90\text{ g/cm}^3} = 51.0\text{ cm}^3$

20. $\frac{10^6\text{ ergs}}{4.184 \times 10^{10}\text{ ergs/kcal}} \times \frac{1000\text{ cal}}{1\text{ kcal}} = 2.390 \times 10^{-2}\text{ cal}$

21. $\frac{0.708\text{ g/mL} \times 1000\text{ mL/L}}{1.057\text{ qt/L}} \times \frac{4\text{ qt/gal}}{453.6\text{ g/lb}} \times \$4.00\text{/lb} = \$23.63$

22. $°\text{C} = \frac{5}{9}(°\text{F} - 32)$

$°\text{C} = °\text{F}$

$°\text{C} = \frac{5}{9}°\text{C} - \frac{5}{9}(32)$

$°\text{C} = -40$

23. $73(0.20) + 55(0.20) + 80(0.20) + 70(0.40) = 70\%$

24. $1.0\text{ ton} \times \frac{0.1\text{ part Zn}}{1\text{ part alloy}} \times \frac{2000\text{ lb Zn}}{1\text{ ton Zn}} \times \frac{453.6\text{ g}}{1\text{ lb}} =$
$9.07 \times 10^4\text{ g}$

25. $\frac{6\text{ carbon atoms}}{14\text{ total atoms}} \times 100 = 43\%$ carbon atoms

26. (a) The diameter of one atom is 2 × 0.79 Å or 1.58 Å.

one mole of H atoms $\times \frac{6.02 \times 10^{23}\text{ atoms}}{\text{mole}} \times \frac{1.58\text{ Å}}{1\text{ atom}} =$

$9.51 \times 10^{23}\text{ Å}$

$9.51 \times 10^{23}\text{ Å} \times \frac{1\text{ m}}{10^{10}\text{ Å}} \times \frac{1\text{ km}}{1000\text{ m}} = 9.51 \times 10^{10}\text{ km}$

or, in miles

$9.51 \times 10^{10}\text{ km} \times \frac{1\text{ mile}}{1.609\text{ km}} = 9.51 \times 10^{10}\text{ miles}$

(b) The length of one mole of hydrogen atoms is 16.1 times longer than the average distance of Pluto from our sun.

$\frac{5.91 \times 10^{10}\text{ miles}}{3.67 \times 10^9\text{ miles}} = 16.1$

(c) Light would take 3.67 days to travel the length of the hydrogen atom chain.

$9.51 \times 10^{10}\text{ km} \times \frac{100\text{ m}}{1\text{ km}} \times \frac{\text{second}}{3.00 \times 10^8\text{ meter}} =$

3.17×10^5 seconds

$3.17 \times 10^5\text{ seconds} \times \frac{1\text{ hour}}{3600\text{ seconds}} \times \frac{1\text{ day}}{24\text{ hours}} =$

3.67 days

27. a. $500\text{ sheets} \times \frac{9.22\text{ g}}{1\text{ sheet}} \times \frac{1.00\text{ lb}}{453.6\text{ g}} = 10.2\text{ lb}$

b. $6.0 \times 10^6\text{ sheets} \times \frac{1\text{ ream}}{500\text{ sheets}} = 1.2 \times 10^4\text{ reams}$

c. $10.0\text{ tons/day} \times \frac{2000\text{ lb}}{1\text{ ton}} \times \frac{1\text{ ream}}{10.2\text{ lb}} \times \frac{365\text{ days}}{1\text{ year}} =$
7.16×10^5 reams/year

d. $1.0\text{ ton} \times \frac{2000\text{ lb}}{1\text{ ton}} \times \frac{1\text{ ream}}{10.2\text{ lb}} \times \frac{0.12\text{ ft}^3}{1\text{ ream}} = 24\text{ ft}^3$

28. a. $1.0\text{ tat} \times \frac{1000\text{ seeds}}{1\text{ tat}} \times \frac{57\text{ mg}}{1\text{ seed}} = 5700\text{ mg} = 57\text{ g}$

b. $15\text{ tats} \times \frac{57\text{ g}}{1\text{ tat}} = 855\text{ g}; 855\text{ g} \times \frac{1.00\text{ lb}}{453.6\text{ g}} = 1.88\text{ lb}$

c. $\frac{10\text{ days}}{1\text{ week}} \times \frac{5\text{ meals}}{1\text{ day-Schafkin}} \times \frac{15\text{ tats}}{1\text{ meal}} =$

$750\text{ tats/week-Schafkin}\ \frac{1.68 \times 10^8\text{ tats/week}}{750\text{ tats/week-Schafkin}} =$

224,000 Schafkins

d. $\frac{3.23 \times 10^9\text{ Schafkins}}{2.24 \times 10^5\text{ -Schafkins/factory}} = 1.44 \times 10^4\text{ factories}$

e. $750\text{ tats/week} \times \frac{57\text{ g}}{1\text{ tat}} = 4.3 \times 10^4\text{ g} = 43\text{ kg}$

29. a. 1.51×10^2 b. 1.51×10^{23}
c. 1.000012×10^2 d. 6.2×10^{27}

30. a. 2 b. 4 c. 2 d. 1

31. a. $\frac{100.34}{0.34} = 3.0 \times 10^2$

b. $\frac{6.78 \times 10^3}{10^5} \times 1.0045 = 7 \times 10^{-2}$

c. $\frac{17.12}{0.25} \times 1.0 \times 10^5 = 6.8 \times 10^6$

d. $\frac{7.467 \times 10^2}{5.23 \times 10^2} \times \frac{12.3}{0.12} = 1.5 \times 10^2$

32. no

Chapter 2

1. Indicate the difference between the terms in each of the following pairs:

(a) The nucleus is the positively charged core of an atom. This core accounts for virtually all the mass of the atom. A nucleon is a nuclear particle that is present in the nucleus of the atom; i.e., a proton or a neutron.

(b) The atomic number is the total positive charge in an atom's nucleus; i.e., it is the number of protons. The mass number is the sum of the number of nucleons of an atom; i.e., the atomic number plus the number of neutrons.

(c) Atoms with the same atomic number but different masses are isotopes. Isobars are atoms that have the same mass but different atomic numbers.

(d) The atomic weight is the mass of an atom relative to the mass of ^{12}C, which is assigned a mass of 12 amu. The atomic mass is a weighted-average of the masses for all the naturally occurring isotopes of an element. The mass number of an atom is determined by the number of nucleons and therefore is not an average value.

(e) Alpha particles are helium ions; i.e., they are composed of two protons and two neutrons. Beta particles are free electrons.

(f) The atomic number for an element is equivalent to the number of protons in the nucleus. The atomic weight is the average mass of an element relative to ^{12}C, which has an assigned mass of 12 amu.

6. ${}^{3}_{1}\text{H}$: 1 proton, 2 neutrons
${}^{31}_{15}\text{P}$: 15 protons, 16 neutrons
${}^{34}_{16}\text{S}$: 16 protons, 18 neutrons
${}^{206}_{82}\text{Pb}$: 82 protons, 124 neutrons
${}^{99}_{43}\text{Tc}$: 43 protons, 56 neutrons
${}^{235}_{92}\text{U}$: 92 protons, 143 neutrons

7. lithium, boron, phosphorous, aluminum, cobalt, selenium, gold, cadmium, antimony, bromine, copper, magnesium, sodium

8. S, K, Zn, Mn, U, Sr, Sn, As, Ar, Be, Ni, Hg, Pb, Si, I, Cl

13. $12.00 \times 0.9889 = 11.87$
$13.003 \times 0.0111 = 0.14$
$11.87 + 0.14 = 12.01$

14. $(34.96885 \times 0.7553) + 0.2447x = 35.453$
$x = 36.95$

15. (a) $$\frac{1.0\text{g}}{197\text{ g/mol}} \times 6.022 \times 10^{23}\text{ atoms/mol} =$$
10^{21} atoms

(b) $$\frac{1.0\text{ kg} \times 1000\text{ g/kg}}{55.8\text{ g/mol}} \times 6.022 \times 10^{23}\text{ atoms/mol} =$$
1.1×10^{25} atoms

(c) $$\frac{5.0\text{ L} \times 0.18\text{ g/L}}{4.0\text{ g/mol}} \times 6.022 \times 10^{23}\text{ atoms/mol} =$$
1.4×10^{23} atoms

16. $$\frac{28.086\text{ g/mol}}{6.022 \times 10^{23}\text{ atoms/mol}} = 4.664 \times 10^{-23}\text{ g/atom}$$

17. $$\frac{10^{6}\text{ atoms}}{6.022 \times 10^{23}\text{ atoms/mol}} \times 107.9\text{ g/mol} = 1.791 \times 10^{-16}\text{ g}$$

18. $0.5\text{ mol} \times 40.08\text{ g/mol} = 20\text{ g Ca}$
$0.2\text{ mol} \times 137.34\text{ g/mol} = 27\text{ g Ba}$
Therefore, 0.2 mol of barium weighs more.

19. $$1.5\text{ carat} \times \frac{200\text{ mg}}{1\text{ carat}} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol}}{12.01\text{ g}} = 0.025\text{ mol}$$

20. $$\frac{15.5\text{ g}}{65.4\text{ g/mol}} = 0.237\text{ mol}$$

21. $$\frac{90\text{ g}}{63.6\text{ g/mol}} = 1.4\text{ mol Cu}$$
$$\frac{10\text{ g}}{65.4\text{ g/mol}} = 0.15\text{ mol Zn}$$
$$\frac{\text{Cu atoms}}{\text{Zn atoms}} = \frac{1.4}{0.15} = 9.3$$

22. $$V = \frac{1}{6} \times \pi\,\text{D}^3$$
$$\text{atom: } V = \frac{1}{6} \times 3.14\left(2\text{ Å} \times 10^{-8}\frac{\text{cm}}{\text{Å}}\right)^3 = 4 \times 10^{-24}\text{ cm}^3$$
$$\text{nucleus: } V = \frac{1}{6} \times 3.14\left(10^{-4}\text{ Å} \times 10^{-8}\frac{\text{cm}}{\text{Å}}\right)^3$$
$$= 5 \times 10^{-40}\text{ cm}^3$$

23. $$\frac{9.11 \times 10^{-28}\text{ g/electron}}{1.67 \times 10^{-24}\text{ g/atom}} \times 100\% = 5.46 \times 10^{-2}\ \%$$

24. $$31.54 \times 10^{-23}\text{ g/atom} \times \frac{6.022 \times 10^{23}\text{ atoms}}{1\text{ mol}} = 18.99\text{ g/mol}$$

25. (a) $$6.635 \times 10^{-23}\text{ g/atom} \times \frac{6.022 \times 10^{23}\text{ atoms}}{1\text{ mol}} =$$
39.96 g/mol

(b) There must be at least one other isotope of calcium with a greater mass.

26. $$2 \times \frac{0.117\text{ nm}}{1\text{ atom}} \times \frac{10^{-9}\text{ m}}{1\text{ nm}} \times \frac{10^{-3}\text{ km}}{1\text{ m}} \times \frac{6.022 \times 10^{23}\text{ atoms}}{1\text{ mol}}$$
$$= 1.41 \times 10^{11}\text{ km/mol}$$

27. (a) 4.00260 amu

(b) $$\frac{4.00260\text{ g/mol}}{6.022 \times 10^{23}\text{ atoms}} = 6.647 \times 10^{-24}\text{ g/atom}$$

28. (a) $$1\text{ mol} \times \frac{6.022 \times 10^{23}\text{ molecules}}{1\text{ mol}} \times \frac{2\text{ atoms}}{1\text{ molecule}} =$$
1.204×10^{24} atoms

(b) $$1\text{ mol} \times \frac{6.022 \times 10^{23}\text{ molecules}}{1\text{ mol}} =$$
6.022×10^{23} molecules

29. $$\frac{1\text{ kg} \times 1000\text{ g/kg}}{26.98\text{ g/mol}} \times \frac{6.022 \times 10^{23}\text{ atoms}}{1\text{ mol}} \times \frac{1\text{ sample}}{10^9} =$$
2.232×10^{16} samples

30. 1. c; 2. b; 3. b; 4. d; 5. a
6. a; 7. b; 8. b; 9. a; 10. d

Chapter 3

5. $$\frac{6.626 \times 10^{-34}\text{ J-s}}{(9.1091 \times 10^{-31}\text{ kg/16700}) \times 3.00 \times 10^{8}\text{ m/s}} =$$
4.05×10^{28} m
$$\frac{3.00 \times 10^{8}\text{ m/s}}{4.05 \times 10^{-8}\text{ m}} = 7.41 \times 10^{15}\text{ sec}^{-1}$$

6. $$\lambda = \frac{3.00 \times 10^{8}\text{ m/s}}{89.1 \times 10^{6}\text{ s}^{-1}} = 3.37\text{ m}$$
$$E = \frac{6.626 \times 10^{-34}\text{ J-s} \times 89.1 \times 10^{6}\text{ s}^{-1}}{4.184\text{ J/cal}}$$
$$= 1.41 \times 10^{-26}\text{ cal}$$

7. (a) $\lambda\nu = \text{c}$
$$\nu = \frac{\text{c}}{\lambda} = \frac{3.00 \times 10^{8}\text{ m/s}}{4.047 \times 10^{-7}\text{ m}} - 7.41 \times 10^{14}\text{ s}$$

(b) $E = \text{h}\nu = 6.626 \times 10^{-34}\text{ J-s} \times 7.41 \times 10^{14}\text{ s}^{-1} =$
4.91×10^{-19} J

(c) $4.91 \times 10^{-19}\text{ J} \times 6.022 \times 10^{23} = 2.96 \times 10^{5}\text{ J}$

(d) $$\frac{5\text{ g NO}_2}{46\text{ g/mol}} \times \frac{6.022 \times 10^{23}\text{ molecules}}{1\text{ mol}} =$$
7×10^{22} photons

8. (a) At the lower wavelength:
$$\nu = \frac{\text{c}}{\lambda} = \frac{3.00 \times 10^{8}\text{ m/s}}{2.10 \times 10^{-7}\text{ m}} - 1.43 \times 10^{15}\text{ s}^{-1}$$

At the upper wavelength:

$$\nu = \frac{\mathrm{c}}{\lambda} = \frac{3.00 \times 10^{8}\ \mathrm{m/s}}{3.10 \times 10^{-7}\ \mathrm{m}} - 9.68 \times 10^{14}\ \mathrm{s}^{-1}$$

(b) $E = \mathrm{h}\nu = 6.62 \times 10^{-34}\ \mathrm{J\text{-}s} \times 9.68 \times 10^{14}\ \mathrm{s}^{-1} =$ $6.41 \times 10^{-19}\ \mathrm{J}$

11. (a) An orbit is a well-defined path followed by one object as it revolves about a central position; e.g., the moon around the earth. An orbital is a description of the location in space about a nucleus in which an electron is likely to be found. An orbital also describes the energy of an electron in the orbital.

(b) Frequency is a measure of the number of wave crests that pass a specific point in a given time period (for example, 100 per second). Wavelength is the distance between wave crests.

(c) The Heisenberg uncertainly principle states that the position and the velocity of an electron cannot both be known or measured with certainty. The Pauli exclusion principle states that no two electrons of an atom may have the same four quantum numbers (n, l, m and s).

(d) A wave has a regular oscillating motion that is propagated from point to point. A particle is a small hard object with well-defined physical properties.

(e) A quantum number gives information about the energy of an electron and the probability of finding it at a given point in space about the nucleus. An energy level refers to the potential energy associated with a given electron of an atom.

(f) An energy level refers to the potential energy associated with a given electron of an atom. An electron configuration describes the distribution of electrons in the various energy levels of an atom.

12. (a) In the Bohr model the electron is a particle whereas the electron is a wave in the other model.

(b) In the Bohr model the electron revolves about the nucleus in a circular orbit, but in the wave model the electron position is defined in terms of the probability of finding it in a given location about the nucleus.

(c) The total energy of the electron in the wave model is the same as that derived from the Bohr model.

(d) Because there is a small, but finite, probability of finding an electron even at large distances from the nucleus, the wave model does not define the size of an atom. The Bohr model's circular orbits would clearly define the radius and thus the size of an atom.

14.

$$r = \frac{n^2h^2}{4\pi kme^2}$$

$$= \frac{(1)^2(6.626 \times 10^{-14}\ \mathrm{J\text{-}s})^2}{4(3.14)^2(8.99 \times 10^{9}\mathrm{J\text{-}s})}$$

$$(9.11 \times 10^{-31}\ \mathrm{kg})(-1.60 \times 10^{-19}\ \mathrm{C})^2$$

$$= 5.3 \times 10^{-11}\ \mathrm{m}$$

15.

$$\frac{1}{\lambda} = 1.09678 \times 10^{7}\ \mathrm{m}^{-1}\left(\frac{1}{4} - \frac{1}{\pi^2}\right)$$

$$= 1.09678 \times 10^{7}\ \mathrm{m}^{-1}\left(\frac{1}{4} - \frac{1}{(4)^2}\right) = 2056460\ \mathrm{m}^{-1}$$

$$\lambda = 4.86 \times 10^{-7}\ \mathrm{m}$$

$$E = \frac{\mathrm{hc}}{\lambda} = \frac{6.626 \times 10^{-34}\ \mathrm{J\text{-}s} \times 3.00 \times 10^{8}\ \mathrm{m/s}}{4.86 \times 10^{-7}\ \mathrm{m}}$$

$$= 4.09 \times 10^{-19}\ \mathrm{m}$$

$$E_2 = \frac{-21.7 \times 10^{-19}\ \mathrm{J}}{(2)^2} = -5.43 \times 10^{-19}\ \mathrm{J}$$

$$E_4 = \frac{-21.7 \times 10^{-19}\ \mathrm{J}}{(4)^2} = -1.36 \times 10^{-19}\ \mathrm{J}$$

$$E_4 - E_2 = 4.07 \times 10^{-19}\ \mathrm{J}$$

19. (a) (1) No, this is just the expression for the quantized separation of the electron and proton = n(1Å). (2) No, this is just the expression for the potential energy of any pair of charged particles. (3) Correct = $kq_1q_2/(n \times 1 \times 10^{-10}\ \mathrm{m})$

(b) The electron is closest to the proton when $n = 1$ and $r = 1 \times 10^{-10}$ m.

Thus,

$$\frac{kq_1q_2}{n \times 1 \times 10^{-10}}$$

$$= \frac{(8.99 \times 10^{9}\ \mathrm{J\text{-}m/C^2})(-1.60 \times 10^{-19}\ \mathrm{C}-1.60 \times 10^{-19}\ \mathrm{C})}{1 \times 10^{-10}\ \mathrm{m}}$$

$$= 2.3 \times 10^{-18}\ \mathrm{J}$$

(c) The atom is in its ground state when $r = 1$ Å. The potential energy, which is also the total energy of this hypothetical system, is -2.3×10^{-18} J . When the electron is completely removed from the atom the separation between the proton and electron is infinity and the potential energy is zero ($V = q_1q_2/\text{infinity} = 0$). The energy required to remove the electron is the difference between these two states,

$$\Delta E = 0 - (-2.3 \times 10^{-18}\ \mathrm{J}) = 2.3 \times 10^{-18}\ \mathrm{J}.$$

(d) $\mathrm{V} = kq_1q_2/(n \times 1 \times 10^{-10}\ \mathrm{m})$
In the first excited energy level $n = 2$
Thus, $\mathrm{V} = 22.3 \times 10^{-18}\ \mathrm{J}/2 = 21.15 \times 10^{-18}\ \mathrm{J}$

(e) $\Delta E = -1.15 \times 10^{-18}\ \mathrm{J} - (-2.3 \times 10^{-18}\ \mathrm{J}) = 1.15 \times 10^{-18}\ \mathrm{J}$

(f) The most convenient source of energy in the laboratory is electromagnetic radiation, which is most commonly encountered as visible light. Other types of radiation, for example, microwave, radio waves, ultraviolet, infrared, and x-rays, are also electromagnetic radiation, but have different energies. The energy of one photon of radiation is given by the Planck relationship

$$E = \mathrm{h}\nu$$

where h is Planck's constant [6.626×10^{-34} J-s] and ν is the frequency of the radiation.

(g) $E = \mathrm{h}\nu$
$n = \mathrm{E/h} = 1.15 \times 10^{-18}\ \mathrm{J}\ /6.626 \times 10^{-34}\ \mathrm{J\text{-}s} = 1.7 \times 10^{15}\ \mathrm{s}^{-1}$

(h) The wavelength, frequency, and velocity of light (and other radiation) are related by the equation

$$c = \nu\lambda$$

where c is the speed of light, ν is the frequency, and λ is the wavelength of light.

$$\nu = c/\lambda = 3.00 \times 10^{8}\ \text{m/s}/1.7 \times 10^{15}\ \text{s}^{-1}$$
$$= 1.8 \times 10^{-7}\ \text{m}$$
$$= 180\ \text{nm}$$

This is in the ultraviolet region of the electromagnetic spectrum. The visible region extends from about 400 nm to 800 nm [not a very large portion of the spectrum]

24. $n = 4$ to $n = 3$; $n = 4$ to $n = 2$; $n = 4$ to $n = 1$; $n = 3$ to $n = 2$; $n = 3$ to $n = 1$; $n = 2$ to $n = 1$
total = 6 lines

25. a. $$\Delta E = \frac{-2 \times 10^{-1}}{1} - \frac{2 \times 10^{-11}}{2} = +1 \times 10^{-11}\ \text{ergs}$$

$$E = h\nu = \frac{hc}{\lambda}$$

$$c = \lambda\nu$$

$$\nu = \frac{c}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.6 \times 10^{-27}\ \text{erg-sec})(3 \times 10^{10}\ \text{cm/sec})}{1 \times 10^{-11}\ \text{erg}}$$
$$= 20 \times 10^{-6}\ \text{cm} = 2 \times 10^{-5}\ \text{cm}$$

b. $$V = \frac{q_1 q_2}{r} = -2 \times 10^{-11} = \frac{-(4.8 \times {}^{-10})^2}{r}$$

$$r = \frac{-(4.8 \times 10^{-10})^2}{-2 \times 10^{-11}} = 1.2 \times 10^{-8}\ \text{cm}$$

c. Number of lines 5 3.

27. a. wavelength = $2\pi r/2n$, where $n = 1, 2, 3, \ldots$

28. $$E = mc^2$$

$$E = h\nu = \frac{hc}{\lambda}$$

$$\frac{hc}{\lambda} = mc^2 \quad \text{and} \quad \lambda = \frac{h}{mc}$$

$$\lambda = \frac{h}{mv}$$

29. $$\frac{6.626 \times 10^{-34}\ \text{J-s}}{5.979 \times 10^{24}\ \text{g} \times 29.771 \times 10^{3}\ \text{m/s}} = 3.722 \times 10^{63}\ \text{m}$$

30. (a) $$\lambda = \frac{h}{mv}$$
$$= \frac{6.626 \times 10^{-34}\ \text{J-s}}{9.11 \times 10^{-31}\ \text{kg} \times 3.00 \times 10^{8}\ \text{m/s} \times 0.12}$$
$$= 2.0 \times 10^{-11}\ \text{m}$$

(b) $$\frac{6.63 \times 10^{-34}\ \text{J-s}}{0.454\ \text{kg} \times 3.00 \times 10^{8}\ \text{m/s} \times 0.12} = 4.0 \times 10^{-41}\ \text{m}$$

31. Imagine that velocity could only increase by increments of 5 miles per hour for any object. In this circumstance driving an automobile would be a little uncomfortable as the car and driver jumped from a stop to exactly 5 mph; i.e., there would be no smooth acceleration. However, it would be relatively easy for everyone to drive exactly 55 mph. Sports that use balls would be very different as well. For example, a baseball player trying to hit a pitch would have a difficult time judging the speed of a good fastball as it approaches home plate because it could, at any point in its trajectory, drop from 90 mph instantaneously to 85 mph.

32. $E_{n=1} = n^2h^2/8\,ml^2 = 5.49 \times 10^{-67}$ J

$E_{n=2} = 5.49 \times 10^{-67}\ \text{J} \times (2)^2 = 22.0 \times 10^{-67}$ J

$E_{n=2} - E_{n=1} = 16.5 \times 10^{-13}$ J

no effect

33. 21.7×10^{-19} J/atom × 6.022×10^{23} atoms/mol × 10^{23} kJ/J = 1.31×103 kJ/mol

This value is in excellent agreement with the reported value of 1,312 kJ/mol.

34. a. Both have a spherical shape, however the 1*s* orbital is closer to the nucleus and would be of lower energy.
b. Both would be the same distance from the nucleus and have the same energy, but their shapes would differ.
c. Their shapes and energies are the same, while their orientations with respect to an applied magnetic field would be different (i.e., *px* vs *py*).
d. An orbital is a description of a spatial region where an electron can be found with some degree of probability, and this description is a product of the wave model of the electron. An orbit is a product of the Bohr model of the atom and describes a particular set path of an electron around a nucleus.

35.

n	*l*	*m*	*s*	*n*	*l*	*m*	*s*
4	0	0	+1/2	4	2	2	+1/2
4	0	0	−1/2	4	2	2	−1/2
4	1	−1	+1/2	4	3	−3	+1/2
4	1	−1	−1/2	4	3	−3	−1/2
4	1	0	+1/2	4	3	−2	+1/2
4	1	0	−1/2	4	3	−2	−1/2
4	1	1	+1/2	4	3	−1	+1/2
4	1	1	−1/2	4	3	−1	−1/2
4	2	−2	+1/2	4	3	0	+1/2
4	2	−2	−1/2	4	3	0	−1/2
4	2	−1	+1/2	4	3	1	+1/2
4	2	−1	−1/2	4	3	1	−1/2
4	2	0	+1/2	4	3	2	+1/2
4	2	0	−1/2	4	3	2	−1/2
4	2	1	+1/2	4	3	3	+1/2
4	2	1	−1/2	4	3	3	−1/2

36. a, c, and d

37. For the *s* orbitals the quantum number $l = 0$, therefore, $m = 0$ and only zero for one *s* orbital. For the quantum number $l = 1$, $m = -1$, 0 or +1, and therefore, there are three *p* orbitals.

38. 25; 7; 4

39. d

40. In the hydrogen atom the 2*s* and 2*p* orbitals have identical energies. (Hydrogen is unique among the elements in this regard.) In the carbon atom the 2*p* orbitals are higher in energy than the 2*s* orbital.

41. (a) $1s^22s^22p^5$
(b) $1s^22s^22p^63s^23p^64s^1$
(c) $1s^22s^22p^63s^23p^63d^74s^2$
(d) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^75s^25p^26s^2$
(e) $1s^22s^22p^63s^23p^63d^6$
(f) $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$

42. Fe^{3+}: $1s^22s^22p^63s^23p^63d^5$
K^+: $1s^22s^22p^63s^23p^6$
Cl^-: $1s^22s^22p^63s^23p^6$
Sn^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^75s^2$
O^{2-}: $1s^22s^22p^6$

44. Kr: $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$
As^{3-}, Se^{2-}, Br^-, Rb^+, Sr^{2+}, Y^{3+}
$Y^{3+} < Sr^{2+} < Rb^+ < Br^- < Se^{2-} < As^{3-}$; Because all of these ions have the same number of electrons, the ions with the greater number of protons in the nucleus will be smaller.

47. lower energy: 2*p*
farther from nucleus: 4*s*
spherical: 4*s*

48. The nonmetals have valence electrons in *p* orbitals, whereas the metals generally only have valence electrons in *s* and *d* orbitals.

49. (a) One. When $l = 0$ we have an *s* orbital. *m* can have only one value (1), and so there is only one orbital for $n = 1$ that has $l = 1$ [$n = 1$, $l = 0$, $m = 1$]; Likewise there is only one s orbital for $n = 2$.
(b) One. A *p*-orbital occurs when $l = 1$, but *m* can have only one value so there can be only one *p*-orbital in every quantum level (every value of *n*) except the first. Clearly, the values permitted for *m* determine the number of *s*, *p*, *d*, *f* orbitals.

50. (a) 2
(b) 6
(c) $$E = \frac{(1)^2(1 \times 10^2\ \text{J-s})^2}{8(0.100\ \text{kg})(60\ \text{ft} \times 12\ \text{in/ft} \times 0.0254\ \text{m/in})^2} =$$
4×10 J
(d) $4 \times 10\ \text{J} \times (2)^2 = E = 160\ \text{J} = 1/2\, mv^2$
$v = 6 \times 10$ m/s

55. 1. degenerate, 2. principal, 3. wavelength, 4. photon, 5. quantized, 6. orbits, 7. position, velocity, 8. spin, 9. shape, spatial orientation, 10. Pauli exclusion, 11. valence, 12. IA, IIA, 13. inert gases, 14. spherical

56. 1. c 2. d 3. a 4. b 5. d

Chapter 4

1. (a) Period 4 of the periodic table includes potassium, K, through krypton, Kr.
(b) The oxygen group includes the elements O, S, Se, Te and Po.
(c) Group VIIB includes Mn, Tc and Re.
(d) The iron triad includes Fe, Ru and Os.
(e) The inert gases are in Group VIIIA and include He, Ne, Ar, Kr, Xe and Rn.
(f) The inner transition elements include the actinides and lanthanides.
(g) The nonmetals include B, Si, As, Te and At and all elements to the right of these on the periodic table. These elements generally have high ionization energies, electron affinities and electronegativities. The metals are the elements that appear to the left of the five elements listed above. The metals have low ionization potentials, electron affinities and electronegativities.
(h) The representative elements are those in the "A" groups of the periodic table including H through Fr, Be through Ra, B through Tl, C through Pb, N through Bi, O through Po, and F through At.
(i) The transition elements are members of the "B" groups on the periodic table, which are located in periods 4, 5 & 6 between Groups IIA and IIIA.

2. (a) Atomic radii generally increase with increasing atomic number in a group, and they generally decrease with increasing atomic number in a period.
(b) The first ionization energy of the elements decrease with increasing atomic number in a group, and they generally increase with increasing atomic number in a period.
(c) Electronegativity increases with increasing atomic number in a period and decreases with increasing atomic number within a group.
(d) Metallic properties are related to electronegativity, electron affinity and ionization energy. Metallic character increases with increasing atomic number within a group, but it decreases with increasing atomic number within a period.

3. Mendeleev placed tellurium before iodine because he based his periodic table on the chemical properties of the elements not on their atomic weights. Iodine has properties like the other halogens, and tellurium has properties like other elements in the oxygen group. In his mind, one or both of the atomic weights of these elements must have been in error.

4. The alkali metals are the first elements in each period and have one electron in the outermost quantum level. They therefore are larger (atomic radius) than the preceeding elements and have the greatest size and lowest mass of any element within a period. This means a lower density than the preceeding elements. The alkaline earth metals, which follow the alkalis, have two electrons in the outermost quantum level (two ns electrons) and have considerably stronger bonding between the atoms in the metal. Consequently, the density of the alkaline earth metals is greater than the alkalis and their molar volumes are lower.

5. The additional representative element would be located below Tl on the periodic table and would have 113 as its atomic number.

6. Predicted density is about 2.15 g per cm^3. Predicted melting point is 10–20 °C. Predicted boiling point is 650–680 °C. These estimates can be made by extrapolation of plots of the data in each set.

8. a.

XF	XF_2	XF_3	XF_4	XF_3	XF_2	XF
1	2	3	4	5	6	7
1	2	3	4	3	2	1

The ratio of F to X increases to the middle of the period and then decreases. From XF_4 to XF the total number of electrons is eight. To the left of XF_4, the total number of electrons is 2, 4, and 6.

b. The first three compounds can be thought of as containing ionic bonding. From XF_4 to XF (left to right), the number of electrons remains at eight and the bonding is primarily covalent.

c. It is generally true that compounds formed between the members of a group and another atom have the same formula. For example, BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$. It is also true, however, that some of the second-period compounds can be quite different from others in the group. Also, as a group is descended, compounds with a different atom ratio can become more stable. For example, in Group IV, both CO and CO_2 are well known oxides of carbon. For silicon and germanium, the second and third members of Group IV, only SiO_2 and GeO_2 are stable at room temperature. For tin, SnO_2 is more stable than SnO, but for lead, the bottom member of Group IV, PbO is more stable than PbO_2.

9. All three species have an outermost quantum level of 2 and the neutral atoms should be of roughly equal size. As electrons are removed to form the positive ions, the electrons that remain are exposed to a greater share of the nucleus's positive charge and are more strongly attracted to the protons in the nucleus, with the greatest attraction experienced by the electrons in the most positive ion, Be^{2+}. The stronger the attraction of the electrons to the nucleus, the more the electrons' orbital will shrink, and the smaller the species will be.

12. For Li^{2+}:

$$\frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{11815 \times 10^{3}\ \text{J/mol} \div 6.022 \times 10^{23}\ \text{ions/mol}} = 1.012 \times 10^{-8}\ \text{m} = 10.12\ \text{nm}$$

For Li:

$$\frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{520.3 \times 10^{3}\ \text{J/mol} \div 6.022 \times 10^{23}\ \text{ions/mol}} = 2.299 \times 10^{-7}\ \text{m} = 229.9\ \text{nm}$$

13. (a) Be (b) S (c) Mg^{2+} (d) Cl

14. (a) Ca (b) S

15. (a) Ge (b) Tl

16. (a) Se (b) Br

17. (a) Mg (b) Fe c) Cl^- (d) F^-

18. $Ba < Na < Li < Sn < S < Br < Cl < O$

19. a. Be has a filled 2*s* orbital which imparts particular stability to the atom. The outermost electron in B is in a 2*p* orbital which has a higher energy than a 2*s*. Moreover, removal of this electron gives the Be^+ ion which has a stable filled 2s orbital. Therefore, it requires less energy to remove the electron from boron and boron has the lower ionization energy.

b. Nitrogen has a valence shell of $2s^22p^3$ while oxygen has a valence shell of $2s^22p^4$. Nitrogen is stable with a half-filled orbital, while oxygen can obtain a half-filled orbital by removal of one electron. Therefore, less energy is required to remove an electron from oxygen than from nitrogen.

20. (a) periods (b) actinides (c) alkali, alkaline earth (d) atomic number (e) groups (f) Mendeleev (g) halogens (h) representative (i) ionization energy (j) fluorine (k) positive (l) evolved (m) inert or noble gases (n) the IB group (o) smaller (p) bismuth (q) oxygen (r) lanthanides (s) beryllium (t) decrease

21. 1. b 2. b 3. a 4. b 5. c
6. d 7. d 8. d 9. b 10. a

CHAPTER 5

1. Some physical and chemical properties that would be important in the classification of AB_2 include melting point, boiling point and the electrical conductivity of the molten state. If the compound is ionic, then it will possess relatively high melting and boiling points and, in its molten state, the compound will conduct electricity. Conversely, if the compound is covalent, then the melting and boiling points will be relatively low and the molten compound will not be conductive. Additionally, x-ray diffraction may be used to categorize the compound as covalent if the bonds show a high degree of directional character.

2. a. moles C must equal moles CO_2 produced, 0.0300 mol
moles H must equal twice the moles H_2O produced, 0.0800 mol

b. $\dfrac{\text{moles H}}{\text{moles C}} = \dfrac{0.0800}{0.0300} = 2.67 = \dfrac{8}{3}$

$C_1H_{2.67} = C_3H_8$

c. 44 g/mol

3. (a) $1.0\ \text{kg}\ KAl(SO_4)_2{\cdot}12\ H_2O \times \dfrac{100\ \text{g}}{1\ \text{kg}} \times \dfrac{27.0\ \text{g Al}}{133.4\ \text{g}\ AlCl_3} =$

2.0×10^2 g Al

(b) $1.0\ \text{kg}\ KAl(SO_4)_2{\cdot}12\ H_2O \times \dfrac{1000\ \text{g}}{1\ \text{kg}} \times$

$$\frac{27.0\ \text{g Al}}{474\ \text{g}\ KAl(SO_4)_2{\cdot}12\ H_2O} = 57\ \text{g Al}$$

4. $$\frac{6.00\ \text{g}\ Na_2B_4O_7{\cdot}10\ H_2O}{381\ \text{g/mol}\ Na_2B_4O_7{\cdot}10\ H_2O} \times \frac{4\ \text{mol B}}{1\ \text{mol}\ Na_2B_4O_7{\cdot}10\ H_2O} \times \frac{10.8\ \text{g B}}{1\ \text{mol B}} = 0.680\ \text{g B}$$

5. (a) $\dfrac{6.941\ \text{g Li}}{86.845\ \text{g total}} \times 100\% = 7.992\%$ Li and

$\dfrac{79.904\ \text{g Br}}{86.845\ \text{g total}} \times 100\% = 92.008\%$ Br

(b) $\dfrac{55.847\ \text{g Fe}}{112.84\ \text{g total}} \times 100\% = 49.492\%$ Fe

$\dfrac{(3 \times 18.998\ \text{g F})}{112.84\ \text{g total}} \times 100\% = 50.509\%$ F

(c) $\dfrac{(2 \times 39.098\text{ g K})}{138.20\text{ g total}} \times 100\% = 56.580\%\text{ K}$

$\dfrac{12.011\text{ g C}}{138.20\text{ g total}} \times 100\% = 8.6910\%\text{ C}$

$\dfrac{(3 \times 15.9994\text{ g O})}{138.20\text{ g total}} \times 100\% = 34.730\%\text{ O}$

6. (a) Nitrogen: $\dfrac{46.68\text{ g N}}{14.0\text{ g/mol N}} = 3.33\text{ mol N}$

Oxygen: $\dfrac{53.32\text{ g O}}{16.0\text{ g/mol O}} = 3.33\text{ mol O}$

Ratio: 3.33 : 3.33, so the empirical formula = NO

(b) Carbon: $\dfrac{85.62\text{ g C}}{12.0\text{ g/mol C}} = 7.14\text{ mol C}$

Hydrogen: $\dfrac{14.38\text{ g H}}{1.008\text{ g/mol H}} = 14.24\text{ mol H}$

Ratio: 7.14 : 14.24 = 1 : 2, so the empirical formula = CH_2

(c) Carbon: $\dfrac{75.92\text{ g C}}{12.0\text{ g/mol C}} = 6.33\text{ mol C}$

Hydrogen: $\dfrac{6.37\text{ g H}}{1.01\text{ g/mol H}} = 6.31\text{ mol H}$

Nitrogen: $\dfrac{17.70\text{ g N}}{14.0\text{ g/mol N}} = 1.26\text{ mol N}$

Ratio: 6.33 : 6.31 : 1.26 = 5 : 5 : 1, so the empirical formula = C_5H_5N

(d) Carbon: $\dfrac{58.53\text{ g C}}{12.0\text{ g/mol C}} = 4.88\text{ mol C}$

Hydrogen: $\dfrac{4.09\text{ g H}}{1.01\text{ g/mol H}} = 4.05\text{ mol H}$

Nitrogen: $\dfrac{11.38\text{ g N}}{14.0\text{ g/mol N}} = 0.812\text{ mol N}$

Oxygen: $\dfrac{25.99\text{ g O}}{16.0\text{ g/mol O}} = 1.62\text{ mol O}$

Ratio: 4.88 : 4.05 : 0.812 : 1.62 = 6 : 5 : 1 : 2, so the empirical formula = $C_6H_5NO_2$

7. $\dfrac{90\text{ g/mol}}{30\text{ g/emp.form.}} = 3$, so the molecular formula = $C_3H_6O_3$

$\dfrac{50.0\text{ g }C_3H_6O_3}{90.08\text{ g/mol }C_3H_6O_3} = 0.55\text{ mol }C_3H_6O_3$

$0.555\text{ mol }C_3H_6O_3 \times 6.022 \times 10^{23}\text{ molecules/mol} = 3.34 \times 10^{23}\text{ molecules }C_3H_6O_3$

$3.34 \times 10^{23}\text{ molecules }C_3H_6O_3 \times \dfrac{3\text{ atoms C}}{1\text{ molecule}} = 1.00 \times 10^{24}\text{ atoms C}$

8. Carbon: $\dfrac{40.00\text{ g C}}{12.0\text{ g/mol C}} = 3.33\text{ mol C}$

Hydrogen: $\dfrac{6.72\text{ g H}}{1.01\text{ g/mol H}} = 6.65\text{ mol H}$

Oxygen: $\dfrac{53.29\text{ g O}}{16.0\text{ g/mol O}} = 3.33\text{ mol O}$

Ratio: 3.33 : 6.65 : 3.33 = 1 : 2 : 1, so the empirical formula = CH_2O

$\dfrac{180\text{ g/mol}}{30\text{ g/emp.form.}} = 6$, so the molecular formula = $C_6H_{12}O_6$

9. Carbon: $\dfrac{42.35\text{ g C}}{12.0\text{ g/mol C}} = 3.53\text{ mol C}$

Hydrogen: $\dfrac{3.53\text{ g H}}{1.01\text{ g/mol H}} = 3.50\text{ mol H}$

Nitrogen: $\dfrac{16.48\text{ g N}}{14.0\text{ g/mol N}} = 1.18\text{ mol N}$

Oxygen: $\dfrac{12.55\text{ g O}}{16.0\text{ g/mol O}} = 0.784\text{ mol O}$

Sulfur: $\dfrac{25.18\text{ g S}}{32.1\text{ g/mol S}} = 0.784\text{ mol S}$

Ratio: 4.5 : 4.5 : 1.5 : 1 : 1, multiplying by two gives $C_9H_9N_3O_2S_2$ for the empirical formula

10. (a) $\dfrac{150\text{ g}}{119.4\text{ g/mol }CHCl_3} = 1.26\text{ mol }CHCl_3$

(b) $1.26\text{ mol }CHCl_3 \times \dfrac{6.022 \times 10^{23}\text{ molecules}}{1\text{ mol}} = 7.59 \times 10^{23}\text{ molecules }CHCl_3$

(c) $1.26\text{ mol }CHCl_3 \times \dfrac{1\text{ mol C}}{1\text{ mol }CHCl_3} \times \dfrac{12.01\text{ g C}}{1\text{ mol C}} = 15.1\text{ g C}$

(d) $7.59 \times 10^{23}\text{ molecules }CHCl_3 \times \dfrac{3\text{ atoms Cl}}{1\text{ molecule}} = 2.28 \times 10^{24}\text{ atoms Cl}$

(e) $1.26\text{ mol }CHCl_3 \times \dfrac{1\text{ mol H}}{1\text{ mol }CHCl_3} = 1.26\text{ mol H}$

11. $\dfrac{10^6\text{ molecules}}{6.022 \times 10^{23}\text{ molecules/mol}} \times 28.01\text{ g/mol CO} = 4.650 \times 10^{-17}\text{ g CO}$

12. Assume a 100.0-g sample of the compound. Then, the compound would consist of 23.1 g K, 14.3 g Ti, and 62.7 g Cl.

$$\frac{23.1\text{ g K}}{39.10\text{ g/mol K}} = 0.591\text{ mol K}$$

$$\frac{14.3\text{ g Ti}}{47.90\text{ g/mol Ti}} = 0.299\text{ mol Ti}$$

$$\frac{62.7\text{ g Cl}}{35.45\text{ g/mol Cl}} = 1.77\text{ mol Cl}$$

$$K_{1.98}Ti_{1.00}Cl_{5.92} = K_2TiCl_6$$

13. a. yes because it contains a metal, iron

b. Fe

c. CO_3^{2-}

d. $FeCO_3$

e. No. Many ionic compounds are not soluble in water.

14. Lithium fluoride and beryllium fluoride have high melting points because they are ionic compounds. These compounds have three-dimensional structures in which the cations and anions are arranged in the lattice to minimize the potential energy of the solid. The other five compounds, which possess substantially lower melting points, are covalent compounds. Structurally, these compounds differ from LiF and BeF_2 in that they form discrete small molecules and not extended lattices with ionic interactions.

15. Although the first ionization potential for an element will be lower than the second or third ionization potential, it is not necessarily the case that the monovalent cation will be the most common ionic form of the element. For example, the calcium ion is essentially only thought of as a divalent cation. This observation is rationalized by noting that the loss of two electrons from the calcium atom, although more costly than the loss of a single electron, produces an ion with an inert-gas electron configuration.

16. (a) calcium carbonate (b) cuprous sulfate (c) ferric chloride (d) lithium phosphate (e) cobaltous fluoride (f)cupric hydroxide (g) potassium sulfite (h) zinc bromide (I) ammonium nitrate

17. (a) sodium dihydrogen phosphate (b) ferric chloride hexahydrate (c) cesium hydrogen phosphate (d) nickel oxide (e) sodium hydrogen carbonate (f) lithium chlorite (g) barium perchlorate (h) rubidium hydrogen sulfite (i) sodium carbonate heptahydrate (j) sodium carbide (k) boron phosphate (l) mercuric sulfate

18. (a) carbonic acid (b) chlorous acid (c) phosphoric acid (d) sulfurous acid (e) perchloric acid (f) phosphorous acid (g) hypochlorous acid (h) nitrous acid (i) acetic acid (j) oxalic acid (k) nitric acid (l) sulfuric acid

19. (a) K_2CO_3 (b) $CsClO_3$ (c) HClO (d) NaBr (e) H_2S (f) $SrSO_3$ (g) $Cu_3(PO_4)_2$ (h) CuCl (i) $Ni(MnO_4)_2$ (j) $Cr_2(SO_4)_3$ (k) $Hg(NO_3)_2$ (l) $LiBrO_3$ (m) In_2O_3 (n) $Al(OH)_3$ (o) $BiCl_3$ (p) $Fe(NO_2)_3$ (q) Ag_2S (r) AuCN (s) HF (t) $RbHSO_3$ (u) $Ba(H_2PO_4)_2$

20. (a) $HBrO_2$ (b) $NaBrO_2$ (c) HIO (d) $Ba(IO_4)_2$ (e) H_3AsO_3 (f) H_2SeO_4 (g) $FeAsO_4$ (h) $HBrO_3$

21. a. $Fe(OH)_2$, b. ZnC_2O_4, c. HIO_3, d. $Al_2(TeO_4)_3$, e. $NH_4C_2H_3O_2$

22. b, The hydrogen is almost always attached to oxygen.

23. a. molybdate, b. tungstate, c. vanadate, d. manganate

24. cupric chloride, $CuCl_2$
Cu^{2+}: $1s^22s^22p^63s^23p^64s^03d^9$
Cl^{1-}: $1s^22s^22p^63s^23p^6$

ferric oxide, Fe_2O_3
Fe^{3+}: $1s^22s^22p^63s^23p^64s^03d^5$
O^{2-}: $1s^22s^22p^6$

manganese(II) sulfide, MnS
Mn^{2+}: $1s^22s^22p^63s^23p^64s^03d^5$
S^{2-}: $1s^22s^22p^63s^23p^6$

25. There are four attractions and two repulsions:

$$PE = -\frac{4(8.99 \times 10^9 \text{ J-m/C}^2)(1.6 \times 10^{-19}\text{ C})^2}{1.00 \times 10^{-10}\text{ m}} + \frac{2(8.99 \times 10^9 \text{ J-m/C}^2)(1.6 \times 10^{-19}\text{ C})^2}{1.41 \times 10^{-10}\text{ m}}$$
$$= -5.9 \times 10^{-18}\text{ J}$$

26. (a) As the cations increase in size from lithium through potassium, the distances between ions in the lattice increase which results in decreased attractive forces between anions and cations. Thus, the potential energy is lowest for LiF and greatest for KF.
(b) As the anions' radii increase from fluoride through bromide, the distances between ions in the lattice increase which results in decreased attractive forces between anion and cations. Thus, the potential energy is the lowest for NaF and greatest for NaBr.
(c) Because the magnesium ion has a greater charge than the sodium ion and because it is slightly smaller than the sodium ion, the MgF_2 will have the lower potential energy; that is, the greater lattice energy.
(d) The fluoride ion and the oxide ion are very similar in size, but the greater negative charge of the oxide ion will produce stronger ion attractive forces in MgO and thus it will have the greater latttice energy.

27. a. linear

28. $$PE = -\frac{(6.022 \times 10^{23})(1.75)(8.99 \times 10^9 \text{ J-m/C}^2)(3.2 \times 10^{-19}\text{ C})^2}{2.56 \times 10^{-10}\text{ m}} \times 0.9 =$$
-3.41×10^3 kJ

30. -328 kJ/mol $= 89.6$ kJ/mol $+ 418.9$ kJ/mol $+ (213.6$ kJ/mol$)/2 + -295.2$ kJ/mol $+$ U
U $= -648$ kJ/mol

31. Because the arrangement of the ions in MgO is the same as arrangement of the ions in NaCl, the major factors to consider in estimating the lattice energy of MgO relative to NaCl are the ionic charges and the ionic radii.

$$\text{Lattice energy} = Mkq_1q_2/r$$

Because the ionic charges in MgO are greater, the lattice energy for MgO should be greater than that for NaCl. Also, because the corresponding ionic radii in MgO are smaller than those in NaCl, the lattice energy should be greater.

ionic radius of sodium:	95 pm
ionic radius of magnesium:	65 pm
ionic radius of chlorine:	181 pm
ionic radius of oxygen:	140 pm

With these two factors combined, the lattice energy of MgO should be much greater than the lattice energy for NaCl. (See Table 6.7.) With a greater lattice energy, MgO should possess a melting point higher than the melting point of NaCl.

32. a. $\Delta E = 979 + (-593) + (-378) = 8$ kJ/mol
b. Because ΔE is positive, heat is absorbed.
c. The first one.
d. $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ $\Delta E = 65$ kJ/mol
e. AgCl, because ΔE for the dissolution is more positive.
f. The silver ion is larger than the cuprous ion and therefore the distance between the center of the silver ion and the center of the chloride ion is greater. This leads to a smaller $\frac{q_1q_2}{r}$ term and a lower lattice energy.

33. Because the alkali metal cations have only a single positive charge, the lattice energy of their compounds is not as high as the lattice energy of compounds containing 2+ or 3+ cations. The lattice energy is an important factor in determining solubility, although it is certainly not the only factor. All else being constant, the greater the lattice energy, the less soluble the compound.

34. Hardness depends on the type of crystal lattice. For ionic compounds it is usually directly related to lattice energy—the greater the lattice energy, the harder the compound. In this case, the carbonate must have a higher lattice energy. Because the cation must have the same charge as the Ba^{2+} ion, it must be smaller. Hence, we can conclude that the carbonate is $MgCO_3$, $CaCO_3$, or $SrCO_3$.

35. (a) NaCl structure, 138/196 = 0.70
(b) NaCl structure, 102/200 = 0.46
(c) zinc blende structure, 30/198 = 0.15
(d) NaCl structure,72/140 = 0.51

36.
$$\frac{(8.99\times 10^{9}\text{ J-m/C}^{2})(1.6\times 10^{-19}\text{ C})^{2}}{0.001\text{ m}} - \frac{(8.99\times 10^{9}\text{ J-m/C}^{2})(1.6\times 10^{-19}\text{ C})^{2}}{0.001\text{ m}} = 2.1\times 10^{-26}\text{ J}$$

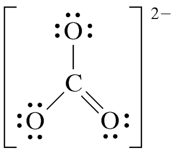
CHAPTER 6

1. (a) $AsCl_3$ (b) BI_3 (c) P_2O_5 (d) H_2Se (e) XeF_6 (f) $GeCl_4$ (g) ZrF_4 (h) SbF_5 (i) BrF_3 (j) Cl_2O

2. (a) nitrogen oxide, (b) dinitrogen oxide, (c) dinitrogen tetroxide, (d) nitrogen dioxide, (e) phosphorous pentachloride, (f) sulfur hexafluoride, (g) sulfur trioxide, (h) diphosphorous pentoxide, (i) silicon tetrabromide, (j) oxygen difluoride, (k) dichlorine oxide, (l) tin tetraiodide

3. (a) LiBr (b) BF_3 (c) LiF (d) CF_4 (e) SiO_2 (f) $SnCl_4$ (g) IF

4.

(a)


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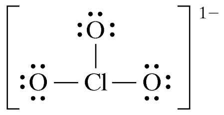

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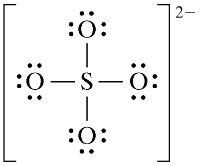

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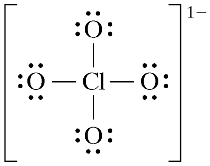

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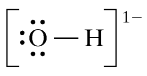

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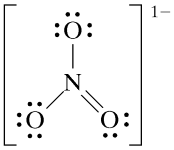

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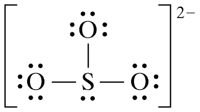

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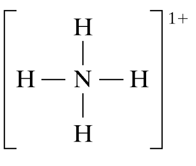
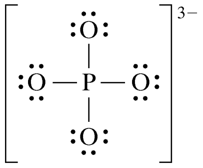
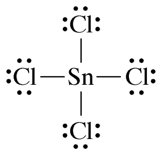


(i)


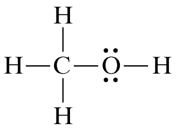
5.

(a) $:\ddot{\mathrm{O}}=\mathrm{C}=\ddot{\mathrm{O}}:$

(b)


(c) $:\mathrm{C}\equiv\mathrm{O}:$

(d) $\mathrm{H}-\ddot{\mathrm{O}}-\mathrm{H}$

(e)


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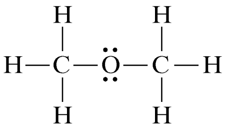

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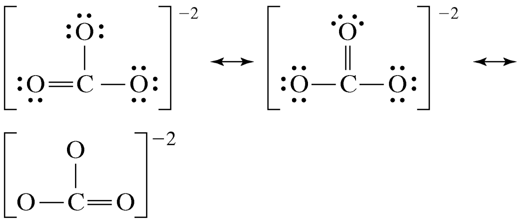
(a)


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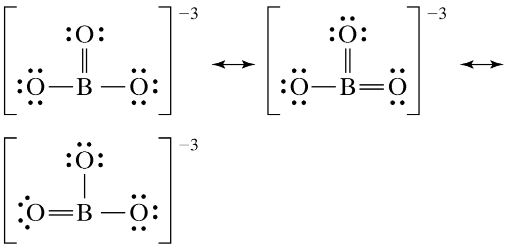

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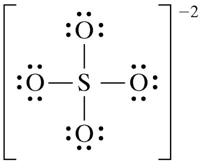
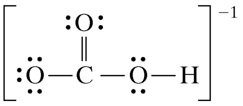
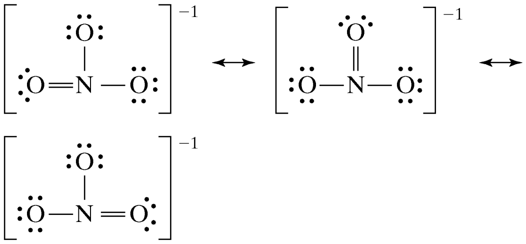
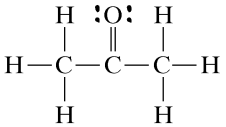


(d)


(e)


(f) $\mathrm{H}-\mathrm{C}\equiv\mathrm{C}-\mathrm{H}$

(g)


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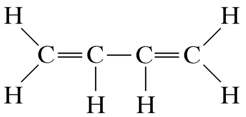

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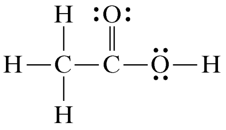

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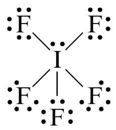

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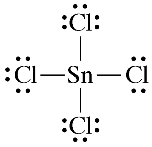

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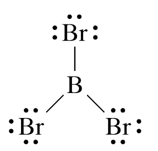

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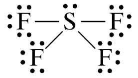

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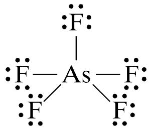

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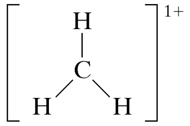

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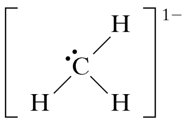

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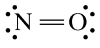
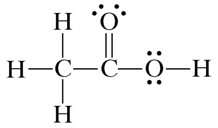


8. BBr$_3$, SF$_4$, AsF$_5$, CH$_{3+}$, NO

9. (a)


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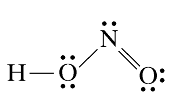

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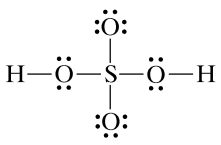

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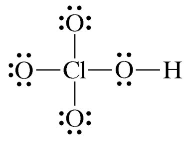

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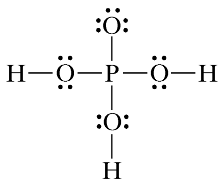

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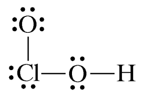
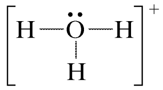


10. (a) and (f)
(b) and (g)
(c) and (d)
(i),(e) and (h)

11. (a)


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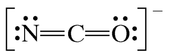

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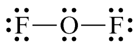

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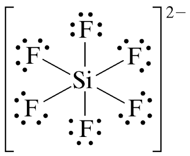
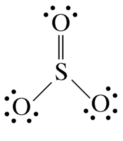


(e) $H-C\equiv N:$

(f)


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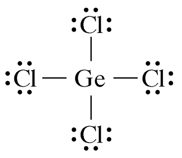
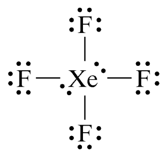
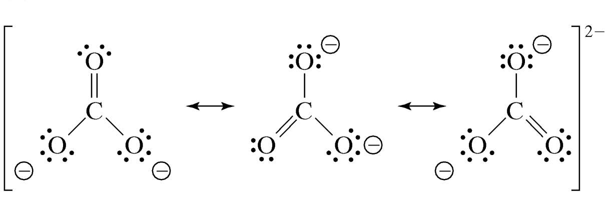
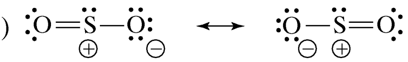


(h)


14. (a)


bond order = 4/3

(b)


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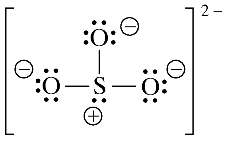


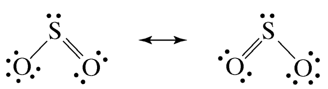
15. As the atom bonded to carbon with a σ bond is changed from carbon to nitrogen to oxygen, the bonding orbitals become progressively smaller, because the nuclear charge is increasing, and thus the bonds are shorter and stronger. This same argument is valid for the second series, in which the atoms are bonded together by a σ bond and a π bond. The trend of the third series is directly related to the bond order; i.e., triple bonds are stronger and shorter than double bonds, which in turn are shorter and stronger than single bonds.

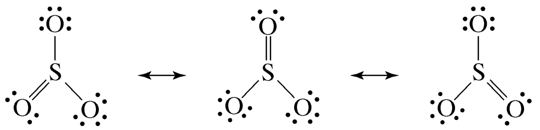
16. a. −1, b. +1, c. 180°, d. sp^2, e. two, f. sp^3

17. This method is based upon the octet rule. Because hydrogen has only two electrons in its valence shell, this method of analysis fails for binary hydrogen compounds.

19. Carbon monoxide is slightly polar, and the greater electron density at one atom can be shared with an electron-deficient center. Diatomic nitrogen is nonpolar, and thus less reactive.

20. Because SO$_4$ is neutral, it may be envisioned as SO$_4^{2-}$ from which two electrons have been taken. This loss of electrons would leave two unpaired electrons on SO$_4$ and thus it would be reactive. Neutral NH$_4$, would have more than eight electrons at the central atom and therefore would be unstable.

21. **1.**


2.


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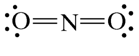

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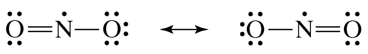
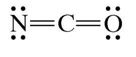
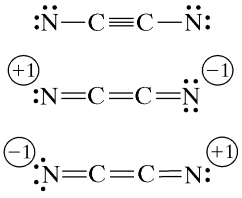


5.


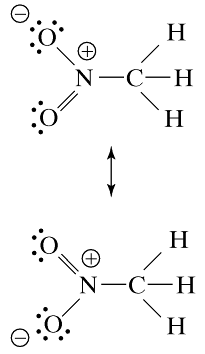
6.



24.

S = +2	C = 0
C = 0	Cl = +3
I = −1	C = 0
N = +1	N = +1
N = 0	N = 0
N = 0	

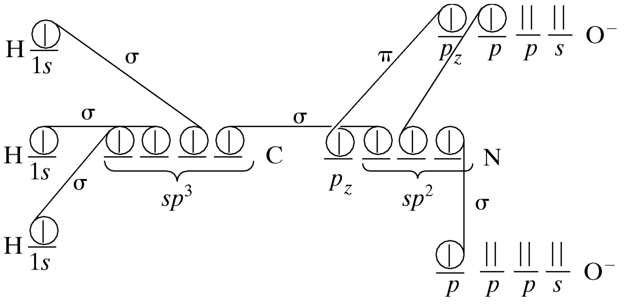
25. a.



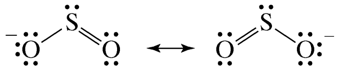
b. BO = 3/2 from resonance structures above. Therefore should be between 1.4 and 1.2, say 1.3 Å.

However, adjacent formal charges will shorten bond somewhat, so NO bond length probably about 1.25.

c. Give the valence bond description of nitromethane in the diagram below. Label every orbital.

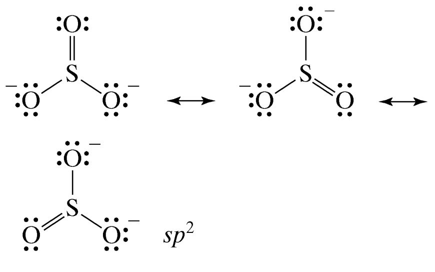


26. (a)



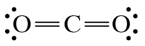
sp^2

(b)



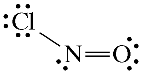
sp^2

(c)



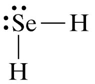
sp

(d)



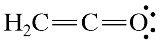
sp^2

(e)



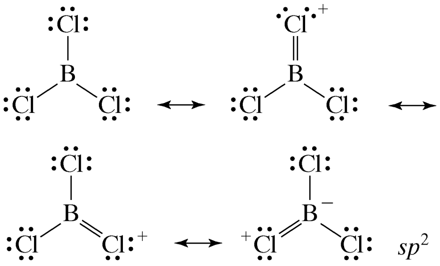
No hybridization

(f)



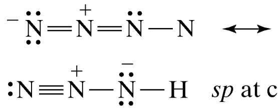
left carbon: sp^2
right carbon: sp

(g)



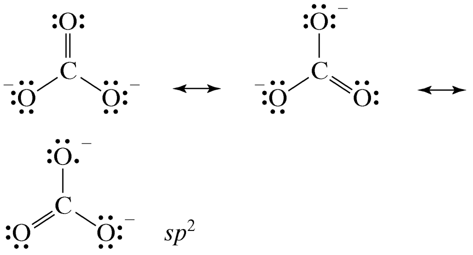
sp^2

(h)



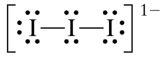
sp at central nitrogen

28. (a)



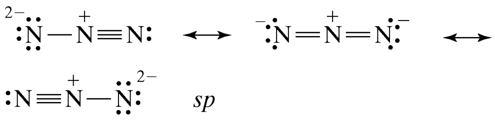
sp^2

(b)



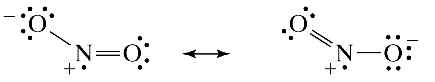
sp^2d

(c)



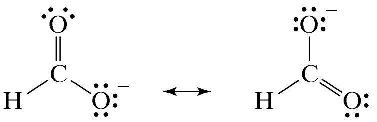
sp

(d)



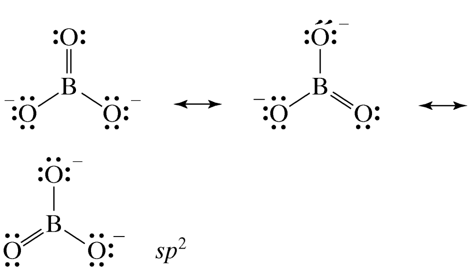
sp^2

(e)



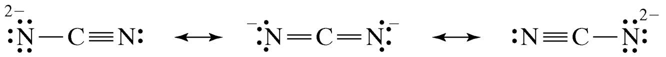
sp^2

(f)

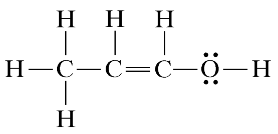


sp^2

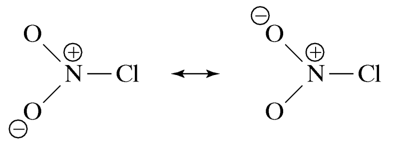
29.



Carbon dioxide is isoelectric; the molecule is linear; bond angle 180°.



34. a.



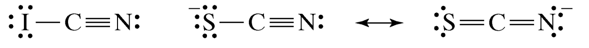
b. trigonal planar

c. *sp*^{2}

d. BO = 1.5

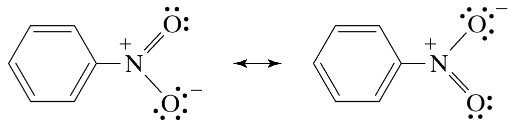
shorter because of opposite formed charges

35.

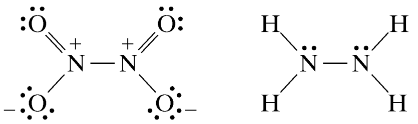


sp hydridization in both species

36.

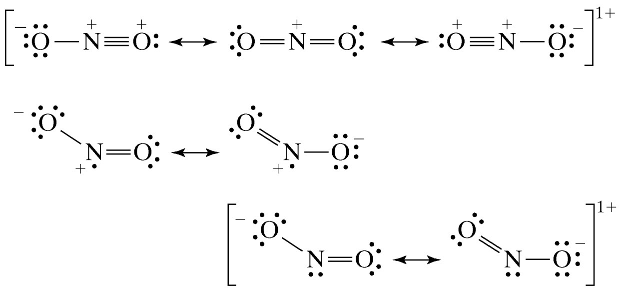


41.



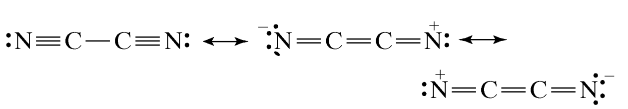
The repulsive interactions between the N_2O_4 nitrogen atoms, which have formal positive charges, force the bond to be longer than the bond in the hydrazine, in which the nitrogen atoms are neutral.

42.



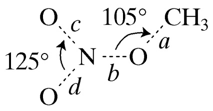
The bond order in the nitronium ion is 2, and the nitrite ion has a bond order of 1.5. Although the bond order in nitrogen dioxide is 1.5, the formal charges should contribute attractive forces that will shorten the bond relative to the nitrite ion.

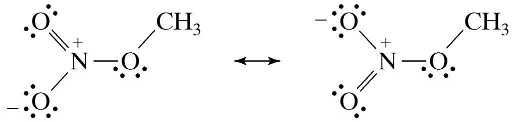
43.



The C—N bond must have considerable triple bond character. Because the C—C bond length is between that of single bonds and that of double bonds, the resonance structures must account for this observation.

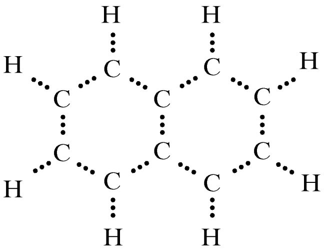
44.

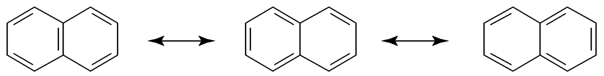




The best structure has an *sp*^{2} hybridized nitrogen atom bonded to three oxygen atoms. This hybridization accounts for the O—N—O bond angle. Additionally, resonance structures help rationalize the equal bond lengths (c and d).

45.





The resonance energy of naphthalene would be greater than that of benzene.

46. The Lewis model is based on the premise that atoms achieve stability by obtaining the electron structure of an inert gas and that covalent bonds are formed by electron pairs. The valence bond model retains the electron-pair bond concept of the Lewis model, but it describes this concept in terms of the overlap of atomic orbitals. The Lewis model rationalizes molecular geometry by assuming that the four electron pairs around an atom are oriented towards the apexes of a tetrahedron. The valence bond model uses hybridization of atomic orbitals and resonance to explain and predict molecular geometry.

47. (a) $(\sigma 1s)^2(\sigma^* 1s)^2$; bond order = 0; unstable

(b) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2$; bond order = 1; stable

(c) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2$; bond order = 0; unstable

(d) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2$; bond order = 3; stable

(e) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2$ $(\pi^* 2p_y)^1(\pi^* 2p_z)^2$; bond order = 2; stable

(f) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2$ $(\pi^* 2p_y)^1$; bond order = 2.5; stable

(g) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2$ $(\pi^* 2p_y)^2(\pi^* 2p_z)^1$; bond order = 1.5; stable

(h) $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2$ $(\pi^* 2p_y)^2(\pi^* 2p_z)^2$; bond order = 1; stable

(i) $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2(\pi^*2p_y)^1$; bond order = 2.5; stable

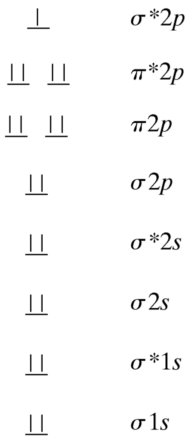
(j) $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2$; bond order = 3; stable

(k) $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2(\pi^*2p_y)^2(\pi^*2p_z)^2$; bond order = 1; stable

48. $O_2^- > O_2 > O_2^+$ parallels bond order trend of 1.5, 2.0, 2.5
$NO > NO^+$ because the bond order for NO is 2.5 whereas the bond order for the cation is 3.0

$NO^+ > N_2$ because oxygen has a greater electronegativity than nitrogen and because oxygen is slightly smaller.

49. a.



b. $\text{BO} = \dfrac{10 - 9}{2} = 1/2$

paramagnetic because of unpaired e^-

c. $F_2 + e^- \rightarrow F_2^-$
No.
BO in $F_2 = 1$
BO in $F_2^- = 1/2$
Therefore F_2^- less stable than F_2.

53. (a) An atomic orbital is a description of the probable location of a given electron about the nucleus of an atom. A molecular orbital is a combination of atomic orbitals and is associated to some extent with the entire molecule.

(b) Bond length is the distance between adjacent atoms that are bonded to each other. The bond order is a measure of the extent of the bonding interaction between adjacent atoms.

(c) An ionic compound is held together by electrostatic attractive forces between ions, which are formed by the transfer of an electron from one species to another. A covalent compound possesses bonds that result when adjacent atoms share electrons.

(d) The valence bond model is based upon the electron-pair concept for bonding and employs atomic orbitals or hybrid orbitals. In the molecular orbital model every electron in a molecule exists in an orbital that is associated with the entire molecule.

(e) A resonance hybrid is the structure of a molecule in which the electrons are delocalized based upon the combination of a number of valence bond descriptions of the molecule. An electron dot structure shows the location of electrons in a molecule for one given structure.

(f) The electron density of a sigma bond (σ bond) is located along the bond axis; i.e., along the line connecting the two nuclei of the atoms involved in the bond. A pi bond (π bond) is formed by the overlap of orbitals above and below the bond axis. A π bond is weaker than a σ bond, and rarely forms between two atoms unless the atoms are also bonded with a σ bond.

(g) Atomic orbitals define the probable locations of electrons around the nucleus of an atom. Hybrid orbitals are combinations of atomic orbitals for a given atom. The number of hybrid orbitals formed is equal to the number of atomic orbitals that are combined. Thus, orbitals are conserved.

54. 1. b 2. a 3. b 4. d 5. b 6. b
7. a 8. b 9. a 10. d 11. c 12. a

CHAPTER 7

4. Both methyl groups would be planar, but they would be in perpendicular, intersecting planes. The confirmation with all of the atoms in the same plane would produce greater repulsions between the hydrogens on adjacent carbons.

5. (a) (c,f) (g,h)
(b) a, h
(c) g, h

6. (a) NH_3 has three sigma bonds and one lone pair, giving it a pyramidal shape. NO_3^- has three sigma bonds, giving it a trigonal planar shape.

(b) Both molecules have the same electron-dot formulas and therefore should have pyramidal shapes. Apparently phosphine uses little hybridization (just its *p*-orbitals) and there seems to be no simple explanation.

(c) NF_3 has three sigma bonds and one lone pair and is therefore pyramidal. BF_3 has three sigma bonds and is trigonal planar.

(d) ClF_3 has three sigma bonds and two lone pairs. The fluorines are located on an equatorial and the two axial positions of a trigonal bipyramid. The molecule is T-shaped.

(e) Although both have the same number of sigma bonds and lone pairs, the bond angle for NF_3 is smaller than that for NH_3. This smaller bond angle could be explained in several ways: a) that the repulsion between the lone pair and the bonded pairs is greater in NF_3, probably because of the presence of fluorine atoms that have three lone pairs of their own, and b) that the repulsion between the bonded pairs is less in NF_3 because the bonded electrons are more tightly confined to the space between the nitrogen and the very electronegative fluorine (moreover, the fluorine's high electronegativity pulls electron density away from the region near the nitrogen where the repulsions are the greatest).

7. (a) linear sp (b) tetrahedral sp^3 (c) square pyramid sp^3d^2 (d) see-saw sp^3d (e) pyramidal sp^3 (f) tetrahedral sp^3 (g) bent sp^2 (h) trigonal planar sp^2 (i) trigonal planar sp^2 (j) bent sp^2 (k) octahedral sp^3d^2 (l) tetrahedral sp^3 (m) square planar sp^3d^2 (n) T-shape sp^3d (o) pyramidal sp^3 (p) linear sp^3d (q) bent sp^3 (r) square planar sp^3d^2 (s) pyramidal sp^3 (t) bent sp^3 (u) tetrahedral sp^3 (v) pyramidal sp^3

8. a. BF_3, CO_3^{2-}, NO_3^-

b. BF_3, CO_3^{2-}, NO_3^- and OH_3^+, NF_3

c. BF_3, CO_3^{2-}, NO_3^- are all trigonal planar OH_3^+, NF_3 are pyramidal

9. a. CO_2 and NO_2^+

H_2O and SCl_2

b. CO_2 and NO_2^+ are linear

H_2O and SCl_2 are bent

10. a. 0; b. 1; c. 0, d. 0, e. 1; f. 2; g. 3; h. 0; i. 1; j. 0

12. The lone pairs are located on the equatorial position of a trigonal bipyramid and therefore exert equal repulsions on both axial iodines.

13. BrF_2^+ bent sp^3 BrF_4^- square planar sp^3d^2

14. (a) $\frac{85.6\text{ g C}}{12.0\text{ g/mol}} = 713\text{ mol C}$

$\frac{14.5\text{ g H}}{1.00\text{ g/mol}} = 14.4\text{ mol H}$

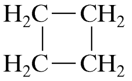
empirical formula = CH_2

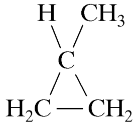
$\frac{56\text{ g/mol}}{14\text{ g/emp}} = 4$

molecular formula = C_4H_8

(b) $CH_2CH{=}CHCH_2$ $H_2C{=}CHCHCH_2$

$H_2C{=}C(CH_3)_2$





(c) six, 2-butene has two geometrical isomers

15. $\frac{0.295\text{ g Xe}}{131\text{ g/mol}} = 0.00225\text{ mol Xe}$

$\frac{0.173\text{ g F}}{19.0\text{ g/mol}} = 0.0091\text{ mol F}$

empirical and molecular formula = XeF_4
The molecule should be square planar.

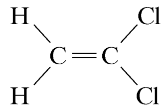
16. (a) trigonal planar (b) pyramidal (d) trigonal bipyramidal (e) octahedral

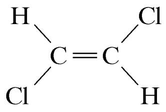
(c) and (d) exhibit geometrical isomerism

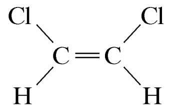
(b) exhibits optical isomerism

17.

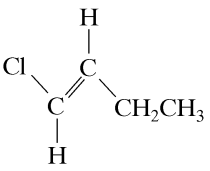
(a)

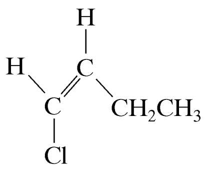


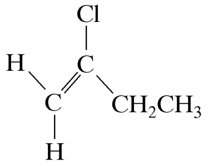


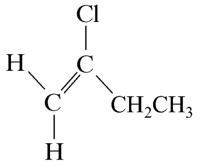


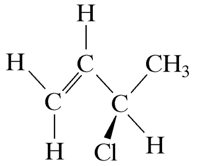
(b)

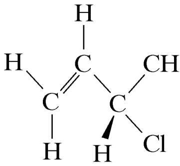


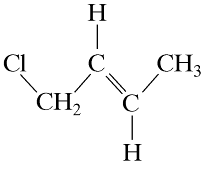


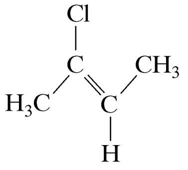


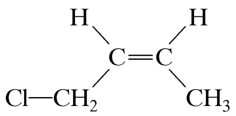


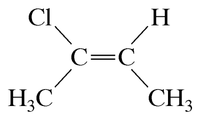


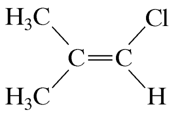


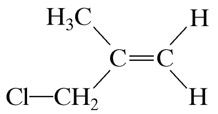






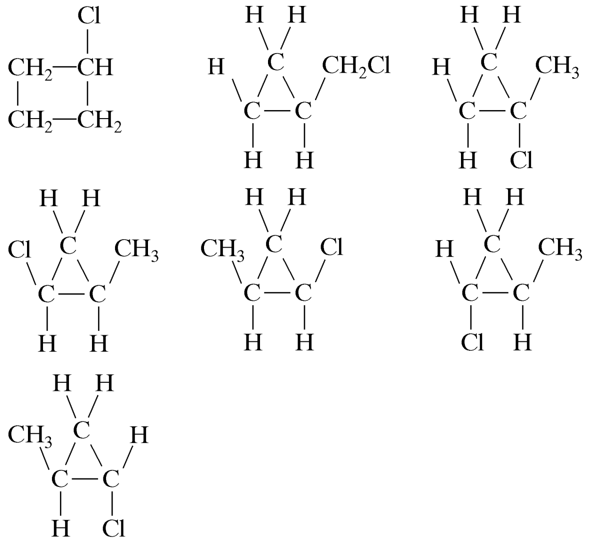




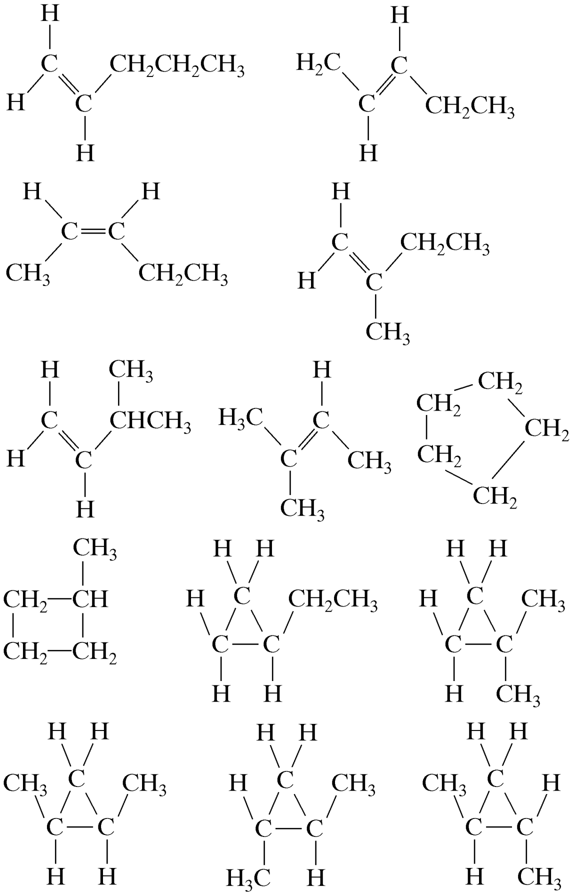


(b) *Continued on next page*

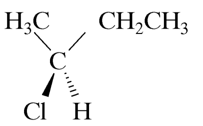
(b)

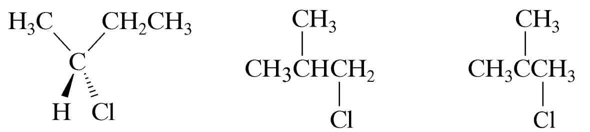


(c)



(d) Cl—$CH_2CH_2CH_2CH_3$



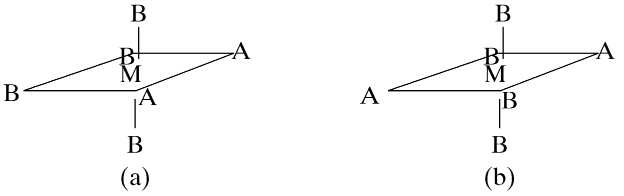


18. No, the carbons containing the triple bond have *sp* hybridization and the carbon skeleton is therefore linear. Hence, only one three-dimensional arrangement of the atoms can exist.

20. a. One

b. Three. Yes, (b) and (c) have nonsuperimposable mirror images.

21. The following are geometric isomers:



(a) (b)

Neither exhibts optical isomerism and (b) has no dipole moment.

23. (a) Structural isomers have the same molecular formulas but different structural formulas. Stereoisomers have the same structural formula but different configurations in three dimensions.

(b) A molecular formula provides the identity and numbers of atoms in a structure. A structural formula indicates the sequence in which the atoms are bonded to each other in the molecule.

(c) Geometrical isomers consist of two different configurations that result from the absence of rotation about a double bond. They are usually designated *cis* or *trans*, and they have different physical properties. Optical isomers, which are also known as enantiomers, are nonsuperimposable mirror images of each other. Optical isomers have identical physical properties except in their abilities to rotate plane-polarized light.

(d) Translation refers to the motion of an entire molecule in three-dimensional space. Rotation refers to the spinning movement of a molecule (or portion of a molecule) about a central axis.

24. (a) 1,1-dichloroethane and 1,2-dichloroethane

(b) 1-chloropropane and 2-chloropropane

(c) 1,1-dibromopropane, 1,2-dibromopropane, 1,3-dibromopropane and 2,2-dibromopropane

25. The color purple results from transmittance of blue and red, thus yellow and green are absorbed. In blue light it will appear blue; in red light it will appear red, and in green light it will appear black.

26. Colored substances absorb visible light and undergo an electronic transition. In many compounds that difference in energy between the electronic energy levels (the molecular orbitals) is larger and requires ultraviolet light for a transition from one level to another. These compounds therefore do not absorb visible light and are not colored.

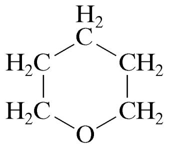
27. black

28. The frequency of the absorptions is controlled by the reduced mass and the strength of the bond. The frequency of the C—H bond is greater than that of the C—O bond primarily because of the reduced mass, while C=O > C—O because of the greater strength of the double bond.

29. The absorption at 3.0 indicates the presence of an O—H bond and therefore the compound is methanol. This assignment is confirmed by the absence of an absorption around 6.0, the area typical for carbonyl groups.

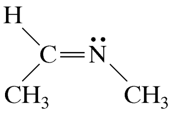
30. empirical formula and molecular formula = $C_5H_{10}O$

The infrared spectrum indicates no OH or C=O or C=C groups. Therefore, the compound is probably an ether with no unsaturation. In order to have five carbons and ten hydrogens and an ether functional group the compound must be cyclic



31. molecular formula = C_3H_7N

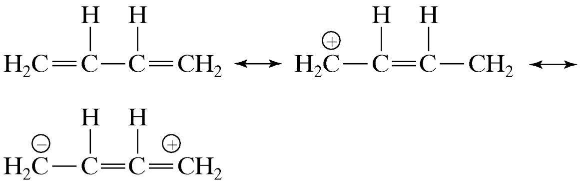
The infrared data indicates that a C=N bond is present. The compound



fits the data and exhibits geometric isomerism.

32. The frequency of the absorptions is controlled by the reduced mass and the strength of the bond. The frequency of the O—H bond is greater than that of the O—D bond because of the smaller reduced mass of the O—H group (deuterium is twice as heavy as hydrogen). [The strength of the O—H and O—D bonds are the same.]

33.



$$H_2C=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=CH_2 \longleftrightarrow \overset{\oplus}{H_2C}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2 \longleftrightarrow$$

$$\overset{\ominus}{H_2C}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}=\overset{\oplus}{CH_2}$$

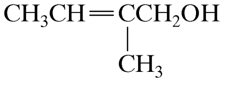
$E = n^2h^2/(8md^2)$

$E_3 - E_2 = 15.06 \times 10^{-19}\,J - 6.69 \times 10^{-19}\,J = 8.37 \times 10^{-12}\,J$

$\lambda = hc/E = (6.6 \times 10^{-34}\,J\text{-sec})(3.00 \times 10^{8}\,m/sec)/(8.37 \times 10^{-19}\,J) = 2.37 \times 10^{-7}\,m = 237\,nm$

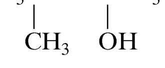
This wavelength is in the ultraviolet and therefore the compound is not colored.

34.
1. b
2. (a)



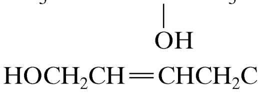
$CH_3CH=\underset{\underset{CH_3}{|}}{C}CH_2OH$

(b)



$CH_3\underset{\underset{CH_3}{|}}{C}=\underset{\underset{OH}{|}}{C}CH_3$

(c)



$CH_3CH=CH\underset{\underset{OH}{|}}{C}HCH_3$

(d) $HOCH_2CH=CHCH_2CH_3$

c

3. c
4. d
5. b
6. d
7. b
8. d
9. a
10. c
11. a
12. b

CHAPTER 8

1. (a) Isotopes are atoms that have the same atomic number but different atomic masses. Allotropes are different forms of a given element that exist in the same physical state; e.g., diatomic oxygen (O_2) and ozone (O_3) are allotropes of oxygen.

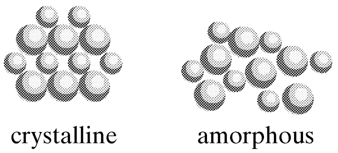
(b) An ionic crystal is composed of ions that are arranged in the lattice and held together by electrostatic forces. In a molecular crystal, individual molecules form the lattice, and they are held together by intermolecular forces; e.g., dipole-dipole, H-bonding, van der Waals.

(c) The heat of fusion is the heat energy required to change a solid to a liquid at its melting point. The heat of crystallization is the energy that is released as a liquid forms a solid at its freezing point.

(d) A polar bond is one in which the electronegativities of the two atoms involved in the bond are different. A polar molecule is one in which the sum of all the bond polarities is not zero; i.e., the electron density of the molecule is distorted by the different electronegativities of the atoms present.

(e) Vapor pressure is the pressure exerted by the molecules of a vapor (gas) that is in equilibrium with its liquid. The rate of evaporation refers to the amount of liquid (below its boiling point) that becomes a gas per unit time.

2.



3. If you use the "sea of electrons" model for a metal, it is reasonable to think of the electrons as being anions randomly (and therefore amorphously) distributed around a well-defined lattice of cations. This view has the advantage of explaining the characteristic malleability and ductility of metals (like tar).

4. Silicon carbide possesses a covalent network crystal structure. In this structure, each carbon atom is covalently bonded to four silicon atoms, and each silicon atom is covalently bonded to four carbon atoms.

5. (a) $MgCl_2$ (b) PCl_5 (c) $MgCl_2$ (d) $MgCl_2$
(e) $MgCl_2$ (f) $MgCl_2$

6. Ionic crystals have higher melting points than molecular crystals because electrostatic forces are much greater than intermolecular forces, such as dipole-dipole interactions and H-bonding. These stronger attractive forces in ionic solids also give ionic solids greater heats of fusion and hardness. The weaker attractive forces in molecular solids account for the higher vapor pressures associated with these solids relative to ionic solids.

7. MX_2

8. $\frac{10.0\text{ g}}{108\text{ g/mol}} \times 11.3\text{ kJ/mol} = 1.05\text{ kJ}$

9. Side of cube $= (8r^2)^{1/2} = (8 \times 170^2)^{1/2} = 481\text{ pm} = 4.81 \times 10^{-8}\text{ cm}$

$$\frac{4\text{ atoms/unit cell} \div 6.022 \times 10^{23}\text{ atoms/mol} \times 196.966\text{ g/mol}}{(4.81 \times 10^{-8}\text{ cm})^3} = 11.8\text{ g/cm}^3$$

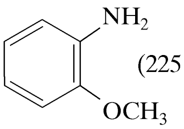
11. PH_3 and H_2S

12. Although the dipole moment of CH_3F is greater (because of the greater difference in electronegativity between C and F vs that of C and I), the greater number of electrons in CH_3I gives that compound the stronger van der Waals forces. CH_3I has the higher boiling point.

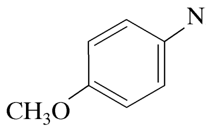
13. $CH_3CH_2CH_3$, C_6H_{12} (cyclohexane), and C_6H_6 (benzene)

14.
a. H_2O
b. H_2O
c. H_2S
d. H_2S
e. H_2O can form hydrogen-bonds between its molecules but H_2S is not capable of forming hydrogen-bonds.

15. (f)



(225 °C)



(243 °C)

(a) greater van der Waals forces in 1-heptene, (b) dipole-dipole interaction in PCl_3, none in $SiCl_4$, (c) unbranched alcohol molecules can get closer, therefore all interactions stronger, (d) acetic acid is molecular, sodium acetate is ionic, (e) greater hydrogen bonding in alcohol, (f) intramolecular H-bonding in ortho derivative, intermolecular H-bonding in para, (g) H-bonding in acid

16. In each pair, the compound with the higher boiling point has the lower vapor pressure, the greater viscosity, and the greater surface tension.

19. The density of the liquid decreases because of the increased molecular motion at higher temperature. The density of the vapor increases at higher temperature because of the greater concentration of molecules in the vapor phase (more liquid has evaporated).

20. If the two phases did not have the same vapor pressure, one phase would be evaporating at a higher rate than the other, with the result that the phase with the higher vapor pressure would be decreasing in amount while the phase with the lower vapor pressure would be increasing in amount. Obviously, if this situation existed, the solid and liquid would not be in equilibrium.

21. (a) Solid $TeCl_4$ is more dense than liquid $TeCl_4$, and increased pressure favors the smaller volume, thus raising the freezing point.
(b) AlF_3 is more ionic than $AlCl_3$.
(c) Ethyl alcohol exhibits hydrogen bonding; methyl ether does not.

22. Because alcohol "wets" the glass, it gives a concave meniscus. Mercury does not "wet" the glass; thus its meniscus is convex.

23. Slow evaporation occurs through the pores of the clay. Because this is an endothermic process, the water inside the pot cools.

24. At 90 °C the water molecules have higher kinetic energy. Therefore, less energy is required to convert water to vapor at 90 °C than at the lower temperature.

25. H_2O exhibits hydrogen bonding; H_2S does not.

26. The boiling point of ethyne is about −85 °C while the boiling point of hydrogen cyanide is about 25 °C. Ethyne is a nonpolar hydrocarbon that experiences only van der Waals interactions, but hydrogen cyanide is polar and therefore experiences stronger dipole-dipole interactions. Also, because HCN is slightly acidic, it may be able to form hydrogen bonds between molecules.

27. (a) HF forms H—bonds but the other acids do not form them. Thus, HF has the highest boiling point. The boiling points decrease from HI through HCl as molecular weight decreases.
(b) As the atomic number decreases, the size of the electron clouds for these atomic species decreases. Larger electron clouds provide stronger van der Waals interactions, and therefore higher boiling points.
(c) These are non-polar compounds so van der Waals interactions will determine the boiling points. Tin tetrachloride, with its high molecular weight and large size, will have the highest boiling point, and carbon tetrachloride, which is the smallest in the series, will have the lowest boiling point.
(d) Water forms a better network of hydrogen bonds than the other two species because it can donate two hydrogens and accept two hydrogens simultaneously.
(e) As the polarity of the molecules in this series decreases so does the boiling point.
(f) Water forms hydrogen bonds and the other compounds do not form them. The boiling point trend for the other three compounds parallels the decrease in their sizes.

29.

	DIPOLE-DIPOLE	VAN DER WAALS	HYDROGEN BONDING
Isopropyl alcohol	X	X	X
Ethyl methyl ether	X	X	
Ethyl fluoride	X	X	
Tin tetrachloride		X	
Acetic acid	X	X	X
Hydrogen sulfide	X	X	

30. 1. van der Waals forces 2. vapor pressure 3. amorphous 4. allotropes 5. Sublimation 6. unit cell 7. x-rays 8. dynamic equilibrium 9. cubic hexagonal 10. covalent network 11. stronger 12. hydrogen-bonding 13. dipole-dipole attraction 14. dipole-dipole interaction 14. vapor pressure 15. decreases

31. 1. (a) 2. (c) 3. (a) 4. (d) 5. (c) 6. (c) 7. (b) 8. (b) 9. (d) 10. (a) 11. (b) 12. (d) 13. (d) 14. (b) 15. (a)

CHAPTER 9

1. $450\text{ mL} \times \dfrac{800\text{ torr}}{760\text{ torr}} = 474\text{ mL}$

2. $800\text{ torr} \times \dfrac{450\text{ mL}}{100\text{ mL}} = 3600\text{ torr}$

3. $1.00\text{ L} \times \dfrac{523\text{ K}}{273\text{ K}} = 1.92\text{ L}$

4. $22.4\text{ L} \times \dfrac{348\text{ K}}{273\text{ K}} \times \dfrac{760\text{ torr}}{850\text{ torr}} = 25.5\text{ L}$

5. $1\text{ atm} \times \dfrac{10\text{ L}}{3.5\text{ L}} \times \dfrac{323\text{ K}}{273\text{ K}} = 3.4\text{ atm}$

8. $742\text{ torr} \times \dfrac{373\text{ K}}{301\text{ K}} = 919\text{ torr}$

9. $\dfrac{98.92\text{ g/mol}}{22.4\text{ L/mol}} = 4.42\text{ g/L}$

10. $V = \dfrac{nRT}{P}$

$$V = \frac{50\text{ g}}{2.0\text{ g/mol}} \times \frac{0.0821\text{ L-atm/mol-K} \times 298\text{ K}}{740\text{ torr/(760 torr/atm)}} = 628\text{ L}$$

11. $\dfrac{g}{V} = \dfrac{PM}{RT}$

$$\frac{g}{V} = \frac{1\text{ atm} \times 38\text{ g/mol}}{0.0821\text{ L-atm/mol-K} \times 305\text{ K}} = 1.52\text{ g/L}$$

12. $P = \dfrac{g}{M}\dfrac{RT}{V}$

$$P = \frac{10.0\text{ g}}{16.0\text{ g/mol}} \times \frac{0.0821\text{ L-atm/mol-K} \times 323\text{ K}}{250\text{ cm}^3/(1000\text{ cm}^3/\text{L})}$$

$= 66.3\text{ atm}$

13. $n = \dfrac{PV}{RT}$

$$n = \frac{750\text{ torr/(760 torr/atm)} \times 200\text{ mL/(1000 mL/L)}}{0.0821\text{ L-atm/mol-K} \times 300\text{ K}}$$

$= 0.00801\text{ mol}; 0.133\text{ mg}$

14. $T = \dfrac{PVM}{gR}$

$$T = \frac{2.0\text{ atm} \times 1.0\text{ L} \times 44\text{ g/mol}}{25\text{ g} \times 0.0821\text{ L-atm/mol-K}} = 43\text{ K}$$

15. $n = \dfrac{PV}{RT}$

$$n = \frac{[1.0 \times 10^{-5}\text{ torr/(760 torr/atm)}][1 \times 10^{-3}\text{ L}]}{0.0821\text{ L-atm/mol-K} \times 373\text{ K}}$$

$= 4.3 \times 10^{-13}\text{ mol}$

$(4.3 \times 10^{-13}\text{ mol})(6.022 \times 10^{23}\text{ molecules/mol})$

$= 2.6 \times 10^{11}\text{ molecules}$

16. $17.0\text{ g/mol} \times \dfrac{742\text{ torr}}{760\text{ torr/atm}} \times \dfrac{1}{(0.0821\text{ L-atm/mol-K} \times 303\text{ K})} = 0.667\text{ g/L}$

17.
$$\frac{0.993\text{ atm} \times (0.87 \times 16.043\text{ g/mol} + 0.13 \times 30.069\text{ g/mol})}{0.08205\text{ L-atm/mol-K} \times 285\text{ K}}$$

$= 0.759\text{ g/L}$

18. $\dfrac{1.075\text{ g} \times 0.0821\text{ L-atom/mol-K} \times 302\text{ K}}{0.275\text{ L} \times 744\text{ torr/760 torr/atm}} = 99.0\text{ g/mol}$

21. $\dfrac{4.98\text{ g/L} \times 0.08205\text{ L-atom/mol-K} \times 323\text{ K}}{0.484\text{ atm}} = 273\text{ g/mol}$

Empirical formula: $C_{8.78/12.011}Cl_{77.32/35.453}F_{13.90/18.9984}C_{0.731}Cl_{2.181}F_{0.732}C_1Cl_3F_1$

Molecular formula: $C_2C_{l6}F_2$

22. $M = \dfrac{gRT}{PV}$

$$M = \frac{0.110\text{ g} \times 0.0821\text{ L-atom/mol-K} \times 301\text{ K}}{744\text{ torr/(760 torr/atm)} \times 51.0\text{ mL/(100 mL/L)}}$$

$= 54.4\text{ g/mol}$

23. $\dfrac{1.5\text{ g} \times 0.0821\text{ L-atom/mol-K} \times 303\text{ K}}{0.350\text{ L} \times (740 - 32\text{ torr})/760\text{ torr/atm}} = 114\text{ g/mol}$

24. $M = \dfrac{gRT}{VP}$

$$M = \frac{2.37\text{ g} \times 0.0821\text{ L-atom/mol-K} \times 298\text{ K}}{1\text{ L} \times 735\text{ torr/(760 torr/atm)}}$$

$= 60.0\text{ g/mol}$

25. $PV = nRT$

$$n = \frac{PV}{RT} = \frac{\left(\frac{500}{760}\right)(1.0)}{(0.0821)(298)} = 2.7 \times 10^{-2}\text{ mol}$$

$2.7 \times 10^{-2} \times m = 0.20\text{ g}$

$m = 7.4$

26. $M = \dfrac{gRT}{PV}$

$$M = \frac{0.523\text{ g} \times 0.0821\text{ L-atom/mol-K} \times 303\text{ K}}{(752 - 32)\text{ torr/(760 torr/atm)} \times 0.456\text{ L}}$$

$= 30.1\text{ g/mol}$

27. (a) $\dfrac{88.8\text{ g}}{12\text{ g/mol}} = 7.4\text{ mol C}$ $\dfrac{11.2\text{ g}}{1.0\text{ g/mol}} = 11.2\text{ mol H}$

$7.4{:}11.2 = 2{:}3$

empirical formula = C_2H_3

(b) $M = \dfrac{gRT}{VP}$

$$M = \frac{2.12\text{ g} \times 0.0821\text{ L-atm/mol-K} \times 304\text{ K}}{1\text{ L} \times 742\text{ torr/(760 torr/atm)}}$$

$= 54.2\text{ g/mol}$

(c) $\dfrac{54.2\text{ g/mol}}{27\text{ g/emp.form.}} = 2$

molecular formula = C_4H_6

28. (a) $\dfrac{34.30}{58.7} = 0.584\text{ mol Ni}$

$\dfrac{28.10}{12.0} = 2.34\text{ mol C}$

$\dfrac{37.60}{16.0} = 2.35\text{ mol O}$

empirical formula = $Ni(CO)_4$

(b) $\dfrac{6.57\text{ g} \times 0.0821\text{ L-atm/mol-K} \times 313\text{ K}}{1\text{ L} \times 750\text{ torr/(760 torr/atm)}} = 171\text{ g/mol}$

molecular formula = $Ni(CO)_4$

29. (a) $10\text{ g} \times 0.0922 = 0.922\text{ g}$

$\dfrac{0.922}{10.811} \times 6 \times 10^{23} 5.1 \times 10^{22}$ atoms

(b) $\dfrac{9.22\text{ g}}{10.811} = 0.853$ moles boron 1

$\dfrac{91.78}{35.45} = 2.589$ moles Cl

BCl_3

(c) $10.4\text{ g/L} \times 22.4\text{ L/mol} = 233$

(d) $10.81 + 3(35.45) = 117.16$

B_2Cl_6

30. $P_{H_2} = 750\text{ torr} \times \dfrac{50\text{ mL}}{150\text{ mL}} = 250\text{ torr}$

$P_{At} = 450\text{ torr} \times \dfrac{75\text{ mL}}{150\text{ mL}} = 225\text{ torr}$

$P_{O_2} = 350\text{ torr} \times \dfrac{100\text{ mL}}{150\text{ mL}} = 233\text{ torr}$

708 torr = total pressure

31. (a) $\dfrac{20.95\text{ mol }O_2}{100\text{ mol air}} \times \dfrac{32.00\text{ g }O_2}{1\text{ mol }O_2} = 6.704\text{ g }O_2\text{/mol air}$

$\dfrac{78.09\text{ mol }N_2}{100\text{ mol air}} \times \dfrac{28.01\text{ g }N_2}{1\text{ mol }N_2} = 21.87\text{ g }N_2\text{/mol air}$

$\dfrac{0.93\text{ mol Ar}}{100\text{ mol air}} \times \dfrac{39.95\text{ g Ar}}{1\text{ mol Ar}} = 0.37\text{ g Ar/mol air}$

$\dfrac{0.03\text{ mol }CO_2}{100\text{ mol air}} \times \dfrac{44.01\text{ g }CO_2}{1\text{ mol }CO_2} = \dfrac{0.01\text{ g }CO_2\text{/mol air}}{28.95\text{ g/mol air}}$

(b) $\dfrac{0.93\text{ mol Ar}}{100\text{ mol air}} = 0.0093\text{ mol Ar/mol air}$

(c) $\dfrac{0.03\text{ mol }CO_2}{100\text{ mol air}} \times 1\text{ atm} = 0.0003\text{ atm}$

32. $222\text{ mL} \times \dfrac{273\text{ K}}{303\text{ K}} \times \dfrac{(750 - 32)\text{ torr}}{760\text{ torr}} = 189\text{ mL}$

33. $V = \dfrac{gRT}{MP}$

$V = \dfrac{5.00\text{ g} \times 0.0821\text{ L-atm/mol-K} \times 298\text{ K}}{16.0\text{ g/mol} \times (758 - 24)\text{ torr/(760 torr/atm)}}$

$= 7.92\text{ L}$

34. (a) $P_{H_2O} = \dfrac{gRT}{MV}$

$P_{H_2O} = \dfrac{0.234\text{ g} \times 0.0821\text{ L-atm/mol-K} \times 298\text{ K}}{18.02\text{ g/mol} \times 10\text{ L}}$

$= 0.03128\text{ atm}$

$0.03128\text{ atm} \times 760\text{ torr/atm} = 23.8\text{ torr}$

(b) $P_{air} = 760\text{ torr} - 23.8\text{ torr} = 736\text{ torr}$

$10\text{ L} \times \dfrac{736\text{ torr}}{760\text{ torr}} = 9.68\text{ L}$

35. $P_{C_6H_6} = \dfrac{1.5912\text{ g} \times 0.0821\text{ L-atm/mol-K} \times 293\text{ K}}{78.11\text{ g/mol} \times 5.0\text{ L}}$

$= 0.098\text{ atm}$

$0.098\text{ atm} \times 760\text{ torr/atm} = 74.5\text{ torr}$

36. $V = \dfrac{(13 \times 10^2\text{ cm})(5.5 \times 10^2\text{ cm})(3.5 \times 10^2\text{ cm})}{1000\text{ cm}^2\text{/L}}$

$= 2.5 \times 10^5\text{ L}$

$g = \dfrac{PVM}{RT}$

$$g = \frac{(0.40 \times 25.2)\text{ torr/(760 torr/atm)} \times 2.5 \times 10^5\text{ L} \times 18\text{ g/mol}}{0.0821\text{ L-atm/mol-K} \times 299\text{ K}} = 2.4 \times 10^3\text{ g}$$

37. $Cl_2 < SO_2 < CO_2 < H_2S < N_2 < CH_4$

38. $\dfrac{\text{rate(gas)}}{\text{rate}(O_2)} = \sqrt{\dfrac{M(O_2)}{M(\text{gas})}}$

$M(\text{gas}) = \dfrac{\text{rate}(O_2)^2 \times M(O_2)}{\text{rate(gas)}^2}$

$M(\text{gas}) = \dfrac{(14.1\text{ mL/s})^2 \times 32\text{ g/mol}}{(10.0\text{ mL/s})^2} = 63.6\text{ g/mol}$

39. $\dfrac{\text{rate}(235)}{\text{rate}(238)} = \text{R352 g/mol, 349 g/mol)} = 1.004$

40. (a) As the temperature of the gases inside the bottle increases, the internal pressure increases ($P = nRT/V$). Eventually, the internal pressure is so much greater than the atmospheric pressure on the outside of the bottle, that the bottle must break to relieve the stress.

(b) The molecules of a real gas experience some attractive forces. When the gas expands, these forces must be broken and energy must be absorbed. Thus, the expansion of a gas, which is compressed, is analogous to the evaporation of a liquid, which is also an endothermic process.

(c) At low pressures the volume occupied by the molecules is negligible because they are so far apart. At high pressures the gas molecules are forced into a smaller volume (i.e., closer together), and their volumes are not negligible.

(d) Ammonia is capable of hydrogen bonding, and therefore a higher temperature is required to prevent these intermolecular forces from "taking over" even at extremely high pressures. Nitrogen has only van der Waals attractive forces, and thus a lower temperature is required to prevent any intermolecular forces from being able to produce condensation.

(e) Although both species can experience only weak van der Waals interactions, argon, which is larger, will have stronger inter-atomic attractive forces than helium. Therefore, it will require a lower temperature to prevent the attractive forces of helium from producing a liquid regardless of the pressure than will be required for argon.

(f) Although these compounds have the same molecular formula, the alcohol is capable of forming hydrogen bonds and the ether is not. Thus, a higher temperature will be required to prevent H-bonding from producing a liquid, regardless of the pressure.

41. Diatomic hydrogen has extremely weak attractive forces because it is nonpolar and has a small electron cloud. Therefore, very little kinetic energy (i.e., low temperature) is required to prevent these molecules from condensing.

42. $\Delta G = \Delta H - T\Delta S$; $\Delta G = 0$

$$\Delta S = \frac{\Delta H}{T} = \frac{10.9 \text{ kJ/mol}}{(660 + 273)\text{ K}} = 0.0117 \text{ kJ/mol-K}$$

$$= 11.7 \text{ J/mol-K}$$

43. $$\Delta S = \frac{\Delta H}{T} = \frac{6020 \text{ J/mol}}{273 \text{ K}} = 22.1 \text{ kJ/mol-K}$$

$$T = \frac{\Delta H}{\Delta S} = \frac{6490 \text{ J/mol}}{22.1 \text{ J/mol-K}} = 294 \text{ K}$$

$294 - 273 = 21$ °C

44. For H_2O: $$\Delta S = \frac{6020 \text{ J/mol}}{273 \text{ K}} = 22.1 \text{ J/mol-K}$$

For D_2O: $$\Delta S = \frac{6490 \text{ J/mol}}{276.8 \text{ K}} = 23.4 \text{ J/mol-K}$$

46. 98.6 °F = 37 °C = 310 K
$\Delta G = \Delta H - T\Delta S = 2090 \text{ J/mol} - 310 \text{ K}(6.95 \text{ J/mol-K})$
$\Delta G = -64.5 \text{ J/mol}$
Because $\Delta G < 0$, the cesium will spontaneously melt at 98.6 °F (37 °C)

47. $$\Delta S = \frac{\Delta H}{T} = \frac{35200 \text{ J/mol}}{337.7 \text{ K}} = 104 \text{ J/mol-K}$$

48. rhombic → monoclinic $\Delta H = 71, \Delta S = 0.16$
$\Delta G = 71 \text{ cal/mol} - (298 \text{ K} \times 0.16 \text{ cal/mol-K})$
$\Delta G = +23 \text{ cal/mol}$
not spontaneous; rhombic is stable

49. 1. (d) 2. (c) 3. (d) 4. (a) 5. (b) 6. (c) 7. (a) 8. (b) 9. (b) 10. (b) 11. (d) 12. (d) 13. (c) 14. (d) 15. (d) 16. (c) 17. (b) 18. (c) 19. (d) 20. (d) 21. (c) 22. (b) 23. (c) 24. (c) 25. (c) 26. (c)

50. 1. (a), 2. (b), 3. (b), 4. (c), 5. (d) 6. (c), 7. (c), 8. (e), 9. (b), 10. (a), 11. (c), 12. (b), 13. (d), 14. (b), 15. (a), 16. (b), 17. (d), 18. (e), 19. (c), 20. (c)

CHAPTER 10

1. (a) The solute of a solution is the species that is dissolved in the solvent, and the solvent is the component of the solution that retains its original physical state.

(b) Solubility refers to the amount of a given substance that may be dissolved in a specified volume of solvent. The rate of solution refers to the time required for a given quantity of solute to dissolve in the solvent.

(c) In a saturated solution the dissolved solute is in equilibrium with undissolved solute. An unsaturated solution contains less solute than the saturated equilibrium amount.

(d) Molarity (M) is the concentration of a solution given in terms of moles of solute per liter of solution, but molality (m) is the concentration of a solution in terms of moles of solute per kilogram of solvent.

(e) An electrolyte is any substance that, when dissolved in water, produces a solution that conducts electric current.

(f) A strong electrolyte is one that ionizes completely in solution, and a weak electrolyte is one that does not completely dissociate (ionize) in solution.

(g) An acid anhydride is an oxide of a nonmetal that forms an aqueous acid when it reacts with water. A basic anhydride is a metal oxide that forms a basic solution when it reacts with water.

(h) A solution is a single-phase, homogeneous mixture. A colloid is a mixture in which the dispersed particles are too large to yield a true solution but are too small to be visible or to "settle out."

2. (a) and (d) are more soluble in water; all others are more soluble in benzene.

3. $$0.7809 \times \frac{742 \text{ torr}}{760 \text{ torr}} \times 0.0162 \text{ g/L} \times 1 \text{ L} = 0.0124 \text{ g}$$

4.
$$\begin{array}{rr}
\text{AgF}(s) \longrightarrow \text{Ag}^+(g) + \text{F}^-(g) & \Delta H = 967 \text{ kJ/mol} \\
\text{Ag}^+(g) + \text{F}^-(g) \longrightarrow \text{Ag}^+(aq) + \text{F}^-(aq) & \Delta H = 987 \text{ kJ/mol} \\
\hline
\text{AgF}(s) \longrightarrow \text{Ag}^+(aq) + \text{F}^-(aq) & \\
 & \Delta H_{\text{soln}} = 967 \text{ kJ/mol}
\end{array}$$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = -20 \text{ kJ/mol} - 298 \text{ K}(-0.0198 \text{ kJ/mol-K})$

$\Delta G = -14.1 \text{ kJ/mol}$

Because $\Delta G < 0$ AgF should dissolve

$$\begin{array}{rr}
\text{AgCl}(s) \longrightarrow \text{Ag}^+(g) + \text{Cl}^-(g) & \Delta H = 918 \text{ kJ/mol} \\
\text{Ag}^+(g) + \text{Cl}^-(g) \longrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq) & \Delta H = 852 \text{ kJ/mol} \\
\hline
\text{AgCl}(s) \longrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq) & \\
 & \Delta H_{\text{soln}} = 66 \text{ kJ/mol}
\end{array}$$

$\Delta G = 66 \text{ kJ/mol} - 298\ (0.0317 \text{ kJ/mol-K})$

$\Delta G = 56.5 \text{ kJ/mol}$

Because $\Delta G > 0$, AgCl is not soluble

5. The dissolution of ammonium nitrate is an endothermic process. Therefore, as it dissolves it will cause the temperature of the solution to drop to a temperature below the freezing point of water.

6. $\dfrac{25 \text{ g NaCl}}{25 \text{ g NaCl} + x \text{ g H}_2\text{O}} \times 100\% = 10.0\%$

$x = 225 \text{ g H}_2\text{O}$

7. $25.0 \text{ g solution} \times \dfrac{42.5 \text{ g riboflavin}}{10^6 \text{ g solution}} = 1.06 \times 10^{-3} \text{ g}$

8. (a) $\dfrac{5.00 \text{ mL}}{1000 \text{ mL}} \times 100\% = 0.500 \text{ vol-\%}$

(b) $\dfrac{5.00 \text{ mL}}{1000 \text{ mL}} \times 10^6 = 5.00 \times 10^3 \text{ ppm (vol)}$

9. $\text{Molarity} = \dfrac{\text{moles solute}}{\text{liter of solution}}$

$= \dfrac{1.50 \text{ g}/164 \text{ g/mol Ca(NO}_3)_2}{0.0200 \text{ L}}$

$= 0457 \text{ M Ca(NO}_3)_2,$

10. $M_1V_1 = M_2V_2$

(3.0 mol/L) (0.100 L) = (0.65 mol/L) (X L)

X L = 0.461 L = 461 mL total volume of solution after dilution water added is: 461 mL − 100 mL = 361 mL

11. (a) $0.50 \text{ mol/L} \times 1 \text{ L} \times 101 \text{ g/mol} = 51 \text{ g KNO}_3$

Dissolve KNO_3 in enough water to make 1.00 L of solution.

(b) $\dfrac{0.25 \text{ mol}}{1 \text{ L}} \times \dfrac{250 \text{ mL}}{1000 \text{ mL/L}} \times \dfrac{1\text{L}}{1 \text{ mol}} = 0.063 \text{ L} = 63 \text{ mL}$

Dilute 63 mL of the stock solution to a total volume of 250 mL.

(c) $\dfrac{0.15 \text{ mol Cl}^{-+}}{1 \text{ L}} \times \dfrac{1 \text{ mol CaCl}_2{\cdot}2 \text{ H}_2\text{O}}{2 \text{ mol Cl}^-} \times$

$\dfrac{500 \text{ mL}}{1000 \text{ mL/L}} \times 147 \text{ g/mol} = 5.5 \text{ g CaCl}_2$

Dissolve the $\text{CaCl}_2{\cdot}2\text{H}_2\text{O}$ in enough water to make 500 mL of solution.

(d) $0.50 \text{ mol} \times 82 \text{ g/mol} = 41 \text{ g NaC}_2\text{H}_3\text{O}_2$

Dissolve the sodium acetate in 1.00 kg of water.

(e) $\dfrac{15 \text{ g NaOH}}{85 \text{ g H}_2\text{O}} \times 500 \text{ g H}_2\text{O} = 88 \text{ g NaOH}$

Dissolve the NaOH in 500 g of water.

12. $\dfrac{0.997 \text{ g} \div 18.015 \text{ g/mol}}{1.00 \times 10^{-3} \text{ L}} = 55.3 \text{ M}$

13. (a) $\dfrac{0.20 \text{ mol AgNO}_3}{1 \text{ L}} \times \dfrac{1 \text{ mol Ag}^+}{1 \text{ mol AgNO}_3} \times 0.100 \text{ L} \times$

$108 \text{ g/mol Ag}^+ = 2.2 \text{ g Ag}^+$

(b) $0.75 \text{ mol CuSO}_4\text{/L} \times \dfrac{1 \text{ mol Cu}^{2+}}{1 \text{ mol CuSO}_4} \times 0.020 \text{ L} \times$

$63.5 \text{ g/mol} = 0.95 \text{ g Cu}^{2+}$

(c) $1.2 \times 10^{-3} \text{ mol MgCl}_2\text{/L} \times \dfrac{1 \text{ mol Mg}^{2+}}{1 \text{ mol MgCl}_2} \times 3.0 \text{ L} \times$

$24.3 \text{ g/mol} = 0.087 \text{ g Mg}^{2+}$

(d) $1.06 \text{ g/mL} \times 500 \text{ mL} \times 0.050 \times \dfrac{200.6 \text{ g Hg}^{2+}}{324.6 \text{ g Hg(NO}_3)_2} =$

16 g Hg^{2+}

14. (a) $\dfrac{1.0 \times 10^{-6} \text{ g Ag}}{107.87 \text{ g/mol}} = 9.3 \times 10^{-6}$ mol Ag per milliter of solution

$\dfrac{9.3 \times 10^{-6} \text{ mol Ag}}{0.0010 \text{ L}} = 9.3 \times 10^{-3} \text{ M Ag}$

$M_1V_1 = M_2V_2$

(0.50 M Ag)(X L) = $(9.3 \times 10^{-3}$ M Ag) (0.500 L)

X L = 9.3×10^{-3} L = 9.3 mL of 0.5 M AgNO_3 would be diluted with water to a total volume of 500 mL.

(b) $\dfrac{1.0 \times 10^{-3} \text{ mg Ag}}{107.87 \text{ g/mol}} = 9.3 \times 10^{-6}$ mol Ag per millilter of solution

$\dfrac{9.3 \times 10^{-6} \text{ mol Ag}}{\text{mL}} \times 500 \text{ mL} = 4.7 \times 10^{-3} \text{ mol Ag}$

$4.7 \times 10^{-3} \text{ mol Ag} \times \dfrac{1 \text{ Ag}}{1 \text{ AgNO}_3} \times 169.9 \text{ g/mol}$

$\text{AgNO}_3 = 0.80 \text{ g AgNO}_3$ would be dissolved in sufficient water to generate 500 mL of solution

(c) $1.0 \text{ L} \times \dfrac{1000 \text{ mL}}{\text{L}} \times \dfrac{1.0 \times 10^{-3} \text{ g}}{\text{mL}} = 1.0 \text{ g Cu required}$

$\dfrac{1.0 \text{ g Cu}}{63.55 \text{ g/mol}} \times \dfrac{1 \text{ mol CuSO}_4{\cdot}5 \text{ H}_2\text{O}}{1 \text{ mol Cu}} \times 249.55 \text{ g/mol}$

$\text{CuSO}_4{\cdot}5 \text{ H}_2\text{O} = 3.9 \text{ g}$

3.9 g $\text{CuSO}_4{\cdot}5 \text{ H}_2\text{O}$ would be dissolved in sufficient water to give 1 L of solution.

(d) $1.0 \text{ L} \times \dfrac{1000 \text{ mL}}{\text{L}} \times \dfrac{1.0 \times 10^{-3} \text{g}}{\text{mL}} = 1.0 \text{ g Cu required}$

$\dfrac{1.0 \text{ g Cu}}{63.55 \text{ g/mol}} = 0.016 \text{ mol per liter Cu} = 0.016\ M \text{ Cu}$

$M_1V_1 = M_2V_2$

(0.050 M CuSO_4)(X L) = (0.016 M Cu) (1.000 L)

X L = 0.32 L = 320 ml of 0.05 M CuSO_4 would be diluted with water to a total volume of 1 L

(e) $250 \text{ mL} \times 1.0 \times 10^{-3} \text{ g/mL} = 0.25 \text{ g Al required}$

Dissolve 0.25 g Al in sufficient HCl to give 250 mL of solution

(f) $2 \text{ L} \times \dfrac{1000 \text{ mL}}{\text{L}} \times \dfrac{1.0 \times 10^{-3} \text{ g}}{\text{mL}} = 2.0 \text{ g Na required}$

$\dfrac{2.0 \text{ g Na}}{22.99 \text{ g/mol}} \times \dfrac{1 \text{ Na}_2\text{CO}_3}{2 \text{ Na}} \times 105.98 \text{ g/mol Na}_2\text{CO}_3 =$

$4.6 \text{ g Na}_2\text{CO}_3$

4.6 g Na_2CO_3 would be dissolved in sufficient water to give 2 L of solution.

15. (a) $1.185 \text{ g/mL solution } 3\ 1000 \text{ mL/L} \times \dfrac{36.5 \text{ g HCl}}{100 \text{ g solution}} \times$

$\dfrac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 11.9 \text{ mol HCl/L solution}$

(b) $\dfrac{36.5\text{ g HCl}}{63.5\text{ g H}_2\text{O}} \times \dfrac{1000\text{ g}}{1\text{ kg}} \times \dfrac{1\text{ mol HCl}}{36.5\text{ g HCl}} = 15.7\text{ mol}$ HCl/kg H_2O

(c) $\dfrac{36.5\text{ g HCl/(36.5 g/mol)}}{36.5\text{ g HCl/(36.5 g/mol)} + 63.5\text{ g H}_2\text{O/(18.0 g/mol)}} = 0.221$

16. $1.082\text{ g/mL} \times 1000\text{ mL/L} \times 0.09000 \times \dfrac{1}{56.11\text{ g/mol}} =$ 1.74 M KOH stock solution $\dfrac{1.0\text{ mol/L} \times 1\text{ L}}{1.74\text{ mol/L}} = 0.576\text{ L} =$ 576 mL of stock solution should be diluted to 1.00 L with water.

17. 1.86 mol/L × 98.1 g/mol = 182 g H2SO4/L solution (1.115 g/mL × 1000 mL/L) − 182 g = 933 g H_2O/L solution

$$\frac{1.86\text{ mol H}_2\text{SO}_4}{933\text{ g H}_2\text{O}} \times \frac{1000\text{ g}}{1\text{ kg}} = 1.99\text{ m}$$

18. (a) $\dfrac{4.35\text{ g}}{79.35\text{ g}} \times 100 = 5.48\%$

(b) Volume of solution $= \dfrac{79.35\text{ g}}{1.05\text{ g/mL}} = 75.6\text{ mL}$

Moles of $CaCl_2$ $= \dfrac{4.35\text{ g}}{110.99\text{ g/mol}} = 0.0392\text{ mol}$

$\text{M} = \dfrac{0.0392\text{ mol}}{0.0756\text{ L}} = 0.519\text{ M}$

(c) Moles of water $= \dfrac{75.0\text{ g}}{18.02\text{ g/mol}} = 4.16\text{ mol}$

Mole fraction of $CaCl_2$ $= \dfrac{0.0392\text{ mol}}{(4.16 + 0.0392)\text{ mol}} = 0.00934$

19. (a) $\dfrac{\text{x grams Na}_2\text{CO}_3}{\text{x grams Na}_2\text{CO}_3 + 100\text{ grams water}} \times 100 = 10.0\%$

mass of Na_2CO_3 = 11.1 g

(b) $\dfrac{1.10\text{ g solution}}{\text{mL}} \times \dfrac{1000\text{ mL}}{1\text{ L}} \times \dfrac{10.0\text{ g Na}_2\text{CO}_3}{100\text{ g solution}} =$ 110 g/L

(c) $\dfrac{10.0\text{ g Na}_2\text{CO}_3 \div 105.99\text{ g/mol}}{(10.0\text{ g Na}_2\text{CO}_3 \div 105.99\text{ g/mol}) + (9.0\text{ g H}_2\text{O} \div 18.015)} = 0.0185$

(d) $\dfrac{110\text{ g Na}_2\text{CO}_3\text{/L}}{105.99\text{ g/mol}} = 1.04\ m$

(e) $\dfrac{110.0\text{ g Na}_2\text{CO}_3 \div 105.99\text{ g/mol}}{990\text{ g} \times 1\text{ kg/1000 g}} = 1.05\ m$

20. $\dfrac{2.0\text{ mol HNO}_3}{1000\text{ g H}_2\text{O}} \times \dfrac{63\text{ g HNO}_3}{1\text{ mol HNO}_3} = 126\text{ g HNO}_3\text{/1000 g H}_2\text{O}$

$$\frac{126\text{ g HNO}_3}{(1000 + 126\text{ g solution}} \times 100\% = 11\%\text{ HNO}_3$$

21. 0.156 mol/L × 1 L × 80.96 g/mol = 12.63 g HBr needed

$$\frac{12.63\text{ g}}{0.470} \times \frac{1\text{ mL}}{1.50\text{ g}} = 17.9\text{ mL}$$

22. $0.0393\text{ g/L} \times \dfrac{1\text{ mol}}{32\text{ g}} = 1.23 \times 10^{-3}\ M$

23. (a) $\dfrac{25\text{ g methanol}}{25.0\text{ g methanol} + 100\text{ g water}} \times 100\% = 20.0\%$ methanol

(b) $\dfrac{25\text{ g methanol}}{100\text{ g water}} \times \dfrac{100\text{ g/kg}}{32.0\text{ g/mol methanol}} = 7.81\ m$ methanol

(c) $\dfrac{25.0\text{ g/32.0 g/mol}}{25.0\text{ g/32 g/mol} + 100\text{ g/18 g/mol}} = 0.123$

24. $\dfrac{1.063\text{ g/L}}{136.1\text{ g/mol}} = 7.810 \times 10^{-3}\ M$

25. (a) $\dfrac{1.10\text{ g/mL} \times 1000\text{ mL/L} \times 0.200}{158\text{ g/mol}} = 1.39\ M\text{ Na}_2\text{S}_2\text{O}_3$

(b) $20\text{ g Na}_2\text{S}_2\text{O}_3\text{/80 g H}_2\text{O} \times \dfrac{1000\text{ g/kg}}{158\text{ g/mol Na}_2\text{S}_2\text{O}_3} = 1.58\ m$ $Na_2S_2O_3$

26. $\dfrac{60.0\text{ g/119.4 g/mol CHCl}_3}{60.0\text{ g/119.4 g/mol CHCl}_3 + 80.0\text{ g/153.8 g/mol CCl}_4} = 0.491$ mol-fraction $CHCl_3$

1.000 − 0.491 = 0.509 mol-fraction CCl_4

27. (a) $\dfrac{0.99\text{ g PbCl}_2}{100\text{ mL}} \times 1000\text{ mL/L} \times \dfrac{1}{278\text{ g/mol PbCl}_2} =$ 0.036 M $PbCl_2$ at 20 °C

$\dfrac{3.14\text{ g PbCl}_2}{100\text{ mL}} \times 100\text{ mL/L} \times \dfrac{1}{278\text{ g/mol PbCl}_2} =$ 0.036 M $PbCl_2$ at 20 °C

(b) endothermic

28. (a) $\dfrac{1050 \times 0.20}{36.5} = 5.75\ m$

(b) 1050 × .20 = 210.00
1050 − 210 g HCl = 840 g H_2O

$\dfrac{210}{36.5} \times \dfrac{1000}{840} = 6.8$

(c) $\dfrac{\frac{210}{36.5}}{\frac{210}{36.5} + \frac{840}{18}} = \dfrac{5.75}{5.75 + 46.7} = \dfrac{5.75}{52.4} = 0.11$

(d) $\dfrac{0.1\text{ mol}}{5.75\ m} = 0.017 = 17\text{ mL}$

(e) $Na_2CO_3 + 2HCl \rightarrow H_2CO_3 + 2NaCl$

$\dfrac{10}{106} \times 2 \times 36.5 \times \dfrac{1}{0.20} = 34\text{ g}$

29. $\dfrac{150\text{ g/18 g/mol H}_2\text{O}}{150\text{ g/18 g/ml H}_2\text{O} + 100\text{ g/92.1 g/mol C}_3\text{H}_8\text{O}_3} = 0.885$

23.8 torr × 0.885 = 21.1 torr

30. The ethanol penetrates the ice and becomes an impurity within the ice that acts to lower the freezing point of the water below that of the existing conditions. Thus, the ice melts.

31. (a) $\Delta T_{fp} = K_{fp}\text{m}$

$$m = \frac{\Delta T_{fp}}{K_{fp}} = \frac{10.0}{1.86} = 5.38\ m$$

Because the solution is sufficiently dilute, the molarity is essentially equivalent to the molality, so the solution is 5.38 *M*.

$10.0\text{ L} \times 5.38\text{ mol/L} = 53.8\text{ mol}$

(b) $53.8\text{ mol} \times 32.0\text{ g/mol} = 1.72 \times 10^3\text{ g}$

32. $$\frac{45\text{ mL} \times 0.789\text{ g/mL}}{46.069\text{ g/mol}} = 0.77\text{ mol } CH_3CH_2OH$$

$$\frac{55\text{ mL} \times 0.997\text{ g/mL}}{18.015\text{ g/mol}} = 3.0\text{ mol } H_2O$$

$$\frac{0.77\text{ mol}}{0.77 + 3.0\text{ mol}} \times 65.0\text{ torr} = 13\text{ torr } CH_3CH_2OH$$

$$\frac{3.0\text{ mol}}{0.77 + 3.0\text{ mol}} \times 23.8\text{ torr} = 19\text{ torr } H_2O$$

33. $\pi = MRT\ = \frac{n}{V}RT$

$$\left(\frac{12.8\text{ torr}}{760\text{ torr/atm}}\right) = \frac{\left(\frac{0.125\text{ g}}{\text{MW}}\right)}{0.2500\text{ L}}\left(0.08205\,\frac{\text{L-atm}}{\text{mol K}}\right)(288\text{ K})$$

MW = 702 g/mol

34. $$\frac{46\text{ g} \div 62.068\text{ g/mol}}{54\text{ g} \times (1\text{ kg}/1000\text{ g})} \times 1.86\ °\text{C}\cdot\text{kg/mol} = 26\ °\text{C}$$

Thus, the new freezing point is −26 °C.

35. $\Delta T_f = (6 - -14)°\text{C} = 20\ °\text{C} = K_f m$

$$\text{m} = \frac{2.35\text{ g } CCl_4/153.82\text{ g/mol}}{0.015\text{ kg solvent}} - 1.02\ m$$

$K_f = 20\ °\text{C}/1.02\text{ m} = 20\ °\text{C/m}$

36. Freshly boiled water has lower concentrations of dissolved gases, such as carbon dioxide, than does unboiled tap water. Thus, the tap water with its higher concentration of solutes will have a lower freezing point than that of the boiled water.

37. $$\frac{4.785\text{ g } HgCl_2}{60\text{ g } H_2O} \times \frac{1000\text{ g}}{\text{kg}} \times \frac{1\text{ mol}}{271.5\text{ g}} = 0.29\ m$$

$\Delta T_{bp} = K_{bp}\text{m} = 0.52 \times 0.29 = 0.151\ °\text{C}$

The experimental boiling point matches the one calculated assuming that $HgCl_2$ does not dissociate. Thus, $HgCl_2$ does not dissociate in water.

38. $$\frac{10.00\text{ g}/(78.11\text{ g/mol})}{10.00\text{ g}/(78.11\text{ g/mol}) + 1.00\text{ g}/(75.2\text{ g/mol})} = 0.906$$

Vapor pressure = 0.906 × 95.5 torr = 86.5 torr

39. $P_{CHCl_3} = 178\text{ torr} \times 0.068\text{ mol } C_6H_4Cl_2$

$P_{CCl_4} = 100\text{ torr} \times 0.509 = 50.9\text{ torr}$

$P_{\text{total}} = 87.4\text{ torr} + 50.9\text{ torr} = 138.3\text{ torr}$

40. (a) $$\frac{10\text{ g } C_6H_4Cl_2}{146.9\text{ g/mol}} = 0.068\text{ mol } C_6H_4Cl_2$$

$$\frac{0.068\text{ mol } C_6H_4Cl_2}{0.350\text{ L}} = 0.19\ M\ C_6H_4Cl_2$$

(b) $$\frac{10\text{ g } C_6H_4Cl_2}{350\text{ mL} \times 1.60\text{ g/mL solution}} \times 100\% = 1.8\ \%\ \text{para-dichlorbenzene}$$

(c) $$\frac{10\text{ g } C_6H_4Cl_2}{146.9\text{ g/mol}} = 0.068\text{ mol } C_6H_4Cl_2$$

$350\text{ mL} \times 1.60\text{ g/mL} = 560\text{ g solution}$

$560\text{ g solution} - 10\text{ g } C_6H_4Cl_2 = 550\text{ g } CCl_4 = 0.55\text{ kg } CCl_4$

$$\frac{0.068\text{ mol } C_6H_4Cl_2}{0.55\text{ kg } CCl_4} = 0.12\text{ molal}$$

(d) $$\frac{550\text{ g } CCl_4}{153.8\text{ g/mol}} = 3.58\text{ mol } CCl_4$$

$$\frac{0.068\text{ mol } C_6H_4Cl_2}{0.068\text{ mol } C_6H_4Cl_2 + 3.58\text{ mol } CCl_4} = 0.019$$

(e) $C_{CCl_4} = 1.00 - 0.019 = 0.981$

$P = C_{CCl_4}\,P°_{CCl_4} = 0.981\ (100\text{ mm}) = 98.1\text{ mm}$

(f) $\Delta T_{b.p.} = K_b \times \text{m}$

$$\text{m} = \frac{\Delta T_{b.p.}}{K_b} = \frac{(78.6\ °\text{C} - 76.6\ °\text{ C})}{5.0\ °\text{ C-kg/mol}} = 0.40\text{ molal}$$

moles $C_6H_4Cl_2$ = m × kg CCl_4 = 0.40 mol/kg × 0.100 kg = 0.040 mol $C_6H_4Cl_2$

g $C_6H_4Cl_2$ = 0.040 mol $C_6H_4Cl_2$ × 146.9 g/mol = 5.9 g $C_6H_4Cl_2$

41. (a) $\Delta T = \text{m}\,K_f \qquad K_f = 5.12\ °\text{C-kg/mol for benzene}$

$$\text{moles } C_{10}H_8 = \frac{1.28\text{ g}}{128\text{ g/mol}} = 0.0100\text{ mol}$$

$$\text{m} = \frac{0.0100\text{ mol}}{0.0100\text{ kg}} = 1.00\text{ molal}$$

$\Delta T = 1.00\text{ mol/kg} \times 5.12\ °\text{C-kg/mol} = 5.12\ °\text{C}$

(b) F.P. = 5 °C − 5.12 °C = − 0.12 °C

(c) $$\text{mol } C_{10}H_8 = \frac{1.28\text{ g}}{128\text{ g/mol}} = 0.0100\text{ mol } C_{10}H_8$$

$$\text{mol benzene } (C_6H_6) = \frac{10.0\text{ g}}{78.0\text{ g/mol}} = 0.128\text{ mol } C_6H_6$$

$$X_{C_6H_6} = \frac{0.128}{(0.128 + 0100)} = 0.928$$

(d) $\text{V.P.} = X_{C_6H_6}\,P^0 = 0.928\ (100\text{ mm}) = 928\text{ mm}$

(e) $\Delta T = \text{m}\,K_b \qquad K_b = 2.53\ °\text{C kg/mol for benzene}$

$\Delta T = 1.00\text{ mol/kg} \times 2.53\ °\text{C kg/mol} = 2.53\ °\text{C}$

B.P. = 80 °C + 2.53 °C = 82.53 °C

43. (a) $$\frac{(12.21\text{ g}/110.99\text{ g/mol})}{0.05000\text{ L}} = 2.200\ M$$

(b) Total mass = 50.00 mL × 1.19 g/mL = 59.5 g

$$\text{mass \% } CaCl_2 = \frac{12.21\text{ g}}{59.5\text{ g}} \times 100 = 20.5\%$$

(c) mass H_2O = 59.5 g − 12.21 g = 47.3 g

number of moles of H_2O = 2.62

$$X_{H_2O} = \frac{\text{moles } H_2O}{\text{total \# moles}} = \frac{2.62}{2.62 + 0.33} = 0.888$$

number of moles of ions = 3 × number of moles

$$CaCl_2 = 3 \times \frac{12.21 \text{ g}}{110.99 \text{ g/mol}} = 0.330$$

P = 0.888 × 760 torr = 675 torr

(d) $\Delta T_f = (i)(K_f)(m) = (3)(1.86\ ^\circ\text{C/m})\ (2.33 \text{ m}) = 13.0\ ^\circ\text{C}$

$$m = \frac{\left(\dfrac{12.21 \text{ g}}{110.99 \text{ g/mol}}\right)}{0.0473 \text{ kg}} = 2.33$$

Solution starts to freeze at −13.0 °C

44. (a) $M = \dfrac{2.5 \text{ g/}293.887 \text{ g/mol}}{0.750 \text{ L}} = 0.011\ M$

(b) Mass of solution = 750.0 mL × 1.003 g/mL = 752.3 g

$$\%\ CaI_2 = \frac{2.5 \text{ g}}{752.3 \text{ g}} \times 100 = 0.33\%$$

45. (a) $\dfrac{10.0 \text{ g}}{95 + 10} \times 100 = 9.5\%$

(b) $\dfrac{105 \text{ g}}{100 \text{ mL}} = 1.05 \text{ g/mL}$

(c) $\dfrac{10.0 \text{ g}}{122 \text{ g/mol}} \times \dfrac{1000 \text{ mL}}{100 \text{ mL}} = 0.82\ M$

(d) $\dfrac{10.0 \text{ g}}{122 \text{ g/mol}} \times \dfrac{1000 \text{ g}}{95 \text{ g}} = 0.86\ m$

(e) $\dfrac{\dfrac{10}{122}}{\dfrac{10}{122} + \dfrac{95}{18}} = 0.0153$

(f) $\Delta T = K_b m = 1.86\ (0.86) = 1.60$

bp = 101.6

(g) $P = P^\circ X$

P = 24.6 = 0.985

X = 1.00 − 0.0153

46. (a) Endothermic

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 20{,}000 \text{ J/mol} - (298 \text{ K})\ (70 \text{ J/mol-K})$

$\Delta G^\circ = -860$ J/mole

$\Delta G^\circ < 0$ therefore the dissolution process will be spontaneous which agrees with observed experimental results; i.e., the dissolution was indeed spontaneous.

47. $P_{O_2} = 760 \text{ torr} \times 0.2094 = 159.1 \text{ torr}$

$P_{N_2} = 760 \text{ torr} \times 0.7809 = 593.5 \text{ torr}$

$P_{Ar} = 760 \text{ torr} \times 0.0093 = 7.1 \text{ torr}$

$$\frac{159.1 \text{ torr}}{760 \text{ torr}} \times 4.89 \text{ mL} = 1.024 \text{ mL } O_2$$

$$\frac{593.5 \text{ torr}}{760 \text{ torr}} \times 2.35 \text{ mL} = 1.835 \text{ mL } N_2$$

$$\frac{7.1 \text{ torr}}{760 \text{ torr}} \times 5.6 \text{ mL} = 0.0523 \text{ mL Ar}$$

Total volume of gases dissolved is 2.91 mL

$$\frac{2.91 \text{ mL air}}{(22{,}400) \text{ mL/mol}} \times \frac{1000 \text{ g/kg}}{100 \text{ g } H_2O} = 1.30 \times 10^{-3}\ m$$

$\Delta T_{fp} = K_{fp}m = 1.86 \times 1.30 \times 10^{-3} = 2.41 \times 10^{-3}\ ^\circ\text{C}$

freezing point = −0.00241 °C

48. Water fills the red blood cells in order to equalize the osmotic pressure on both sides of the cell wall. Before equal pressures are established, so much water has built up in the cell that the cell membrane cannot contain it.

49. $P = P^\circ X$

$$X = \frac{P}{P^\circ} = \frac{94.8 \text{ torr}}{95.5 \text{ torr}} = 0.993 \text{ mol-fraction } C_6H_6$$

$$\frac{90.0 \text{ g/}(78.11 \text{ g/mol})}{90.0 \text{ g/}(78.11 \text{ g/mol}) + 10.0 \text{ g/}(x \text{ g/mol})} = 0.993$$

$x = 1.24 \times 10^3$ g/mol

50. $\dfrac{50.0 \text{ g}}{100.0 \text{ g } H_2O} \times \dfrac{1000 \text{ g}}{\text{kg}} \times \dfrac{1 \text{ mol}}{92 \text{ g}} = 5.43\ m$

$\Delta T_{bp} = 0.512 \times 5.43 = 2.78\ ^\circ\text{C}$

boiling point = 100 °C + 2.78 °C = 102.78 °C

51. $\Delta T_{bp} = 81.4 - 80.1 = 1.3\ ^\circ\text{C}$

$$m = \frac{T_{bp}}{K_{bp}} = \frac{1.3}{2.53} = 0.514 \text{ mol Y/kg } C_6H_6$$

$$\frac{40.0 \text{ g Y}}{500.0 \text{ g } C_6H_6} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ kg } C_6H_6}{0.514 \text{ mol Y}} = 156 \text{ g/mol}$$

52. $\Delta T_{fp} = 1.86 \times 0.50 = 0.93\ ^\circ\text{C}$

freezing point = 0.00 − 0.93 = −0.93 °C

53. $\dfrac{1.0 \text{ g } C_{10}H_8}{100 \text{ g camphor}} \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times \dfrac{1 \text{ mol } C_{10}H_8}{128 \text{ g } C_{10}H_8} = 0.078\ m$

$\Delta T_{fp} = 39.7 \times 0.078 = 3.1\ ^\circ\text{C}$

melting point = 179.7 − 3.1 = 176.6 °C

54. $\Delta T_{fp} = 5.5\ ^\circ\text{C} - (-1.3\ ^\circ\text{C}) = 6.8\ ^\circ\text{C}$

$$\frac{6.8\ ^\circ\text{C}}{5.12\ ^\circ\text{C-kg/mol}} = 133\ m$$

$$\frac{1.00 \text{ g A}}{10.0 \text{ g } C_6H_6} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ kg } C_6H_6}{0.33 \text{ mol A}} = 75.2 \text{ g/mol}$$

55. $\Delta T_{fp} = 70.00\ ^\circ\text{C} - 68.44\ ^\circ\text{C} = 1.56\ ^\circ\text{C}$

$$\frac{1.56\ ^\circ\text{C}}{8.00\ ^\circ\text{C-kg/mol}} = 0.195\ m$$

$$\frac{0.650 \text{ g compound}}{27.80 \text{ g diphenyl}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ kg diphenyl}}{0.195 \text{ mol compound}} = 120 \text{ g/mol}$$

56. $\Delta T_{fp} = 6.00 - 1.00 = 5.00\ ^\circ\text{C}$

$$\frac{5.00\ ^\circ\text{C}}{20.00\ ^\circ\text{C-kg/mol}} = 0.250\ m$$

$$\frac{0.100 \text{ g compound}}{10.00 \text{ g cyclohexane}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ kg cyclohexane}}{0.250 \text{ mol compound}} = 40.0 \text{ g/mol}$$

57. (a) $\dfrac{93.75 \text{ g C}}{12.01 \text{ g/mol}} = 7.81 \text{ mol C}\ \dfrac{6.25 \text{ g H}}{1.01 \text{ g/mol}} = 6.19 \text{ mol H}$

7.81 : 6.19 = 5 : 4

empirical formula = C_5H_4

(b) $\Delta T_{fp} = 5.50 - 4.20 = 1.30\ ^{\circ}\text{C}$

$$\frac{1.3\ ^{\circ}\text{C}}{5.12\ ^{\circ}\text{C-kg/mol}} = 0.254\ m$$

$$\frac{0.320 \text{ g compound}}{10.0 \text{ g } C_6H_6} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times$$

$$\frac{1 \text{ kg } C_6H_6}{0.254 \text{ mol compound}} = 126 \text{ g/mol}$$

(c) $\dfrac{126 \text{ g/mol}}{64 \text{ g/formula}} = 2$

The molecular formula is $C_{10}H_8$

58. (a) $K_2O(s) + H_2O \rightarrow 2\ KOH$
(b) $CO_2(g) + H_2O \rightarrow H_2CO_3$
(c) $SO_2(g) + H_2O \rightarrow H_2SO_3$
(d) $MgO(s) + H_2O \rightarrow Mg(OH)_2$
(e) $N_2O_5(s) + H_2O \rightarrow 2\ HNO_3$
(f) $B_2O_3(s) + H_2O \rightarrow 2\ H_3BO_3$

59. The strong electrolytes are: (a), (b), (f), (h), (j), (k), (o), (r)
The weak electrolytes are: (c), (d), (e), (g), (n), (s)
The nonelectrolytes are: (i), (l), (m), (p), (q), (t)

60. a. N, b. N, c. S, d. W, e. W, f. W, g. S, h. W

61. $\dfrac{0.245\ ^{\circ}\text{C}}{1.86\ ^{\circ}\text{C-kg/mol}} = 0.132\ m$

let x = number of moles of HA dissociated
$HA \rightleftharpoons H^+ + X^-$
$(0.01 - x) \quad x \quad x$
$(0.01 - x) + x + x = 0.132$
$x = 0.032$

$$\frac{0.032 \text{ mol}}{0.100 \text{ mol}} \times 100\% = 32\%$$

62. $\dfrac{1.70\ ^{\circ}\text{C}}{1.86\ ^{\circ}\text{C-kg/mol}} = 0.914\ m$

$NaCl \rightleftharpoons Na^+ + Cl^-$
$(0.50 - x) \quad x \quad x$
$(0.50 - x) + x + x = 0.914$
$x = 0.414$

$$\frac{0.414 \text{ mol}}{0.50 \text{ mol}} \times 100\% = 83\%$$

63. $\dfrac{7.70 \text{ atm}}{0.08205 \text{ L-atm/mol-K} \times 298 \text{ K}} \times \dfrac{1\text{mol NaCl}}{2 \text{ mol ion}} = 0.157 \text{ M}$
NaCl

64. $\dfrac{4.785 \text{ g } HgCl_2}{60 \text{ g } H_2O} \times \dfrac{1000 \text{ g}}{\text{kg}} \times \dfrac{1 \text{ mol}}{271.5 \text{ g}} = 0.29\ m$

$\Delta T_{bp} = K_{bp}m = 0.512 \times\ 0.29 = 0.151\ ^{\circ}\text{C}$
The experimental boiling point matches the one calculated assuming that $HgCl_2$ does not dissociate. Thus, $HgCl_2$ does not dissociate in water.

65. (a) In the 1.0 molal solution a substantial number of ions exist as ion pairs. This pairing reduces the number of particles in solution and therefore the potassium chloride is not as effective at depressing the freezing point as it is in the lower concentration solution, in which ion pairing is minimized.

(b) The solute-solvent interactions make it more difficult for solvent molecules to escape from the surface of the liquid. Thus, at a given temperature, fewer solvent molecules will be entering the vapor phase, and consequently the vapor pressure of the solution will be less than that for the pure solvent.

66. (a) $\dfrac{(12.21 \text{ g}/110.99 \text{ g/mol})}{0.05000 \text{ L}} = 2.200\ M$

(b) Total mass = 50.00 mL × 1.19 g/mL = 59.5 g

$$\text{mass \% } CaCl_2 = \frac{12.21 \text{ g}}{59.5 \text{ g}} \times 100 = 20.5\%$$

(c) mass H_2O = 59.5 g − 12.21 g = 47.3 g
number of moles of H_2O = 2.62

$$X_{H_2O} = \frac{\text{moles } H_2O}{\text{total \# moles}} = \frac{2.62}{2.62 + 0.33} = 0.888$$

number of moles of ions = 3 × number of moles

$$CaCl_2 = 3 \times \frac{12.21 \text{ g}}{110.99 \text{ g/mol}} = 0.330$$

$P = 0.888 \times 760 \text{ torr} = 675 \text{ torr}$

(d) $\Delta T_f = (i)(K_f)(m) = (3)(1.86\ ^{\circ}\text{C/m})\ (2.33 \text{ m}) = 13.0\ ^{\circ}\text{C}$

$$m = \frac{\left(\dfrac{12.21 \text{ g}}{110.99 \text{ g/mol}}\right)}{0.0473 \text{ kg}} = 2.33$$

Solution starts to freeze at −13.0 °C

67. Assuming that the only important effect is the freezing point depression produced by a solute, then one should use NaCl because it will provide the greatest number of ions (particles) that will lower the freezing point of water.

$$\frac{10 \times 10^3 \text{ g NaCl}}{58.442 \text{ g/mol}} \times \frac{2 \text{ mol of ions}}{1 \text{ mol NaCl}} = 342 \text{ mol of ions}$$

$$\frac{10 \times 10^3 \text{ g KCl}}{74.551 \text{ g/mol}} \times \frac{2 \text{ mol of ions}}{1 \text{ mol KCl}} = 268 \text{ mol of ions}$$

$$\frac{10 \times 10^3 \text{ g } CaCl_2}{110.984 \text{ g/mol}} \times \frac{3 \text{ mol of ions}}{1 \text{ mol } CaCl_2} = 270 \text{ mol of ions}$$

68. $\dfrac{10\ ^{\circ}\text{C}}{1.86\ ^{\circ}\text{C-kg/mol}} = 5.38\ m$

$$\frac{5.38 \text{ mol ions}}{1 \text{ kg } H_2O} \times \frac{1 \text{ mol } CaCl_2}{3 \text{ mol ions}} \times 10 \text{ L } H_2O \times \frac{1 \text{ kg } H_2O}{1 \text{ L } H_2O} =$$

17.9 mol $CaCl_2$
Aqueous $CaCl_2$ is not used in automobiles because it is a corrosive solution and would damage metal parts.69

69. 1. (c) 2. (c) 3. (c) 4. (a) 5. (c) 6. (c) 7. (c) 8. (a) 9. (b) 10. (b)

CHAPTER 11

1. (a) $1.0 \text{ kg } AlCl_3 \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times \dfrac{27.0 \text{ g Al}}{133.4 \text{ g } AlCl_3} =$

2.0×10^2 g Al

(b) $1.0 \text{ kg } Kal(SO_4)_2 \cdot 12\ H_2O \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times$

$$\frac{27.0 \text{ g Al}}{474 \text{ g } KAl(SO_4)_2 \cdot 12\ H_2O} = 57 \text{ g Al}$$

2. $$\frac{6.00\text{ g Na}_2\text{B}_4\text{O}_7\cdot 10\text{ H}_2\text{O}}{381\text{ g/mol Na}_2\text{B}_4\text{O}_7\cdot 10\text{ H}_2\text{O}} \times \frac{4\text{ mol B}}{1\text{ mol Na}_2\text{B}_4\text{O}_7\cdot 10\text{ H}_2\text{O}} \times \frac{10.8\text{ g B}}{1\text{ mol B}} = 0.680\text{ g B}$$

3. (a) $$\frac{6.941\text{ g Li}}{86.845\text{ g total}} \times 100\% = 7.992\%\text{ Li}$$

$$\frac{79.904\text{ g Br}}{86.845\text{ g total}} \times 100\% = 92.008\%\text{ Br}$$

(b) $$\frac{55.847\text{ g Fe}}{112.84\text{ g total}} \times 100\% = 49.492\%\text{ Fe}$$

$$\frac{(3 \times 18.998\text{ g F})}{112.84\text{ g total}} \times 100\% = 50.509\%\text{ F}$$

(c) $$\frac{(2 \times 39.098\text{ g K})}{138.20\text{ g total}} \times 100\% = 56.580\%\text{ K}$$

$$\frac{12.011\text{ g C}}{138.20\text{ g total}} \times 100\% = 8.6910\%\text{ C}$$

$$\frac{(3 \times 15.9994\text{ g O})}{138.20\text{ g total}} \times 100\% = 34.730\%\text{ O}$$

4. (a) Nitrogen: $$\frac{46.68\text{ g N}}{14.0\text{ g/mol N}} = 3.33\text{ mol N}$$

Oxygen: $$\frac{53.32\text{ g O}}{16.0\text{ g/mol O}} = 3.33\text{ mol O}$$

Ratio: 3.33 : 3.33, so the empirical formula = NO

(b) Carbon: $$\frac{85.62\text{ g C}}{12.0\text{ g/mol C}} = 7.14\text{ mol C}$$

Hydrogen: $$\frac{14.38\text{ g H}}{1.008\text{ g/mol H}} = 14.24\text{ mol H}$$

Ratio: 7.14 : 14.24 = 1 : 2, so the empirical formula = CH_2

(c) Carbon: $$\frac{75.92\text{ g C}}{12.0\text{ g/mol C}} = 6.33\text{ mol C}$$

Hydrogen: $$\frac{6.37\text{ g H}}{1.01\text{ g/mol H}} = 631\text{ mol H}$$

Nitrogen: $$\frac{17.70\text{ g N}}{14.0\text{ g/mol N}} = 1.26\text{ mol N}$$

Ratio: 6.33 : 6.31 : 1.26 = 5 : 5 : 1, so the empirical formula = C_5H_2N

(d) Carbon: $$\frac{58.53\text{ g C}}{12.0\text{ g/mol C}} = 4.88\text{ mol C}$$

Hydrogen: $$\frac{4.09\text{ g H}}{1.01\text{ g/mol H}} = 4.05\text{ mol H}$$

Nitrogen: $$\frac{11.38\text{ g N}}{14.0\text{ g/mol N}} = 0.812\text{ mol N}$$

Oxygen: $$\frac{25.99\text{ g O}}{16.0\text{ g/mol O}} = 1.62\text{ mol O}$$

Ratio: 4.88 : 4.05 : 0.812 : 1.62 = 6 : 5 : 1 : 2, so the empirical formula 5 $C_6H_5NO_2$

5. $$\frac{90\text{ g/mol}}{30\text{ g/emp.form.}} = 3\text{, so the molecular formula 5 C}_3\text{H}_6\text{O}_3$$

$$\frac{50.0\text{ g C}_3\text{H}_6\text{O}_3}{90.08\text{ g/mol C}_3\text{H}_6\text{O}_3} = 0.55\text{ mol C}_3\text{H}_6\text{O}_3$$

0.555 mol $C_3H_6O_3$ × 6.022 × 10^{23} molecules/mol = 3.34 × 10^{23} molecules $C_3H_6O_3$

$$3.34 \times 10^{23}\text{ molecules C}_3\text{H}_6\text{O}_3 \times \frac{3\text{ atoms C}}{1\text{ molecule}} = 1.00 \times 10^{24}\text{ atoms C}$$

6. Carbon: $$\frac{40.00\text{ g C}}{12.0\text{ g/mol C}} = 3.33\text{ mol C}$$

Hydrogen: $$\frac{6.72\text{ g H}}{1.01\text{ g/mol H}} = 6.65\text{ mol H}$$

Oxygen: $$\frac{53.29\text{ g O}}{16.0\text{ g/mol O}} = 3.33\text{ mol O}$$

Ratio: 3.33 : 6.65 : 3.33 = 1 : 2 : 1, so the empirical formula = CH_2O

$$\frac{180\text{ g/mol}}{30\text{ g/emp.form.}} = 6\text{, so the molecular formula} = \text{C}_6\text{H}_{12}\text{O}_6$$

7. Carbon: $$\frac{40.00\text{ g C}}{12.0\text{ g/mol C}} = 3.33\text{ mol C}$$

Hydrogen: $$\frac{3.532\text{ g H}}{1.01\text{ g/mol H}} = 3.50\text{ mol H}$$

Nitrogen: $$\frac{16.48\text{ g H}}{14.0\text{ g/mol N}} = 1.18\text{ mol N}$$

Oxygen: $$\frac{53.29\text{ g O}}{16.0\text{ g/mol O}} = 0.784\text{ mol O}$$

Sulfur: $$\frac{25.18\text{ g S}}{32.1\text{ g/mol S}} = 0.784\text{ mol S}$$

Ratio: 4.5 : 4.5 : 1.5 : 1 : 1, multiplying by two gives $C_9H_9N_3O_2S_2$ for the empirical formula

8. (a) $$\frac{150\text{ g}}{119.4\text{ g/mol CHCl}_3} = 1.26\text{ mol CHCl}_3$$

(b) $$1.26\text{ mol CHCl}_3 \times \frac{6.022 \times 10^{23}\text{ molecules}}{1\text{ mol}} = 7.59 \times 10^{23}\text{ molecules CHCl}_3$$

(c) $$1.26\text{ mol CHCl}_3 \times \frac{1\text{ mol C}}{1\text{ mol CHCl}_3} \times \frac{12.01\text{ g C}}{1\text{ mol C}} = 15.1\text{ g C}$$

(d) $$7.59 \times 10^{23}\text{ molecules CHCl}_3 \times \frac{3\text{ atoms Cl}}{1\text{ molecule}} = 2.28 \times 10^{24}\text{ atoms Cl}$$

(e) $$1.26\text{ mol CHCl}_3 \frac{1\text{ mol H}}{1\text{ mol CHCl}_3} = 1.26\text{ mol H}$$

9. $$\frac{10^6\text{ molecules}}{6.022 \times 10^{23}\text{ molecules/mol}} \times 28.01\text{ g/mol CO} = 4.650 \times 10^{-17}\text{ g CO}$$

10. (a) $2\,SO_2 + O_2 \rightarrow 2\,SO_3$
(b) $2\,Na + 2\,H_2O \rightarrow 2\,NaOH + H_2$
(c) $2\,Al + 3\,H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\,H_2$
(d) $2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$
(e) $H_3PO_4 + 2\,NaOH \rightarrow Na_2HPO_4 + 2\,H_2O$
(f) $4\,AgNO_3 + 2\,Cl_2 \rightarrow 4\,AgCl + 2\,N_2O_5 + O_2$
(g) $Mg_3As_2 + 6\,HCl \rightarrow 2\,AsH_3 + 3\,MgCl_2$

(h) $Ag_2S + 4\ KCN \rightarrow 2\ KAg(CN)_2 + K_2S$
(i) $Pb + 4\ Na + 4\ C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 4\ NaCl$
(j) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4\ H_2O$

11. (a) $$\frac{10.0\text{ g } C_2H_2}{26.037\text{ g/mol } C_2H_2} \times \frac{4\text{ mol } CO_2}{2\text{ mol } C_2H_2} = 0.768\text{ mol } CO_2$$

(b) $$\frac{10.0\text{ g } C_2H_2}{26.037\text{ g/mol } C_2H_2} \times \frac{1\text{ mol } H_2O}{1\text{ mol } C_2H_2} \times \frac{18.02\text{ g } H_2O}{1\text{ mol } H_2O} = 6.92\text{ g } H_2O$$

(c) $$\frac{10.0\text{ g } C_2H_2}{26.037\text{ g/mol } C_2H_2} \times \frac{5\text{ mol } O_2}{2\text{ mol } C_2H_2} \times \frac{6.022 \times 10^{23}\text{ molecules}}{1\text{ mol } O_2} = 5.78 \times 10^{23}\text{ molecules}$$

12. (a) $$\frac{450\text{ g } C_{12}H_{22}O_{11}}{342.3\text{ g/mol } C_{12}H_{22}O_{11}} \times \frac{4\text{ mol } C_{12}H_{22}O_{11}}{1\text{ mol } C_{12}H_{22}O_{11}} \times \frac{46.07\text{ g } C_2H_5OH}{1\text{ mol } C_2H_5OH} = 242\text{ g } C_2H_5OH$$

(b) $$1\text{ lb} \times \frac{453.6\text{ g}}{1\text{ lb}} \times \frac{1\text{ mol } C_{12}H_{22}O_{11}}{342.3\text{ g } C_{12}H_{22}O_{11}} \times \frac{4\text{ mol } CO_2}{1\text{ mol } C_{12}H_{22}O_{11}} \times \frac{44.01\text{ g } CO_2}{1\text{ mol } CO_2} = 233.3\text{ g } CO_2$$

13. $$\frac{100\text{ g } Mg_3N_2}{101\text{ g/mol } Mg_3N_2} \times \frac{3\text{ mol Mg}}{1\text{ mol } Mg_3N_2} \times \frac{24.3\text{ g Mg}}{1\text{ mol Mg}} = 72.2\text{ g Mg}$$

14. (a) $$5\frac{0\text{ kg } NH_3}{17\text{ kg/kg-mol } NH_3} \times \frac{4\text{ kg-mol NO}}{4\text{ kg-mol } NH_3} \times \frac{30\text{ kg NO}}{1\text{ kg-mol NO}} = 88\text{ kg NO}$$

(b) $$10\text{ mol } NH_3 \times \frac{5\text{ mol } O_2}{4\text{ mol } NH_3} \times \frac{32\text{ g } O_2}{1\text{ mol } O_2} = 4.0 \times 10^2\text{ g } O_2$$

(c) $$10\text{ mol } NH_3 \times \frac{6\text{ mol } H_2O}{4\text{ mol } NH_3} \times \frac{18\text{ g } H_2O}{1\text{ mol } H_2O} = 2.7 \times 10^2\text{ g } H_2O$$

(d) $$10\text{ kg} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{1\text{ mol } NH_3}{17\text{ g } NH_3} \times \frac{5\text{ mol } O_2}{4\text{ mol } NH_3} = 74\text{ mol } O_2$$

15. $$1.00\text{ kg coal} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{5.0\text{ g S}}{100\text{ g coal}} \times \frac{64.06\text{ g } SO_2}{32.06\text{ g S}} = 1.0 \times 10^2\text{ g } SO_2$$

16. (a) $$\frac{1.0 \times 10^2\text{ g } SO_2}{64.06\text{ g/mol } SO_2} \times \frac{1\text{ mol } CaSO_3}{1\text{ mol } SO_2} \times \frac{120\text{ g } CaSO_3}{1\text{ mol } CaSO_3} = 1.9 \times 10^2\text{ g } CaSO_3$$

(b) $$\frac{1.0 \times 10^2\text{ g } SO_2}{64.06\text{ g/mol } SO_2} \times \frac{1\text{ mol } CO_2}{1\text{ mol } SO_2} = 1.6\text{ mol } CO_2$$

17. (a) $$\frac{100\text{ g}}{1.07\text{ g/mL}} = 93.5\text{ mL}$$

(b) $$1\text{ L} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1.07\text{ g}}{1\text{ mL}} \times \frac{18.0\text{ g sucrose}}{100\text{ g solution}} = 193\text{ g sucrose}$$

(c) $$150\text{ mL} \times \frac{1.7\text{ g}}{1\text{ mL}} \times \frac{18.0\text{ g scurose}}{100\text{ g solution}} \times \frac{1\text{ mol sucrose}}{342.5\text{ g sucrose}} = 0.0844\text{ mol sucrose}$$

18. $$\frac{1.0\text{ kg } Br_2 \times 1000\text{ g/kg}}{159.8\text{ g/mol } Br_2} \times \frac{2\text{ mol NaBr}}{1\text{ mol } Br_2} \times \frac{102.9\text{ g NaBr}}{1\text{ mol NaBr}} \times \frac{100\text{ g sea water}}{0.0070\text{ g NaBr}} \times \frac{1\text{ kg}}{1000\text{ g}} = 1.8 \times 10^4\text{ kg of sea water}$$

19. $$\frac{10.00\text{ g } CHCl_3}{10.0\text{ g } CHCl_3 + (1000\text{ mL} \times 0.708\text{ g/mL})\text{ ether}} \times 100\% = 1.39\%\ CHCl_3$$

20. $$1\text{ mol } HNO_3 \times \frac{63.0\text{ g } CHCl_3}{1\text{ mol } HNO_3} \times \frac{100\text{ g solution}}{20.0\text{ g } HNO_3} \times \frac{1\text{ mL solution}}{1.12\text{ g solution}} = 281\text{ mL solution}$$

21. $$\frac{25.0\text{ g } H_2S}{34.1\text{ g/mol } H_2S} \times \frac{2\text{ mol HCl}}{1\text{ mol } H_2S} \times \frac{36.5\text{ g HCl}}{1\text{ mol HCl}} \times \frac{100\text{ g solution}}{36.0\text{ g HCl}} \times \frac{1\text{ mL solution}}{1.18\text{ g solution}} = 126\text{ mL solution}$$

22. (a) $0.25\text{ mol/L } CaCl_2 \times \frac{500\text{ mL}}{1000\text{ mL/L}} \times 111\text{ g/mol } CaCl_2 =$ 14 g $CaCl_2$, dissolved in sufficient water to make 500 mL of solution.

(b) $1.30\text{ mol/L } Na_2CO_3 \times 2.0\text{ L} \times 106\text{ g/mol} = 2.8 \times 10^2\text{g}$ Na_2CO_3, dissolved in sufficient water to make 2.0 L of solution.

(c) $0.102\text{ mol/L KOH} \times \frac{100\text{ mL}}{1000\text{ mL/L}} \times 56.1\text{ g/mol KOH} = 0.572\text{ g KOH}$ dissolved in sufficient water to give 100 mL of solution.

23. $$\frac{27.0\text{ mL}}{1000\text{ mL/L}} \times 0.859\text{ mol/L } H_3PO_4 \times 98.0\text{ g/mol } H_3PO_4 = 2.27\text{ g } H_3PO_4$$

24. $$\frac{50.0\text{ g } Cl_2}{70.9\text{ g/mol } Cl_2} \times \frac{4\text{ mol HCl}}{1\text{ mol HCl}} \times \frac{1\text{ L}}{6\text{ mol HCl}} = 0470\text{ L HCl}$$

25. $$\frac{10.0\text{ g } PbSO_4}{303\text{ g/mol } PbSO_4} \times \frac{2\text{ mol } H_2SO_4}{2\text{ mol } PbSO_4} \times \frac{1\text{ L}}{5.0\text{ mol } H_2SO_4} \times \frac{1000\text{ mL}}{1\text{ L}} = 6.6\text{ mL } H_2SO_4$$

26. $$\frac{50\text{ kg } FeS_2}{120.0\text{ kg/kg-mol } FeS_2} \times \frac{2\text{ kg-mol } FeSO_4}{2\text{ kg-mol } FeS_2} \times \frac{152\text{ kg } FeSO_4}{1\text{ kg/kg-mol } FeSO_4} \times \frac{78\text{ g}}{100\text{ g}} = 49\text{ kg } FeSO_4$$

27. $$2.25\text{ g impure } CaC_2 \times \frac{92\text{ g } CaC_2}{100\text{ g impure } CaC_2} \times \frac{1\text{ mol } CaC_2}{64.10\text{ g } CaC_2} \times \frac{1\text{ mol } C_2H_2}{1\text{ mol } CaC_2} \times \frac{26.03\text{ g } C_2H_2}{1\text{ mol } C_2H_2} = 0.84\text{ g } C_2H_2$$

28. $\dfrac{20.0\text{ g PCl}_5}{208.2\text{ g/mol PCl}_5} \times \dfrac{1\text{ mol H}_3\text{PO}_4}{1\text{ mol PCl}_5} \times \dfrac{98.0\text{ g H}_3\text{PO}_4}{1\text{ mol H}_3\text{PO}_4} \times$

$\dfrac{89\text{ g}}{100\text{ g}}\ 5\ 8.4\text{ g H}_3\text{PO}_4$

29. $\dfrac{100\text{ g Ag}}{107.9\text{ g/mol Ag}} = 0.927\text{ mol Ag}$

$\dfrac{100\text{ g S}}{32.06\text{ g/mol Ag}} = 3.12\text{ mol S}$

sulfur is in excess, silver limits

$0.927\text{ mol Ag} \times \dfrac{1\text{ mol Ag}_2\text{S}}{2\text{ mol Ag}} \times \dfrac{247.8\text{ g Ag}_2\text{S}}{1\text{ mol Ag}_2\text{S}} =$

$115\text{ g Ag}_2\text{S}$

30. (a) $\dfrac{10.0\text{ g PH}_3}{34.0\text{ g/mol PH}_3} = 0.294\text{ mol PH}_3$

$\dfrac{50.0\text{ g CuSO}_4}{160\text{ g/mol CuSO}_4} = 0.313\text{ mol CuSO}_4$

PH_3 is in excess

$0.313\text{ mol CuSO}_4 \times \dfrac{1\text{ mol Cu}_3\text{P}_2}{3\text{ mol CuSO}_4} \times \dfrac{253\text{ g Cu}_3\text{P}_2}{1\text{ mol Cu}_3\text{P}_2} =$

$26.4\text{ g Cu}_3\text{P}_2$

(b) $\dfrac{20.0\text{ g actual}}{26.4\text{ g theoretical}} \times 100\% = 75.8\%$

31. $100\text{ kg ore} \times \dfrac{42.25\text{ kg Fe}_2\text{O}_3}{100\text{ kg ore}} \times \dfrac{111.7\text{ kg Fe}}{159.7\text{ kg Fe}_2\text{O}_3} =$

29.6 kg Fe

32. $\dfrac{0.4671\text{ g PbSO}_4}{303.3\text{ g/mol PbSO}_4} \times \dfrac{1\text{ mol Pb}}{1\text{ mol PbSO}_4} \times \dfrac{207.2\text{ g Pb}}{1\text{ mol Pb}} \times$

$\dfrac{1}{1.6841\text{ g}} \times 100\% = 18.95\%\text{ Pb}$

33. (a) $\dfrac{0.4705\text{ g BaSO}_4}{233.39\text{ g/mol BaSO}_4} \times \dfrac{1\text{ mol Ba}}{1\text{ mol BaSO}_4} \times$

$\dfrac{137.34\text{ g Ba}}{1\text{ mol Ba}} \times \dfrac{1}{0.4324\text{ g}} \times 100\% = 64.03\%\text{ Ba}$

(b) $\dfrac{0.4705\text{ g BaSO}_4}{233.39\text{ g/mol BaSO}_4} \times \dfrac{1\text{ mol BaCO}_3}{1\text{ mol BaSO}_4} \times$

$\dfrac{1.97.35\text{ g BaCO}_3}{1\text{ mol BaCO}_3} \times \dfrac{1}{0.4324\text{ g}} \times 100\% = 92.01\%$

purity

34. $\dfrac{0.2105\text{ g Al}_2\text{O}_3}{101.96\text{ g/mol Al}_2\text{O}_3} \times \dfrac{2\text{ mol Al}}{1\text{ mol Al}_2\text{O}_3} \times \dfrac{26.9815\text{ g Al}}{1\text{ mol Al}} \times$

$\dfrac{1}{0.6036\text{ g}} \times 100\% = 18.46\%\text{ Al}$

35. $\dfrac{0.8530\text{ g SO}_3}{80.06\text{ g/mol SO}_3} \times \dfrac{1\text{ mol Cu}_2\cdot\text{Fe}_2\text{S}_3}{4\text{ mol SO}_3} \times$

$\dfrac{367.03\text{ g Cu}_2\cdot\text{Fe}_2\text{S}_3}{1\text{ mol Cu}_2\text{S}\cdot\text{Fe}_2\text{S}_3} \times \dfrac{1}{1.0230\text{ g}} \times 100\% = 95.57\%$

36. $\dfrac{0.2000\text{ mol NaOH}}{1\text{ L}} \times \dfrac{38.20\text{ mL}}{1000\text{ mL/L}} \times \dfrac{1\text{ mol H}_2\text{SO}_4}{2\text{ mol NaOH}} \times$

$\dfrac{1000\text{ mL/L}}{50.00\text{ mL}} = 0.0764\ M\text{ H}_2\text{SO}_4$

37. $\dfrac{0.2500\text{ g NaCl}}{58.443\text{ g/mol NaCl}} \times \dfrac{1\text{ mol AgNO}_3}{1\text{ mol NaCl}} \times \dfrac{100\text{ mL/L}}{32.85\text{ mL}} =$

$0.1302\ M\text{ AgNO}_3$

38. $\dfrac{0.3030\text{ g K}_2\text{C}_2\text{O}_4}{166.2\text{ g/mol K}_2\text{C}_2\text{O}_4} \times \dfrac{2\text{ mol KMnO}_4}{5\text{ mol K}_2\text{C}_2\text{O}_4} \times \dfrac{100\text{ mL/L}}{46.50\text{ mL}} =$

$0.01568\text{ mol/L KMnO}_4$

39. $0.8000\text{ mol/L K}_2\text{Cr}_2\text{O}_7 \times \dfrac{28.25\text{ mL}}{1000\text{ mL/L}} \times \dfrac{6\text{ mol FeSO}_4}{1\text{ mol K}_2\text{Cr}_2\text{O}_7} \times$

$\dfrac{1\text{ mol Fe}}{1\text{ mol FeSO}_4} \times \dfrac{55.847\text{ g Fe}}{1\text{ mol Fe}} \times \dfrac{1}{4.3128\text{ g}} \times 100\% =$

17.56% Fe

40. $0.2714\text{ mol/L KMnO}_4 \times \dfrac{32.50\text{ mL}}{1000\text{ mL/L}} \times \dfrac{5\text{ mol H}_2\text{O}_2}{2\text{ mol KMnO}_4} \times$

$\dfrac{1000\text{ mL/L}}{25.00\text{ mL}} = 08820\ M\text{ H}_2\text{O}_2$

41. $0.1200\text{ mol/L HCl} \times 0.04242\text{ L} \times \dfrac{1\text{ mol Ca(OH)}_2}{2\text{ mol HCl}} \times$

$\dfrac{74.08\text{ g Ca(OH)}_2}{1\text{ mol Ca(OH)}_2} \times \dfrac{1}{0.2194\text{ g}} \times 100\% = 85.93\%\text{ Ca(OH)}_2$

42. $0.2736\text{ g CO}_2 \times \dfrac{12.01\text{ g C}}{44.01\text{ g CO}_2} \times \dfrac{1}{0.1020\text{ g}} \times 100\% =$

73.20% C

$0.0672\text{ g H}_2\text{O} \times \dfrac{2.0158\text{ g H}}{18.0158\text{ g H}_2\text{O}} \times \dfrac{1}{0.1020\text{ g}} \times 100\% =$

7.37% H

43. $\dfrac{11.5\text{ mL}}{1000\text{ mL/L}} \times 1.11\text{ g/L N}_2 \times \dfrac{1}{0.1000\text{ g}} \times 100\% = 12.8\text{ N}$

44. (a) $0.1826\text{ g H}_2\text{O} \times \dfrac{2.0158\text{ g H}}{18.0158\text{ g H}_2\text{O}} \times \dfrac{1}{0.2340\text{ g}} \times 100\% =$

8.731% H

$0.6329\text{ g CO}_2 \times \dfrac{12.011\text{ g C}}{44.011\text{ g CO}_2} \times \dfrac{1}{0.2340\text{ g}} \times 100\% =$

73.80% C

$100\% - (8.73\% + 73.80\%) = 17.5\%\text{ N}$

(b) $\dfrac{73.80\text{ g C}}{12.01\text{ g/mol C}} = 6.145\text{ mol C}$

$\dfrac{8.737\text{ g H}}{1.01\text{ g/mol H}} = 8.64\text{ mol H}$

$\dfrac{17.47\text{ g N}}{14.0\text{ g/mol N}} = 1.25\text{ mol N}$

Ratio: 6.15 : 8.64 : 1.25 = 5 : 7 : 1, empirical formula = C_5H_7N

45. The compound is 75.36% carbon, 6.62% hydrogen, 8.363% nitrogen and 9.657% oxygen. The empirical formula is $C_{21}H_{22}N_2O_2$, which is the same as the molecular formula.

$\dfrac{334\text{ g/mol}}{334\text{ g/emp.form.}} = 1$, molecular formula = $C_{21}H_{22}N_2O_2$

CHAPTER 12

1. (a) Homogenous reactions occur in a single phase; heterogeneous reactions occur in a system with more than one phase.
(b) The order of the reaction is the sum of the exponents in the rate law; the molecularity of a reaction indicates the number of species that form an activated complex.
(c) The reaction rate is a measure of the speed of a reaction; the reaction mechanism is a set of elementary reactions (steps) that yield the overall reaction.
(d) The activated complex (or transition state) is a structure with no finite lifetime that is intermediate between the reactant(s) and product(s) of a reaction; the activation energy, E_a, is the minimum energy required for a specific reaction to occur.
(e) Total collisions is a measure of the frequency at which reactants collide; effective collisions between reactants are those that have sufficient energy and proper orientation for reaction to occur.

2. The rate of reaction increases with increasing temperature because the collision rate between reactants increases and because the average internal energy of the reactants increases, which allows more colliding reactants to possess energy greater than E_a.

3. Catalysis is the acceleration of a reaction rate that occurs because the catalyst provides an alternative reaction pathway, which has a lower energy of activation.

4. (a) first-order
(b) second-order
(c) third-order
(d) second-order

5. (a) third-order
(b) first-order
(c) first-order
(d) five-halves order; i.e., 5/2's

6. An increase in temperature will increase the average energy of the molecules and thereby provide more internal energy to overcome the energy of activation. Whether the reaction is endothermic or exothermic, overcoming E_a is the important consideration.

7. Rusting is a heterogeneous process. Iron powder has a greater surface area than a nail of the same mass. Therefore, the agents responsible for rusting may attack more iron sites at the same time on the iron powder sample.

8. An increase in pressure at a constant temperature is essentially an increase in concentration of A and B. At higher concentrations more collisions between A and B will occur per unit time.

9. (a) $K = \dfrac{\text{rate}}{[\mathrm{CO}][\mathrm{Cl_2}]^{3/2}} = \dfrac{6.7 \times 10^{-3}\ \text{mol/L-min}}{(0.10\ \text{mol/L})(0.10\ \text{mol/L})^{3/2}} =$
$2.1\ \mathrm{L^{3/2}/mol^{3/2}\text{-min}}$
(b) Rate $= 2.1 \times 0.02 \times (0.02)^{3/2} = 1 \times 10^{-4}$ mol/L-min
(c) The value of the rate constant will be greater.
(d) The reaction rate would be increased.

10. (a) Rate $= k[\mathrm{A}]^2$
(b) The reaction is second-order.
(c) $k = \dfrac{\text{rate}}{[\mathrm{A}]^2} = \dfrac{2.0 \times 10^{-3}\ \text{mol/L-min}}{(0.10\ \text{mol/L})^2} = 0.20$ L/mol-min

11. (a) Rate $= k[\mathrm{ClO_2}]^2[\mathrm{OH^-}]$
(b) The reaction is third-order.
(c) $k = \dfrac{\text{rate}}{[\mathrm{ClO_2}][\mathrm{OH^-}]} = \dfrac{0.46\ \text{mol/L-s}}{(0.10\ \text{mol/L})^2(0.20\ \text{mol/L})} =$
$2.3 \times 10^2\ \mathrm{L^2/mol^2\text{-s}}$

12. (a) Rate $= k[\mathrm{N_2O_5}]$ and order $= 1$
(b) $k = \dfrac{\text{rate}}{[\mathrm{N_2O_5}]} = \dfrac{0.107\ \text{mol/L-min}}{0.15\ \text{mol/L}} = 0.71\ \text{min}^{-1}$

13. Rate $= k[\mathrm{H_2}]^m[\mathrm{Br_2}]^n$

$$\frac{9.07 \times 10^{-2}}{6.05 \times 10^{-2}} = \left(\frac{0.6}{0.4}\right)^m; \quad m = 1$$

$$\frac{6.05 \times 10^{-2}}{4.32 \times 10^{-2}} = \left(\frac{0.4}{0.2}\right)^n; \quad n = \frac{1}{2}$$

Rate $= k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}$

$$k = \frac{6.05 \times 10^{-2}\ \text{mol/L-min}}{(0.40\ \text{mol/L})(0.40\ \text{mol/L})^{1/2}} = 0.24\ \mathrm{L^{1/2}/mol^{1/2}\text{-min}}$$

14. After 400 seconds, one-fourth of *A* remains, and after 800 seconds, one-sixteenth of *A* remains.

15. (a) The plot ln $[\mathrm{C_2H_5Cl}]$ vs. time is linear and therefore the reaction is first-order.
(b) $\ln [\mathrm{A}]_t = -kt + \ln [\mathrm{A}]_0$
$\ln 0.0730 = (-k \times 10\,s) + \ln 0.100\ -2.62 - (-2.30) = (-k \times 10\,s)$

$$k = \frac{0.32}{10\,s} = 0.032\,s^{-1}$$

(c) $\ln [\mathrm{A}]_t = -(0.032\,s^{-1} \times 120\,s) + (-2.30) = -6.14$
$[\mathrm{A}]_t = 2.2 \times 10^{-3}$ mol/L
(d) $\ln (0.050) = -(0.032\,s^{-1})\,t + \ln (0.10)$
$t = 22\,s$

16. (a) $\dfrac{1}{[\mathrm{HI}]_t} = kt + \dfrac{1}{[\mathrm{HI}]_0}$

$$k = \left(\frac{1}{[\mathrm{HI}]_t} - \frac{1}{[\mathrm{HI}]_0}\right)\frac{1}{t}$$

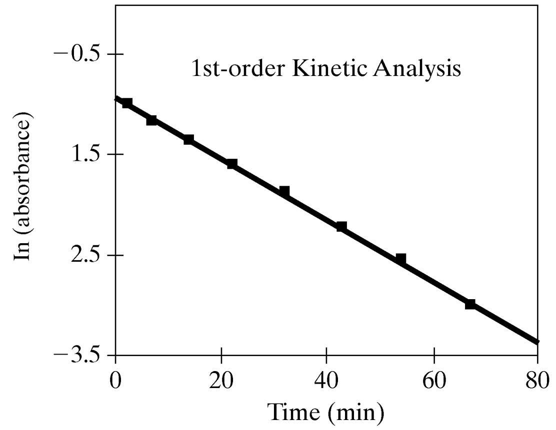
$$k = \left(\frac{1}{0.400} - \frac{1}{0.800}\right)\frac{1}{7.25} = 0.172\ \text{L/mol-min}$$

(b) Rate $= 0.172$ L/mol-min $(0.800\ \text{mol/L})^2 = 0.110$ mol/L-min

17. $k = \dfrac{\text{rate}}{[\mathrm{CO}][\mathrm{NO_2}]} = \dfrac{0.0200\ \text{mol/L-s}}{(0.200\ \text{mol/L})(0.200\ \text{mol/L})}$
$k = 0.500$ L/mol-s

18. $[\mathrm{A}]_t = [\mathrm{A}]_0 - kt$
$[\mathrm{A}]_t = (1.00\ \text{mol/L}) - (3.2 \times 10^{-2}\ \text{mol/L-s})\ (30\ s) = 0.040$ mol/L

19. a. The reaction is first-order with respect to A. See the graph at top of next page.



b. From the slope of the line, $k = 3.04 \times 10^{-2}\ \text{sec}^{-1}$.

c. $\dfrac{\ln 2}{3.04 \times 10^{-2}\ \text{sec}^{-1}} = 2.2\ \text{sec}$

20. From the units on k, the reaction is 2nd order; i.e., Rate = $k[A]^2$.
Also, $[A]$ changes from 1.00 M to 0.10 M.

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + kt \longrightarrow \frac{1}{0.10\ M} = \frac{1}{1.00\ M} + kt$$

$$t = 404\ \text{seconds}$$

21. $t_{1/2} = \dfrac{\ln 2}{3.2 \times 10^{-1}\ \text{sec}^{-1}} = 2.2\ \text{sec}$

22. Rate = $k[\mathrm{F_2}]^1[\mathrm{ClO_2}]^1$

$$k_1 = \frac{7.5 \times 10^{-3}\ \mathrm{M/s}}{(0.125\ M)(0.050\ M)} = 1.2\ \mathrm{M^{-1}\,s^{-1}}$$

$$k_2 = \frac{5.7 \times 10^{-3}\ \mathrm{M/s}}{(0.125\ M)(0.038\ M)} = 1.2\ \mathrm{M^{-1}\,s^{-1}}$$

$$k_3 = \frac{1.1 \times 10^{-2}\ \mathrm{M/s}}{(0.250\ M)(0.038\ M)} = 1.2\ \mathrm{M^{-1}\,s^{-1}}$$

$$k = 1.2\ \mathrm{M^{-1}\,s^{-1}}$$

23. Rate = $k[\mathrm{NO_2}]^2$

$$k = \left(\frac{1}{[\mathrm{NO_2}]_t} - \frac{1}{[\mathrm{NO_2}]_0}\right)\frac{1}{t}$$

$$k = \left(\frac{1}{0.444} - \frac{1}{0.500}\right)\frac{1}{20\ \text{min}}$$

$$k = 0.0125\ \text{L/mol-min}$$

24. $\ln k = \ln \mathrm{A} - \dfrac{E_a}{RT}$

$$\ln k = \ln (8.91 \times 10^{21}\ \text{min}^{-1}) - \frac{349000\ \text{J/mol}}{(8.314\ \text{J/mol-K})(773\ \text{K})}$$

$$= -3.76$$

$$k = 0.0232\ \text{min}^{-1}$$

25. $E_a = R\left(\dfrac{T_1T_2}{T_2 - T_1}\right)\ln\left(\dfrac{k_2}{k_1}\right) = (0.00831\ \text{kJ/mol})$
$\dfrac{298\ \text{K} \times 308\ \text{K}}{308\ \text{K} - 298\ \text{K}}$ ln \B(\F($1.5 \times 10^{-4}\ \text{s}^{-1}$, $3.8 \times 10^{-5}\ \text{s}^{-1}$)) =
1.0×10^2 kJ/mol

$$\ln \mathrm{A} = \ln \frac{E_a}{RT} = (\ln 3.8 \times 10^{-5}) + \frac{1.0 \times 10^5\ \text{J/mol}}{(8.314\ \text{J/K-mol})(298\ \text{K})}$$

$$= 30.2$$

$$\mathrm{A} = 1.3 \times 10^{13}\ \text{s}^{-1}$$

26. (a) The reaction is 2nd-order overall.
(b) $0.37\ M\ \text{sec}^{-1} = k(0.025\ M)(0.025\ M)$; $k = 5.9 \times 10^2\ \mathrm{M^{-1}}\ \text{sec}^{-1}$
(c) Rate $= k[\mathrm{ICl}][\mathrm{H_2}] = 5.9 \times 10^2\ \mathrm{M^{-1}sec^{-1}}(0.35\ \mathrm{M})(0.025\ \mathrm{M}) = 5.2\ \mathrm{M\ sec^{-1}}$

27. (a) $\ln([\mathrm{Cl_2O_7}]_0/[\mathrm{Cl_2O_7}]_t) = kt$; $\ln(47.1\ \text{torr}/16.9\ \text{torr}) = k(165\ \text{sec})$
Therefore, $k = 0.00620\ \text{sec}^{-1}$
(b) $\ln(47.1\ \text{torr}/[\mathrm{Cl_2O_7}]_{330}) = (0.00620\ \text{sec}^{-1})(330\ \text{sec})$
The pressure of $\mathrm{Cl_2O_7}$ after 330 seconds is 6.09 torr.
(c) $\ln(100/1) = (0.00620\ \text{sec}^{-1})t$; Thus, $t = 743$ sec.

28. (a) Answer: c.
(b) Answer: b.
(c) Answer: a.
(d) Answer: b.

29. Step #1 $\ln([\mathrm{A}]_0/[\mathrm{A}]_t) = kt$
Step #2 At the half-life (i.e., $t = t_{1/2}$) $[\mathrm{A}]_t = [\mathrm{A}]_0/2$
Step #3 By substitution $\ln([\mathrm{A}]_0/[\mathrm{A}]_0/2) = kt_{1/2}$
Step #4 $\ln 2 = kt_{1/2}$
Step #5 $(\ln 2)/k = t_{1/2}$

30. (a) $1/[\mathrm{A}]_t - 1/[\mathrm{A}]_0 = kt$; $1/(1.95 \times 10^{-3}\ M) - 1/(2.91 \times 10^{-3}\ M) = k(1825\ \text{sec})$
$k = 9.27 \times 10^{-2}\ M^{-1}\text{sec}^{-1}$
(b) $1/([\mathrm{NO}]_{2825\ \text{sec}}) - 1/(2.91 \times 10^{-3}\ M) = (9.27 \times 10^{-2}\ M^{-1}\text{sec}^{-1})\ (2825\ \text{sec})$
After 2825 second, $[\mathrm{NO}] = 1.65 \times 10^{-3}\ M$
(c) $t_{1/2} = 1/[\mathrm{NO}]_0k$
$t_{1/2} = 3.71 \times 10^3\ \text{sec} = 61.8\ \text{min}$
(d) $t_{1/2} = 1.5 \times 10^2\ \text{sec}$

31. Step #1 $1/[\mathrm{A}]_t - 1/[\mathrm{A}]_0 = kt$
Step #2 At $t = t_{1/2}$, $[\mathrm{A}]_t = [\mathrm{A}]_0/2$
Step #3 $1/([\mathrm{A}]_0/2) - 1/[\mathrm{A}]_0 = kt_{1/2}$
Step #4 $2/[\mathrm{A}]_0 - 1/[\mathrm{A}]_0 = kt_{1/2}$
Step #5 $1/[\mathrm{A}]_0 = kt_{1/2}$
Step #6 Which yields: $1/k[\mathrm{A}]_0 = t_{1/2}$

32. (a) Rate $= k[\mathrm{Br}]^2$
(b) $1/[\mathrm{A}]t - 1/[A]_0 = kt$
$1/(2.43 \times 10^{-6}\ M) - 1/(1.37 \times 10\text{-}5\ M) = k(1.22 \times 10^{-3}\ \text{sec})$
$k = 2.77 \times 10^8\ M^{-1}\text{sec}^{-1}$
(c) $1/(3.67 \times 10^{-6}\ M) - 1/([\mathrm{Br}]_0) = (2.77 \times 10^8\ M^{-1}\ \text{sec}^{-1})(0.82 \times 10^{-3}\ \text{sec})$
$[\mathrm{Br}]_0 = 2.2 \times 10^{-5}\ M$

33. at 293 K:

$$k = \frac{1.2}{(0.100)^2(0.100)} = 1200\ \mathrm{L^2/mol^2\text{-}min}$$

at 303 K:

$$k = \frac{2.4}{(0.100)^2(0.100)} = 2400\ \text{L}^2/\text{mol}^2\text{-min}$$

$$E_a = 8.314\ \text{J/mol-K}\left(\frac{293\ \text{K} \times 303\ \text{K}}{303\ \text{K} - 293\ \text{K}}\right)\ln\left(\frac{2400}{1200}\right)$$

$$= 51\ \text{kJ/mol}$$

34. (a) Rate $= k$
(b) $[\text{A}]_t = [\text{A}]_0 - kt$

$$k = \frac{[\text{A}]_0 - [\text{A}]_t}{t}$$

at 300 K:

$$k_1 = \frac{1.00 - 0.90}{10} = 0.010\ \text{mol/L-min}$$

at 320 K:

$$k_2 = \frac{1.00 - 0.84}{10} = 0.016\ \text{mol/L-min}$$

$$E_a = (8.314\ \text{J/K-mol})\left(\frac{300\ \text{K} \times 320\ \text{K}}{320\ \text{K} - 300\ \text{K}}\right)$$

$$\ln\left(\frac{0.016}{0.100}\right) = 19\ \text{kJ/mol}$$

35. Step 1 (very slow, rate-determining)
Step 2 (fast)

36. (a) Rate $= k[\text{CO}_2]\,[\text{OH}^-]$

(b) $\text{Rate} = 8500\ \text{L/mol-s} \times \dfrac{0.44\ \text{g/L}}{44\ \text{g/mol}} \times 2.2 \times 10^{-4}\ \text{mol/L}$

$\text{Rate} = 1.9 \times 10^{-2}\ \text{mol/L-s}$

37. (a) The reaction is first-order with respect to A.
(b) From the slope of the line, $k = 0.020\ \text{s}^{-1}$.
(c) The half-life for the reaction is $\ln 2/0.020\ \text{s}^{-1} = 35$ sec.
(d) When the reaction is 95% complete, only 5% of the original amount of A will remain. The concentration of A at 95% complete will be:

$$[\text{A}]_{95\%} = 0.05\ (4.48\ \text{mol/L}) = 0.224\ \text{mol/L}$$

First-order: $\ln [\text{A}]_{95\%} = \ln [\text{A}]_0 - kt$

$$\ln (0.224) = \ln (4.48) - 0.020\ \text{s}^{-1}\ (t)$$

$$t = 150\ \text{sec}$$

The reaction will require 150 sec to be 95% complete.

38. Rate $= k[\text{NO}_2]^2$

$$k = \frac{9.0 \times 10^{-7}\ \text{mol/L-min}}{(2.00\ \text{mol/L})^2} = 0.125\ \text{L/mol-s}$$

$$\text{Rate} = (0.125)(1.00)^2 = 0.125\ \text{mol/L-min}$$

39. (a) Rate $= k[\text{CH}_3\text{CHO}]^2$

(b) $k = \dfrac{9.0 \times 10^{-7}\ \text{mol/L-s}}{(0.10\ \text{mol/L})^2} = 9.0 \times 10^{-5}\ \text{L/mol-s}$

(c) Rate $= (9.0 \times 10^{-5})\ (0.25)^2 = 5.6 \times 10^{-6}\ \text{mol/L-s}$

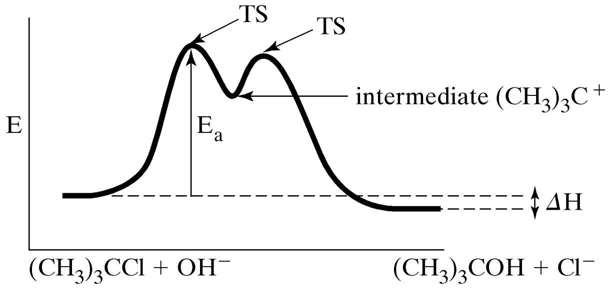
40. (a) Rate $= k[\text{Cl}_2]^1[\text{CO}]^{\text{o}} = k[\text{Cl}_2]^1$
(b) $1 \times 10^{-4}\ \text{M/min} = k(0.1\ \text{M});\ k = 0.001\ \text{min}^{-1}$
(c) Step 1 (rate-determining step)
Step 2 (fast)
Step 3 (fast)

41. (a) second-order
(b) Rate $= k[\text{H}_2][\text{I}_2]$
(c) $k = \dfrac{2.0 \times 10^{-4}}{(0.10)(0.20)} = 1.0 \times 10^{-2}\ \text{L/mol-minL}$

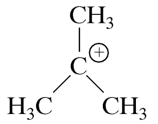
42. Rate $= k[\text{H}_2]$

44. (a) A (b) B (c) B (d) A (e) B

45. answer:



46. answer:



trigonal plane
sp^2 hybrid
< = 120°

47. 1. (d) 2. (b) 3. (c) 4. (b) 5. (d) 6. (a)

CHAPTER 13

1. (a) K will remain the same, but the extent of the reaction will increase.
(b) K will remain the same, but the extent of the reaction will increase.
(c) K will remain the same, but the extent of reaction will increase.
(d) K will decrease, but the change in extent cannot be determined.
(e) The value of K and the extent of reaction will decrease.
(f) No effect on K or the extent of reaction.

2. (a) Mass of CO will increase.
(b) Mass of CO will increase.
(c) No effect.
(d) Mass of CO will increase.
(e) Mass of CO will decrease.

3. (a) 1. The number of moles of carbon dioxide will increase.
2. No effect.
3. No effect.
4. No effect.

(b) $K = \dfrac{[\text{CO}_2]}{[\text{CO}]} = \dfrac{0.25}{0.10} = 2.5$

4. Because the reaction is exothermic the reaction should be done at a relatively low temperature; i.e., as the heat is evolved, it should be removed to maintain the temperature.

Also, steam should be continuously added to the reaction mixture, and the hydrogen should be removed as it is formed.

5. $$K_c = \frac{0.212 \text{ mol/3.00 L}}{(0.364 \text{ mol/3.00 L})(0.264 \text{ mol/3.00 L})} = 6.62$$

$$K_P = \frac{\mathrm{P_{COCL_2}}}{\mathrm{P_{CO}P_{Cl_2}}} = \frac{\mathrm{X_{COCl_2}P}}{(\mathrm{X_{CO}P})(\mathrm{X_{Cl_2}P})}$$

$$= \frac{\dfrac{0.212}{0.840} \times 2.0 \text{ atm}}{\left(\dfrac{0.364}{0.840} \times 2.0 \text{ atm}\right)\left(\dfrac{0.264}{0.840} \times 2.0 \text{ atm}\right)} = 0.93$$

6. (a) $\mathrm{XeF_4} \rightleftharpoons \mathrm{Xe} + 2\,\mathrm{F_2}$ $\quad K = \dfrac{1}{2 \times 10^3} 5 \times 10-4$

(b) $1/2\,\mathrm{Xe} + \mathrm{F_2} \rightleftharpoons 1/2\,\mathrm{XeF_4}$ $\quad K = \sqrt{2 \times 10^3} = 4 \times 10^1$.

(c) $$K_1 = \frac{[\mathrm{Xe}][\mathrm{F_2}]}{[\mathrm{XeF_2}]} = \frac{1}{4 \times 10^2} = 2.5 \times 10^{-3}$$

$$K_2 = \frac{[\mathrm{XeF_6}]}{[\mathrm{Xe}][\mathrm{F_2}]^3} = 40$$

$$K_1K_2 = \frac{[\mathrm{Xe}][\mathrm{F_2}]}{[\mathrm{XeF_2}]} = \frac{[\mathrm{XeF_6}]}{[\mathrm{Xe}][\mathrm{F_2}]^3} = \frac{[\mathrm{XeF^6}]}{[\mathrm{XeF_2}][\mathrm{F_2}]^2}$$

$$= (2.5 \times 10^{-3})(40) = 1 \times 10^{-1}$$

(d) $$K_1 = \frac{[\mathrm{Xe}][\mathrm{F_2}]}{[\mathrm{XeF_4}]} = \frac{1}{2} \times 10^{-3} = 5 \times 10^{-4}$$

$$K_2 = \frac{[\mathrm{XeF_2}]^{-2}}{[\mathrm{Xe}]^2[\mathrm{F_2}]^2} = (4 \times 10^2)^2 = 1.6 \times 10^5$$

$$K_1K_2 = \frac{[\mathrm{Xe}][\mathrm{F_2}]^2}{[\mathrm{XeF_4}]} \times \frac{[\mathrm{XeF_2}]^2}{[\mathrm{Xe}]^2[\mathrm{F_2}]^2} = \frac{[\mathrm{XeF_2}]^2}{[\mathrm{Xe}][\mathrm{XeF_4}]}$$

$$= (5 \times 10^{-4})(1.6 \times 10^5) = 8 \times 10^1$$

(e) $$K_1 = \frac{[\mathrm{XeF_6}]}{[\mathrm{Xe}][\mathrm{F_2}]^3} = 40$$

$$K_2 = \frac{[\mathrm{Xe}]^3[\mathrm{F_2}]^3}{[\mathrm{XeF_2}]^3} = \left(\frac{1}{4 \times \backslash 10^2}\right)^3 = 1.6 \times 10^{-8}$$

$$K_1K_2 = \frac{[\mathrm{XeF_6}]}{[\mathrm{Xe}][\mathrm{F_2}]^3} \times \frac{[\mathrm{Xe}]^3[\mathrm{F_2}]^3}{[\mathrm{XeF_2}]^3} = \frac{[\mathrm{XeF_6}][\mathrm{Xe}]^2}{[\mathrm{XeF_2}]^3}$$

$$= 6 \times 10^{-7}$$

(f) $$K_1 = \frac{[\mathrm{XeF_2}]}{[\mathrm{Xe}][\mathrm{F_2}]} = 4 \times 10^2$$

$$K_2 = \frac{[\mathrm{XeF_4}]}{[\mathrm{Xe}][\mathrm{F_2}]^2} = 2 \times 10^3$$

$$K_3 = \frac{[\mathrm{Xe}][\mathrm{F_4}]^3}{[\mathrm{XeF_6}]} = 1/40 = 2.5 \times 10^{-2}$$

$$K_1K_2K_3 = \frac{[\mathrm{XeF_2}]}{[\mathrm{Xe}][\mathrm{F_2}]} \times \frac{[\mathrm{XeF_4}]}{[\mathrm{Xe}][\mathrm{F_2}]^2} \times \frac{[\mathrm{Xe}][\mathrm{F_2}]^3}{[\mathrm{XeF_6}]}$$

$$= \frac{[\mathrm{XeF_2}][\mathrm{XeF_4}]}{[\mathrm{Xe}][\mathrm{XeF_6}]}$$

$$= (4 \times 10^2)(2 \times 10^3)(2.5 \times 10^{-2})$$

$$= 2 \times 10^4$$

7. (a) $\mathrm{CO_2}(g) + \mathrm{C}(s) \rightleftharpoons 2\,\mathrm{CO}(g)$ $\quad K_p = \dfrac{(\mathrm{P_{CO}})^2}{(\mathrm{P_{CO_2}})}$

(c) $\mathrm{CO_2} = 2$ atm

$$K_p = \frac{(\mathrm{P_{CO}})^2}{\mathrm{P_{CO_2}}}$$

$$p\mathrm{CO} = \sqrt{K_p p\mathrm{CO_2}} = \sqrt{(1.4 \times 10^{-2})(2)}$$

$$= 1.7 \times 10^{-1} \text{ atm}$$

8. (a) $K_p = K_c/(RT)$

$K_p = K_c/(RT)^2$

$K_p = K_c/(RT)$

(b) $PV = nRT$

$$\frac{P}{RT} = \frac{n}{V} = \text{molarity}$$

for $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$

$$K_c = \frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]} = \frac{\left(\dfrac{\mathrm{P_C}}{RT}\right)}{\left(\dfrac{\mathrm{P_A}}{RT}\right)\left(\dfrac{\mathrm{P_B}}{RT}\right)} = \frac{\mathrm{P_C}}{(\mathrm{P_A})(\mathrm{P_B})(RT)}$$

$K_c = K_p(RT)$; $\quad K_p = K_c(RT)^{-1}$

$K_p = K_c\,(RT)^{\Delta n}$

where Δn is the number of moles of gaseousproducts minus the number of moles of gaseous reactants in the balanced equation

9. $$K_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{(\mathrm{P_{N_2O_4}}/RT)}{(\mathrm{P_{NO_2}}/RT)^2} = \frac{\mathrm{P_{N_2O_4}}}{\mathrm{P^2_{NO_2}}} \cdot \frac{\left(\dfrac{1}{RT}\right)}{\left(\dfrac{1}{RT}\right)^2}$$

$$= \frac{\mathrm{P_{N_2O_4}}}{\mathrm{P^2_{NO_2}}} \cdot RT$$

$$\frac{K_c}{RT} = \frac{\mathrm{P_{N_2O_4}}}{\mathrm{P^2_{NO_2}}} = K_p \quad K_p = \frac{7.04}{RT} = 0.288$$

10. Higher pressures will favor $\mathrm{N_2O_4}$ formation.

$$K_p = 0.288 = \frac{\mathrm{P_{N_2O_4}}}{\mathrm{P^2_{NO_2}}}$$

$$\mathrm{P_{N_2O_4}} = 0.392 \text{ atm} \times \frac{250 \text{ mL}}{125 \text{ mL}} = 0.784 \text{ atm}$$

$$\mathrm{P_{NO_2}} = 1.16 \text{ atm} \times \frac{250 \text{ mL}}{125 \text{ mL}} = 2.32 \text{ atm}$$

$$K_p = 0.288 = \frac{(0.784 + x)}{(2.32 - 2x)^2}$$

at equilibrium: $\mathrm{P_{N_2O_4}} = 1.01$ atm or 0.0413 M

$\mathrm{P_{NO_2}} = 1.87$ atm or 0.0765 M

11. a. $$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} = \frac{\mathrm{P^2_{NH_3}}\,(1/RT)^2}{\mathrm{P_{N_2}}\,(1/RT)\,\mathrm{P^3_{H_2}}\,(1/RT)^3} =$$

$$K_p \frac{(1/RT)^2}{(1/RT)^4} = 0.0603$$

b. $[\mathrm{N_2}]_0 = 5.00 \times 10^{-3}\ M$ $\qquad [\mathrm{H_2}]_0 = 6.20 \times 10^{-2}\ M$

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} =$$

$$\frac{(2x)^2}{(5.00 \times 10^{-3} - x)(6.20 \times 10^{-2} - 3x)^3} = 6.04 \times 10^{-2}$$

Assume that $3x \ll 6.2 \times 10^{-2}$, then

$$6.04 \times 10^{-2} = \frac{4x^2}{(5.00 \times 10^{-3} - x)(6.20 \times 10^{-2} - 3x)^3}$$

$x = 1.36 \times 10^{-4}$ $[NH_3] = 2.72 \times 10^{-4}\ M$

Limiting Reagent: N_2 gas

$$\%\ \text{yield} = \frac{2.72 \times 10^{-4}\ M}{2 \times 5.00 \times 10^{-3}\ M} \times 100 - 2.72\%$$

If one assumes $x \ll 5.00 \times 10^{-3}$ then $x = 1.34 \times 10^{-4}$ and % yield = 2.68

12. $$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{0.050\ \text{mol}}{3\ \text{L}}\right)^2}{\left(\frac{0.15\ \text{mol}}{3\ \text{L}}\right)\left(\frac{0.10\ \text{mol}}{3\ \text{L}}\right)^2} = 1.5 \times 10^2$$

13. (a) $N_2 + 3H_2 \rightleftharpoons 2\,NH_3$

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.2/1\ \text{L})^2}{(0.2/1\ \text{L})(0.2/1\ \text{L})^3} = 25$$

(b)

$$\begin{array}{llll} & N_2 + & 3H_2 \rightleftharpoons & 2NH_3 \\ \text{St} & 0.2 & 0.2 & 0.2 \\ \text{Ch} & -0.05 + x & -0.15 & +0.1 \\ \text{Eq} & 0.15 + x & 0.05 & 0.3 \end{array}$$

let $y = 0.15 + x$

$$\frac{(0.3)^2}{y(0.05)^3} = 0.15 + x$$

$y = 28.8 = 0.15 + x$

$x = 28.65$ mol

14. $PCl_{5g} \rightleftharpoons PCl_{3g} + Cl_{2g}$

$x = [PCl_3] = [Cl_2]$, $[PCl_5] = 1 - x$

$$\frac{x^2}{(1 - x)} = 1{,}7 \times 10^{-2}$$

$x = 0.12$ mol PCl_3

0.12 mol × 137 g/mol = 17 g PCl_3

15. (a) $$[CH_3COOCH_2CH_3] = [H_2O] = \frac{0.414\ \text{mol}}{V}$$

$$[CH_3COOH] = \frac{1.00\ \text{mol} - 0.414\ \text{mol}}{V};$$

$$[CH_3CH_2OH] = \frac{0.500 - 0.414}{V}$$

$$K = \frac{\left(\frac{0.414}{V}\right)\left(\frac{0.414}{V}\right)}{\left(\frac{0.586}{V}\right)\left(\frac{0.086}{V}\right)} = 3.40$$

(b) $$K = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1 - x}{V}\right)\left(\frac{1 - x}{V}\right)} = 3.4$$

$x = 0.65$ mol

Therefore, at equilibrium there are 0.65 mol of ethyl acetate, 0.65 mol of water, 0.35 mol of ethanol and 0.35 mol of acetic acid.

16. (a) $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

$$K = \frac{\left(\frac{0.40}{V}\right)\left(\frac{0.40}{V}\right)}{\left(\frac{0.20}{V}\right)\left(\frac{0.20}{V}\right)} = 4.0$$

(b) $[CO] = [H_2O] = 0.50 - x$ $[CO_2] = [H_2] = x$

$$\frac{x^2}{(0.50 - x)^2} = 4.0$$

$x = 0.33$ mol $CO_2 = 0.33$ mol H_2

(c) $[CO] = [H_2O] = x$ $[CO_2] = [H_2] = 0.50 - x$

$$\frac{0.50 - x}{x^2} = 4.0$$

$x = 0.17$ mol CO

(d) from part (b): $\frac{0.33}{0.50} \times 100\% = 67\%$

(e) $[CO_2] = [H_2] = x$ $[CO] = 0.40 - x$ $[H_2O] = 0.60 - x$

$$\frac{x^2}{(0.40 - x)(0.60 - x)} = 4$$

$x = 0.31$ mol CO_2

(f) $$K = \frac{(0.35)(0.35)}{(x - 0.35)(0.25)} = 4$$

$x = 0.47$ mol of CO

17. $$K = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.12}{(0.30)(0.20)} = 2.0$$

$[COCl_2] = 0.24$

$[Cl_2] = 0.20 - 0.12 = 0.08$

$[CO] = 0.30 - 0.12 + x$

$$\frac{0.24}{(0.18 + x)(0.08)} = 2.0$$

$x = 1.3$ mol CO

18. Let x = number of moles CO_2 at equilibrium

Then $[CO_2] = x$ and $[H_2] = x$

$$\frac{x^2}{(0.080 - x)(0.120 - x)} = 6.50$$

Solution of the quadratic equation gives $x = 0.17$ and $x = 0.066$. Only 0.066 is a possible answer. Therefore:

0.066 mol × 44 *g*/mol = 2.9 *g*

19. $K = [N_2][H_2O]^2 = 0.56$

$(x)\,(2x)^2 = 0.56$

$x = 0.52$ mol

0.48 mol NH_4NO_2 remaining = 31 *g* NH_4NO_2

20. (a) $$K_c = [CO_2] = \frac{0.25\ \text{mol}}{10\ \text{L}} = 0.025$$

(b) 0.25 mol × 56 g/mol = 14 g

(c) $K_p = K_c\,(RT)^{\Delta n}$ where Δn is the change in number of moles of gas going from reactants to products (+1 for this reaction)

$K_p = 0.025\ (0.0821 \times 773) = 1.6$

21. (a) $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

$[CO_2] = [H_2] = x$ and $[CO] = [H_2O] = 1 - x$

$$\frac{x^2}{(1-x)(1-x)} = 1.87 \text{ at } 963\ K$$

$x = 0.578$ mol/L
Therefore [CO] = [H_2O] = 0.422 *M*, [CO_2] = [H_2] = 0.578 *M*

(b) at 963 *K*: $\frac{0.58}{1.00} \times 100\% = 5.8\%$

at 1263 *K*: $\frac{0.44}{1.00} \times 100\% = 44\%$

(c) Exothermic because the extent of the reaction decreases as the temperature increases.

(d) [CO_2] = [H_2] = x [CO] = $1 - x$ [H_2O] = $2 - x$

$$\frac{x^2}{(1-x)(2-x)} = 1.87$$

$x = 0.75$

$$\text{Extent} = \frac{0.75}{1.00} \times 100\% = 75\%$$

The extent would therefore increase.

22. (a) No, it means that the ratio of the square of the concentration of NO_2 to the concentration of N_2O_4 is 2. If the reaction were of the type A $\rightleftharpoons$ B, then the number of moles of NO_2 would be twice that of N_2O_4 whenever the system is at equilibrium.

(b) Let x = mol/L of N_2O_4 added
Then [NO_2] = 0.60 and [N_2O_4] = $x - 0.30$ and

$$\frac{(0.60)^2}{(x - 0.30)} = 2.0$$

$x = 0.48$ mol N_2O_4

(c) [N_2O_4] = x [NO_2] = $1.0 - 2x$

$$\frac{(1.0 - 2x)^2}{x} = 2.0$$

$x = 0.19$ mol N_2O_4

(d) $[NO_2] = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 2x$ $[N_2O_4] = x$

$$\frac{(0.5 - 2x)^2}{x} = 2.0$$

$x = 0.068$ mol/L

$$\frac{0.068 \text{ mol } N_2O_4}{1 \text{ L}} \times 2.0 \text{ L} = 0.14 \text{ mol } N_2O_4$$

23. $H_2 + Cl_2 \rightleftharpoons 2\ HCl$

St	0.4	0.5	0
Ch	−0.2	−0.2	+0.4
Eq	0.2	0.3	0.4

$$K = \frac{[HC]^2}{[H_2]\,c\,Cl_2} = \frac{(0.4)^2}{(0.2)(0.3)} = 2.7$$

24. (a) $PCl_3 \longrightarrow PCl_3 + Cl_2$

St	x	0	0
Ch	−0.10	+0.10	+0.10
Eq	$x - 0.10$	0.10	0.10

$$K = \frac{(0.10)^2}{x - 0.10} = 0.10$$

$0.01 = 0.10x - 0.01$

$$x = \frac{0.02}{0.1} = 0.20 \text{ mol}$$

(b) $\frac{(0.3)(0.3)}{(0.05)} = 1.8$

K higher, therefore reaction endothermic.

25. (a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2^{o}$

(b)

	PCl_5	PCl_3	Cl_2
Start	0.10	0.00	0.00
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10\ -x$	x	x

	PCl_5	PCl_3	Cl_2
Start	0.10	0.00	0.00
Change	−0.028	+0.028	+0.028
Equilibrium	0.072	0.028	0.028

K = (0.028)(0.028)/(0.072) = 0.011

(c)

	PCl_5	PCl_3	Cl_2
Start	0.50	0.00	0.00
Change	$-x$	$+x$	$+x$
Equilibrium	$0.50\ -x$	$+x$	$+x$

$K = x^2/(0.50 - x) = 0.011$

Therefore, $x = 0.069$ and [PCl_3] = 0.069 *M*
The amount of PCl_3 produced is 0.14 mol or 19 g.

(d) When the solvent is added the concentrations are decreased by a factor of 10 to 0.0072, 0.0028, and 0.0028 mol/L for PCl_5, PCl_3 and Cl_2, respectively.

	PCl_5	PCl_3	Cl_2
Start	0.0072	0.0028	0.0028
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0072 - x$	$0.0028 + x$	$0.0028 + x$

$K = (0.0028\ 1\ x)^2/(0.0072 - x) = 0.011$

Therefore, $x = 0.00354$, [PCl_5] = 0.0037 *M*, [PCl_3] = 0.0063 *M*, and [Cl_2] = 0.0063 *M*

26. (a) $K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.114)^2}{(0.020)(0.010)} = 65$

(b) [HI] = 0.80 [I_2] = 0.50 − 0.40 [H_2] = $x - 0.40$

$$\frac{(0.80)^2}{(x - 0.40)(0.10)} = 65 \quad x = 0.50 \text{ mol}$$

27. (a)

	C_2H_2 +	$2\ H_2 \longrightarrow$	C_2H_6
St	1.0	1.0	0
C	−0.25	−0.50	+0.25
E	0.75	0.50	0.25

$$K = \frac{[C_2H_2]}{[C_2H_2][H_2]^2} = \frac{(0.25)}{(0.75)(0.50)^2} = 1.33$$

(b)

	C_2H_2 +	$2\ H_2 \longrightarrow$	C_2H_6
St	1.75	0.50	0.25
C	−0.15	−0.30	$+0.15 - x$
E	0.60	0.20	$0.40 - x$

$$K = \frac{(0.4 - x)}{(0.6)(0.2)^2} - 1.33$$

$0.4 - x = 0.032$
$x = 0.37$ mol

28. (a)

$$\begin{array}{lcc} & N_2O_4 \longrightarrow & 2\,NO_2 \\ \text{St} & 1.0 & 0 \\ \text{C} & -x & 2x \\ \text{E} & 1 - x & 2x \end{array}$$

$$K = \frac{[NO_2]}{[N_2O_4]} = 1.0 = \frac{(2x)^2}{1 - x} = 1.0$$

$4x^2 = 1 - x$
$4x^2 + x - 1 = 0$

$$x = \frac{-1 \pm \sqrt{1 + 16}}{8} = 0.39$$

$[NO_2] = 2x = 0.78$ mol

(b)

$$\begin{array}{lcc} & N_2O_4 \longrightarrow & 2\,NO_2 \\ \text{St} & 0 & x \\ \text{C} & +0.2 & -0.4 \\ \text{E} & 0.2 & x - 4 \end{array}$$

$$K = \frac{(x - 0.4)^2}{0.2} \qquad y^2 = 0.2,\ y = 0.45$$

$x - 0.4 = 0.45$

x = 0.85 mol/L

(c) endo

(d) decrease

29. (a) $\dfrac{[CH_3OH][I^-]}{[CH_3][OH^-]} = \dfrac{x^2}{(0.50 - x)(0.50 - x)} = 10$

$x = 0.38$ mol CH_3OH

(b) $[I^2] = [CH_3OH] = x$
$[CH_3I] = 0.50 - x$, $[OH_2] = 1.0 - x$

$$\frac{x^2}{(0.50 - x)(1 - x)} = 10$$

$x = 0.46$ mol CH_3OH

(c) $[CH_3OH] = 0.60 = [I2]$; $[CH_3I] = 0.80 - 0.60$; $[OH^-] = x - 0.60$

$$\frac{(0.60)(0.60)}{(0.20)/(x - 0.60)} = 10$$

$x = 0.78$ mol OH^-

(d) $\dfrac{(0.38 - x)(1.38 - x)}{(0.12 + x)(0.12 + x))} = 10$

$x = 0.08$
$[CH_3OH] = 0.38 - 0.08 = 0.30$ mol/L

30.

$$\begin{array}{lcc} & N_2O_4 \rightleftharpoons & 2\,NO_2 \\ \text{St} & 0.30 & 0.30 \\ \text{Ch} & -0.20 & +0.40 - x \\ \text{Eq} & 0.10 & 0.70 - x \end{array}$$

$$K = \frac{[NO_2]^2}{N_2O_4]} = \frac{(0.3)^2}{0.3} = 0.3$$

$$\frac{(0.70 - x)^2}{0.1} = 0.3$$

$0.49 - 1.4x + x^2 = 0.03$
$0.46 - 1.4x + x^2 = 0$

$$\frac{1.4 \pm \sqrt{(1.4)^2 - 4(0.46)}}{2}$$

$$x = \frac{1.4 \pm \sqrt{0.12}}{2} = 0.53,\ 0.87$$

31. (a) $2\,H_2CO + OH^- \rightleftharpoons CH_3OH + HCOO^-$

$$K = \frac{[CH_3OH][HCOO^-]}{[H_2CO]^2[OH^-]} = \frac{(0.10)(0.60)}{(0.55)^2(0.10)} = 2.0$$

(b) $\dfrac{(0.30)(0.30)}{(0.40)^2(x - \ 0.30)} = 2.0$

$x = 0.58$ mol OH^-

32. (a) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
$[PCl_5] = x \qquad [PCl_3] = [Cl_2] = (0.50 - x)$

$$\frac{(0.50 - x)(0.50 - x)}{x} = 1.7 \times 10^{-2}$$

$x = 0.42$ mol/L $= [PCl_5]$
$[PCl3] = [Cl_2] = 0.080$ mol/L

(b) $K = \dfrac{(0.16)(0.16 - x)}{(0.42 - 0.08)} = 0.017$

$x = 0.12$ mol/L
amount of Cl_2 = 0.12 mol/L × 2.0 L = 0.24 mol

33. $K = \dfrac{[NO_2]^2}{[N_2O_4]} = \dfrac{(0.3)^2}{0.3} = 0.30$

$(0.70 - x)^2/0.1 = 0.3$; Thus, $x = 0.53$ and the amount of NO_2 that must be removed is 0.53 mol.

34. (a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

$$\frac{(0.30)(0.30)}{(0.10)(0.20)} = 4.5$$

(b) $K = \dfrac{(0.40)(0.40)}{(0.10 + x - 0.10)(0.10)} = 4.5$

$x = 0.36$ mol/L of CO

(c) Because the stoichiometry of the reaction indicates that one mole of carbon dioxide is produced from one mole of carbon monoxide, then in order to increase the number of moles of carbon dioxide from 0.3 to 0.4 requires 0.1 mol of carbon monoxide. Therefore, all of the carbon monoxide in this system must be consumed by the reaction, and to accomplish this all of the hydrogen gas would have to be removed.

35. (a) $SO_2 + NO_2 \rightleftharpoons SO_3 + NO$

$$K = \frac{(0.10)(0.10 - x)}{(0.50 - 0.10)} = 0.20$$

(b) $[SO_3] = 0.10 + x$; $[NO] = 0.10 + x$
$[SO_2] = 0.50 + x$; $[NO_2] = 0.20$

$$\frac{(0.10)(0.10)}{(0.50)(0.10)} = 0.20$$

$x^2 + 0.24x - 0.01 = 0$
$x = 0.036$ mol; add 0.036 mol NO
The final concentrations of all species will be:
$[SO_2] = 0.46$ mol/L $\qquad [NO_2] = 0.20$ mol/L
$[SO_3] = 0.14$ mol/L $\qquad [NO] = 0.14$ mol/L

36. (a) $K = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(b) $$K = \frac{\left(\frac{15\text{ mol}}{10\text{ L}}\right)^2}{\left(\frac{3\text{ mol}}{10\text{ L}}\right)^2\left(\frac{2\text{ mol}}{10\text{ L}}\right)} = 125$$

(c) $$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[1.6]^2}{[0.30 + x0.10]^2[0.20 - 0.05]} = 125$$

$x = 0.17$ mol SO_2/L

Therefore, (0.17 mol SO_2/L)(10 L) = 1.7 mol of SO_2.

37. (a) $$\frac{\left(\frac{8\text{ mol}}{10\text{ L}}\right)^2\left(\frac{8\text{ mol}}{10\text{ L}}\right)^2}{\left(\frac{7.5\text{ mol}}{10\text{ L}}\right)^4\left(\frac{0.20\text{ mol}}{10\text{ L}}\right)} = 65$$

(b) $$\frac{(1.0)^2(1.0)^2}{(0.35)^4(0.020 + x - 0.10)} = 65$$

$x = 1.1$ mol O_2/L

(1.1 mol O_2/L)(10 L) = 11 mol O_2

(c) There is not enough oxygen to achieve the increase.

38. (a) $$K = \frac{[XeF_4]}{[Xe][F_2]^2} = \frac{(0.10)}{(0.10)(0.20)^2} = 25$$

(b) $0.80 \times 0.20 = 0.16$ mol XeF_4

$$\frac{(0.16)}{(0.040)(0.20 + x - 0.12)^2} = 25$$

$x = 0.32$ mol F_2

39. (b) To initially reach equilibrium 0.40 mol of $Al_2(CO_3)_3$ reacted to yield 1.20 mol of CO_2, and 0.60 mol of $Al_2(CO_3)_3$ remained. One mole of added CO_2 will generate 0.33 mol of $Al_2(CO_3)_3$. Thus, when equilibrium is reestablished there will be 0.93 mol of $Al_2(CO_3)_3$.

(c) 3.00 mol of CO_2 must be removed.

CHAPTER 14

1. $w = P\Delta V = P(V_2 - V_1)$

$w = 3P_1 \times (1/3\ V_1 - V_1) = -2P_1V_1$

$w = -2(1.01 \times 10^5\text{ N/m}^2) \times 10^{-3}\text{ m}^3$

$= 2.01 \times 10^2$ N-m $= 2.01 \times 10^2$ J

2. $q = -2P_1V_1 = -2.01 \times 10^2$ J

$w = -2P_1V_1 = -2.01 \times 10^2$ J

$\Delta E = 0$

$\Delta H = -\ 2P_1V_1 = -2.01 \times 10^2$ J

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{-1.1\ P_1V_1}{T} = -3.72 \times 10^{-1}\text{ J/K}$$

$$\Delta S_{surr} = \frac{2\ P_1V_1}{T} = 6.78 \times 10^{-1}\text{ J/K}$$

$\Delta G = \Delta H - T\Delta S = -92$ J

3. $\Delta G = \Delta H - T\Delta S = 7113\text{ J} - (298\ K \times 10\text{ J/K}) = 4133$ J; solid

4. $CH_3OH + 3/2\ O_2 \rightarrow CO_2(g) + 2\ H_2O(l)$

$\Delta H° = 2(-285.8) + (-393.5) - (-238.6)$

$= -726.5$ kJ/mol

$$\text{Heat Capacity} = \frac{\Delta H^0}{\Delta T} = \frac{727\text{ kJ/mol} \times 0.10 \times 0.10\text{ mol}}{0.730\text{ °C}}$$

$= 99.6$ kJ/°C

5. (a) increase (b) decrease (c) decrease
(d) increase (e) increase (f) decrease
(g) decrease (h) decrease

6. (a) for CCl_4

$\Delta H° = 4(-92.5) + (-393.5) - (-132.8) - 2(-286)$

$= -58.7$ kJ

$\Delta S° = 4(187) + (214) - (216) - 2(69.9) = 606$ J/K

$\Delta G° = 4(-95.4) + (-395) - (-62.8) - 2(-237)$

$= -240$ kJ

for $SiCl_4$

$\Delta H° = 4(-92.5) + (-859.4) - (-640.2) - 2(-286)$

$= -17.2$ kJ

$\Delta H° = 4(187) + 41.8 - 239 - 2(69.9) = 411$ J/K

$\Delta G° = 4(-95.4) + (-805.0) - (-572.5) - 2(-237)$

$= -140$ kJ

(b) Carbon tetrachloride does not appear to react with water for kinetic reasons; that is, the reaction is slow.

7. $\Delta H° = 2908 + -1926 + 2(-524) = -66$ kJ

8. $\Delta H_{solution} = (-248\text{ kJ/mol} + -57\text{ kJ/mol}) - (-337\text{ kJ/mol})$

$= +32$ kJ/mol

Endothermic.

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta S° = (133 + 107) - (123) = 117$ J/mol K

$\Delta G° = 32\text{ kJ/mol} - (283\text{ K})(0.117\text{ kJ/mol K}) = -1$ kJ/mol

Yes, it is spontaneous.

9. The equation for the heat of formation is: $Li(s) + 0.5\ F_2(g) \rightarrow LiF(s)$ which can be obtained by adding the following steps:

$$\begin{array}{rll}
Li(s) & \longrightarrow Li(g) & \Delta H_f°(\ Li(g)) \\
Li(g) & \longrightarrow Li^+(g) + e^- & \text{onization energy} \\
0.5\ F_2(g) & \longrightarrow F(g) & \Delta H_f°(\ F(g)) \\
F(g) + e^- & \longrightarrow F^-(g) & -\text{electron affinity (EA)} \\
F^-(g) + Li^+(g) & \longrightarrow LiF(s) & -\text{lattice energy (LE)} \\
\hline
\end{array}$$

$Li(s) + 0.5\ F_2(g) \longrightarrow LiF(s)\ \Delta H_f°$

$\Delta H_f° = \Delta H_f°(\ Li(g))$ + ionization energy + $\Delta H_f°(F(g))$ + (−EA) + (−LE) =161 + 520 + 79 + (−328) + (−lattice energy) = −612

lattice energy = 612 + 161 + 520 + 79 −328 = 1044 kJ/mol

10. (a) $\Delta H° > 0, \Delta S° > 0$; (b) $\Delta H° > 0, \Delta S° > 0$;
(c) $\Delta H° > 0, \Delta S° > 0$; (d) $\Delta H° < 0, \Delta S° < 0$

11. *cis* → *trans*

$\Delta H° = 4.2 - 1.9 = 2.3$ kJ/mol

$\Delta S° = 290 - 290 = 0$

$\Delta G° = 26.6 - 24 = 2.6$ kJ/mol

$$\ln K = \frac{\Delta G°}{RT} = \frac{-2600\text{ J/mol}}{(8.314\text{ J/mol-K})(298\ K)} = -1.05$$

$K = 3.5 \times 10^{-1}$

12. $C_6H_{12}O_6(s) + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O(l)$

$\Delta H° = 6(-393.5) + 6(-286) - (-1274) = -2803$ kJ

$\Delta S° = 6(214) + 6(69.9) - (212) - 6(205) = 261$ J

$\Delta G° = 6(-395) + 6(-237) - (-910.4) = -2882$ kJ

$$\ln K = \frac{\Delta G°}{RT} = 1163$$

$K = e^{1163}$ but $\log e^{1163} = \log 10^x$. Therefore $1163 \log e = x \log 10 = x$.
and $x = 505$ so $K = 1 \times 10^{505}$

13. The last reaction is the most likely decomposition because it has $\Delta G = -169$ kJ. The second reaction has a positive change in free energy and therefore is not spontaneous. The first reaction has a small negative free-energy change, so it should be spontaneous, but its extent of reaction at 25 °C should be much less than that of the third reaction.

14. (a) $\Delta H° = -292.3 - [-238.4 + 0] = -53.9$ kJ/mol
(b) $\Delta H° = \Delta(\text{C}{=}\text{O}) + \Delta(\text{H—H})$ - $[\Delta(\text{C— O})$ +
$799 \quad + \quad 432 \qquad 358$
$\Delta(\text{O—H}) + \Delta(\text{C—H})] = 3$ kJ/mol
$459 \qquad 411$
(c) $\Delta S° = 359 - [338 + 131] = -110$ J/K-mol
(d) $\Delta G° = -53.9 - 298(20.110)$
$= -21$ kJ/mol at 25 °C

15. $5/2\ H_2 + 3/2\ N_2 \rightarrow H_2NNHNH_2$
$\Delta H° = 5/2\,(432) + 3/2\,(941.8) - [5(382) + 2(167)]$
$= 2.5 \times 10^2$ kJ

The compound will probably be unstable at room temperature because ΔH for the reverse reaction is negative and the value of ΔS should be positive because one mole of molecules would yield 4 moles of molecules; that is, for the reverse reaction, $\Delta G = \Delta H - T\Delta S = (-) - (+) < 0$.

16. In the preparation of these compounds from the elements, N_2 is a common reactant and nitrogen is 25 mol % in each compound. Therefore, the differences in the heats of formation can be linked to the average bond energies in NF_3, NCl_3, F_2 and Cl_2. The N—F and N—Cl bond energies are within 10% of each other, but the F—F bond (155 kJ/mol) is substantially weaker than the Cl—Cl bond (240 kJ/mol).
$2\Delta H(NF_3) = BE(N_2) + 3BE(F_2) - 6BE(\text{N—F}) = 942 + 3(155) - 6(285) = -303$ kJ
Thus $\Delta H(NF_3) = -303$ kJ/2mol $= -152$ kJ/mol
$2\Delta H(NCl_3) = BE(N_2) + 3BE(Cl_2) - 6BE(\text{N—Cl}) = 942 + 3(240) - 6(301) = -144$ kJ
Thus $\Delta H(NCl_3) = -144$ kJ/2mol $= -72$ kJ/mol
Although these estimates from bond energies (BE), are not very accurate, they do exhibit the appropriate trend in ΔH; that is, the enthalpy of formation of the less stable NCl_3 is clearly more positive than that of NF_3

17. (a) $\Delta G° = -RT \ln K = -(8.314$ J/mol K) (298 K) ln 9.2 $= -5.5 \times 103$ J/mol $= -5.5$ kJ/mol
(b) $\Delta G° = \Delta H° - T\Delta S°$
-5.5 kJ/mol $= -58.2$ kJ/mol $- (298\ K)(\Delta S°)$
$\Delta S = -177$ J/mol K

18. BEs (kJ/mol): Cl—Cl, 240; H—Cl, 428; P—H, 322; P—Cl, 326; H—H, 432; P—P, 201
$\Delta H = \Sigma$ Bonds Broken $- \Sigma$ Bonds Formed $=$
$[(3 \times \text{BDE}_{\text{P—H}}) + (4 \times \text{BDE}_{\text{Cl—Cl}})] -$
$[(5 \times \text{BDE}_{\text{P—Cl}} + (3 \times \text{BDE}_{\text{HCl}})] = [(3 \times 322) + (4 \times 240)] - [(5 \times 326) + (3 \times 428)] = -988$ kJ

19. (a) The compound on the left (the ketone) is more stable.
(b) The compound on the left (the imine) is more stable.
(c) The compound on the left (the amide) is more stable.
(d) The compound on the right (the imine) is more stable.

20. (a) $\Delta G° = 6.01$ kJ/mol $- 273\ K(22.0 \times 10^{-3}$ kJ/K-mol) $=$ 0.00 kJ; $K = 1.0$
(b) $\Delta G° = -46$ kJ/mol $- 298\ K(-96 \times 10^{-3}$ kJ/K-mol) $= -17$ kJ; $K = 9.5 \times 10^2$
$\Delta G° = -46$ kJ/mol $- 523\ K(-96 \times 10^{-3}$ kJ/K-mol) $=$ 4 kJ; $K = 0.4$

21. (a) Method 1
$\Delta H° = 2\,\Delta H_f°(\text{HI(g)}) = 2 \times 26$ kJ/mol $= 52$ kJ
Method 2
$H_2(g) \rightarrow 2\ H(g) \quad D(H_2) = 432$ kJ
$I_2(s) \rightarrow 2\ I(g) \quad 2\Delta H_f°(I(g)) = 2 \times 107$ kJ
$2\ H(g) + 2\ I(g) \rightarrow 2\ HI(g) \quad -2D(\text{H—I}) = 2 \times 295 = -590$ kJ
$\Delta H° = 432 + 214 - 590 = 56$ kJ
(b) $\Delta S° = [2\ S°(HI(g))] - [S°(H_2(g)) + S°(I_2(s))] = 2(206) - 131 - 117 = 164$ J/mol-K.
$\Delta G° = \Delta H° - T\Delta S° = 52{,}000 - 298(164) = 52{,}000 - 48{,}700 = 3$ kJ/mol.
Note: The standard free energy of formation of HI is 1.3 kJ/mol. Thus, $\Delta G°$ for the reaction could be determined as 2(1.3 kJ/mol) = 2.6 kJ/mol
(c) For this reaction, with its positive $\Delta H°$, an increase in temperature will increase the extent of the reaction.
(d) The equilibrium expression is $K = 1.0 = [HI]^2/[H_2]$ If x is the amount of H_2 (and I_2) that is consumed during the reaction, then $2x$ is the amount of HI at equilibrium.
$(2x)^2/(0.010 - x) = 1.0$
$x = 0.0096$ mol/L
amount of HI $= 0.019$ mol

22. (a) Using bond energies:
$\Delta H° = [2\Delta H_f°(PCl_3(g)) + 6\Delta H_f°(HCl(g))] - [2\Delta H_f°(PH_3(g)) + 3\Delta H_f°(Cl_2(g))] = [2(-278.7) + 6(-92.5)] - [2(9.2) + 3(0)] = -1130.8$ kJ/mol
Using bond energies:
$\Delta H° = [6D(\text{P—H}) + 3D(\text{Cl—Cl})] - [6D(\text{P—Cl}) + 6D(\text{H—Cl})] = [6(322) + 3(240)] - [6(326) + 6(428)] = -\ 1872$ kJ/mol
(b) The tabulated bond energies are only average values. They are not the actual values of the bond dissociation energy in these specific molecules. Hence, the $\Delta H°$ calculated from bond energies generally will be less accurate than those obtained from heats of formation.
(c) $\Delta S° = [2S°(PCl_3(g)) + 6S°(HCl(g))] - [2S°(PH_3(g)) + 3S0(Cl_2(g))] = [2(311.7) + 6(186.6)] - [2(210)\ 3(223)] = 654$ J/mole-K
(d) The product of the reaction has three more moles of gas than the reactants. Each mole of gas contributes another set of very closely spaced translational energy levels to the system. The greater the extent that the molecules are spread over different energy levels, the greater the disorder and the greater the entropy.
(e) $\Delta G° = \Delta H° - T\Delta S° = -1130{,}800 - 298(654) = -1134{,}000 - 196{,}000 = -1326$ kJ/mol
(f) $K = e^{-\Delta G°/RT} = e^{(1326\ \text{kJ/mol})/(0.008314\ \text{kJ/mol-K}\ 298K)} = e^{535}$
$K = 2.0 \times 10^{232}$
(Recall that $e^{535} = 10^x$ and $\ln e^{535} = \ln 10^x$ Therefore $535 = x \ln 10$)

(g) The large negative enthalpy change is due mainly to fact that the H—Cl bond is stronger than the Cl—Cl bond. This difference is due to the greater ionic character in the H—Cl bond and the shorter bond distance. The P—Cl is similar to the P—H bond in strength.

(h) A large K means that at equilibrium the reactants will be mostly converted to products. However, in order for a reaction to be useful synthetically, it must have a favorable rate and there should be no significant by-products. Thus, if this reaction of PH_3 with Cl_2 produces PCl_5 with this large equilibrium constant and at a favorable rate, then this might be a good method to prepare PCl_5.

23. (a) C_2H_2 is ethyne or, in the common system, acetylene. It has a linear structure. C_2H_4 is ethene or, in the common system, ethylene. It has a planar structure.

(b) The heat of combustion is the enthalpy change for the complete combustion of a compound to CO_2 and water (assuming the compound contains only carbon, hydrogen, and oxygen). Thus, one must calculate the enthalpy change for the combustion reactions:

$$C_2H_2 + 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O \quad \Delta H^\circ c$$

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O \quad \Delta H^\circ c$$

Using heats of formation for the first reaction:

$$\Delta H^\circ = 2\,(-393) + (-242) - 227 = -1255\ \text{kJ/mol}$$

and for ethene:

$$\Delta H^\circ = 2(-393) + 2(-242) - 52 = -1322\ \text{kJ/mol}$$

(c) The two equations are:

$$C_2H_2 + 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O(g) \qquad \Delta H^\circ c = -1255$$

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O(g) \qquad \Delta H^\circ c = -1322$$

but they do not add up to the required equation. Reversing the second equation gives:

$$C_2H_2 + 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O(g) \qquad \Delta H^\circ c = -1255$$

$$2\ CO_2 + 2\ H_2O(g) \longrightarrow C_2H_4 + 3\ O_2 \qquad \Delta H^\circ = 1322$$

Now, if we were to add these two the CO_2 would cancel, but the O_2 and H_2O would not cancel. Thus another equation is needed; i.e., the formation of H_2O from its elements.

$$H_2 + 1/2\ O_2 \longrightarrow H_2O(g)\ \Delta H_f^\circ = -242\ \text{kJ/mol}$$

Now adding these three equations:

$$\begin{array}{ll}
C_2H_2 + 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O & \Delta H^\circ c = -1255 \\
2\ CO_2 + 2\ H_2O \longrightarrow C_2H_4 + 3\ O_2 & \Delta H^\circ = 1322 \\
H_2 + 1/2\ O_2 \longrightarrow H_2O & \Delta H_f^\circ = -242 \\
\hline
C_2H_2 + H_2 \longrightarrow C_2H_4 & \Delta H^\circ = -175\ \text{kJ/mol}
\end{array}$$

(d) Calculate the ΔH° for the hydrogenation of C_2H_2 using bond energies.

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

$$\Delta H^\circ = [835 + 432] - [602 + 2(411)] = -157\ \text{kJ/mol}$$

24. Fluorine gas (F_2) appears as a reactant in the equation for the heat of formation of compounds containing fluorine. The F—F bond is weak (partly a result of the repulsion of the lone pairs of electrons on the fluorine atoms), so little energy is necessary to break this bond. Moreover, because of its small size and high electronegativity (which gives rise to a high ionic character) fluorine forms strong bonds with most elements.

25. a. $\Delta H^\circ = -428$ kJ/mol
b. $\Delta S^\circ = -115$ J/mol-K
c. Yes, because ΔG is negative.
$\Delta G = \Delta H - T\Delta S = -428\ \text{kJ/mole} - (298K)$ $(-117\ \text{J/mole-K})$
$\Delta G = -393$ kJ/mole

26. a. Answer: a.
b. Answer: d.
c. $\Delta G = \Delta H - T\Delta S = -2880\ \text{kJ/mole} - (298K)$ $(-437\ \text{J/mole-K})$
$\Delta G = -2750$ kJ/mole
Because $\Delta G < 0$, the reaction is spontaneous.

27. a. $\Delta H_{\text{reaction}} = \Sigma$ energies for bonds broken $- \Sigma$ energies for bonds formed

Bonds broken		Bonds formed	
C—H	411 kJ/mole	C—F	485 kJ/mole
C—H	411 kJ/mole	C—F	485 kJ/mole
F—F	155 kJ/mole	H—F	565 kJ/mole
F—F	155 kJ/mole	H—F	565 kJ/mole
	1132 kJ/mole		2100 kJ/mole

$$\Delta H_{\text{reaction}} = 1132\ \text{kJ/mole} - 2100\ \text{kJ/mole} = -968\ \text{kJ/mole}$$

b. The bond energies used to determine ΔH reaction are only average bond energies and they will not be exactly the same as the bond energies associated with the reactants and products for a specific reaction. Thus, enthalpies determined by using bond energies are less accurate.

28. $\Delta H^\circ_{\text{reaction}} = \Sigma\Delta H^\circ_{\text{(products)}} - \Sigma\Delta H^\circ_{\text{(reactants)}}$
$\Delta H^\circ_{\text{reaction}} = 2(33.9\ \text{kJ/mole}) - 2(90.4\ \text{kJ/mole})$
$\Delta H^\circ_{\text{reaction}} = -113$ kJ/mole

29. a. Answer: b.
c. $\Delta H^\circ_{\text{reaction}} = -623$ kJ/mole

Method 1
$\Delta H_{\text{reaction}} = [3(\Delta H_f^\circ(H_2O(g))) + \Delta H_f^\circ(CH_2CO(g))] - 2[(\Delta H_f^\circ(CH_4))]$
The ΔH_f° for ketene must be determined from the combustion data.
$\Delta H_{\text{reaction}} = 2[\Delta H_f^\circ(CO_2(g))] + \Delta H_f^\circ(H_2O(g))] - \Delta H_f^\circ(CH_2CO(g))$
$-981\ \text{kJ/mole} = 2(-393.3\ \text{kJ/mole}) + (-241.8\ \text{kJ/mole}) - \Delta H_f^\circ(CH_2CO(g))$
Therefore, $\Delta H_f^\circ(CH_2CO(g)) = -47.4$ kJ/mole. Now that the enthalpy of formation of ketene is known its value may be substituted into the first equation given in this method.

$\Delta H_{\text{reaction}} = [3(\Delta H_f^\circ(H_2O(g))) + \Delta H_f^\circ(CH_2CO(g))] - 2[(\Delta H_f^\circ(CH_4))] = 3(-241.8 \text{ kJ/mole}) + (-47.4 \text{ kJ/mole}) - 2(-74.9 \text{ kJ/mole}) = -623 \text{ kJ/mole}$

Method 2

$$2[CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)] \qquad \Delta H = 2(-802 \text{ kJ/mole})$$

$$2\,CO_2(g) + H_2O(g) \longrightarrow CH_2CO(g) + 2\,O_2(g) \qquad \Delta H = 981 \text{ kJ/mole}$$

$$2\,CH_4(g) + 2\,O_2(g) \longrightarrow CH_2CO(g) + 3\,H_2O(g) \qquad \Delta H = -623 \text{ kJ/mole}$$

30. a. $\Delta H^\circ = -292.3 - [-238.4 + 0] = -53.9$ kJ/mol
b. $\Delta H^\circ = D(C{=}O) + D(H{-}H) - [D(C{-}O) + D(O{-}H) + D(C{-}H)] = 3$ kJ/mol
c. $\Delta S^\circ = 359 - [338 + 181] = -110$ J/K-mol
d. $\Delta G^\circ = -53.9 - 298(-0.110) = -21$ kJ/mol at 25 °C

31. a. $K = \dfrac{[CH_4]}{[H_2]^2} = \dfrac{0.5 \text{ mol/L}}{(1.0 \text{ mol/L})} = 0.5$

b. $K = \dfrac{x - 0.25}{(0.5)^2} = 0.5$
$x = 0.375\ M$
moles CH_4 needed = $(0.375\ M \times 2.00 \text{ L}) = 0.750$

c. $K = \dfrac{0.07}{(x - 1.4)^2} = 0.5$; $x = 2.58$. Thus, the initial concentration of H_2 must be 2.58 M so 2.58 moles of H_2 must be placed into the flask.

d. If $[H_2] = 1.0\ M$ at equilibrium, then $[CH_4] = 0.5\ M$. Therefore, 1.0 mole of CH_4 must be converted to 1.0 mole of C(s) and 2.0 moles of H_2, and in order to leave 1.0 mole of H_2 in the flask 1.0 mole of H_2 must be removed.

e. $\Delta H^\circ = -74.9 - (0.0 + 2(0.0)) = -74.9$ kJ
$\Delta S^\circ = 186 - (5.9 + 2(130.5)) = -81$ J/mol-K
$\Delta G^\circ = -74.9 - 298\text{K}(-81 \times 10{-}3 \text{ kJ/mol-K}) = -50.8$ kJ

f. 1) The extent would decrease; 2) The extent would increase; 3) The extent would not be altered.

g. $\Delta H^\circ = (720 + 2(432)) - 4(411) = -60$ kJ/mol

32. a. $(CH_3)_3SnCl + H_2O \rightarrow (CH_3)_3SnOH + HCl$

b. $\dfrac{20.0 \text{ g } (CH_3)_3SnCl}{199.25 \text{ g/mol}} = 100 \times 10^{-1}$ mol

$(CH_3)_3SnCl$ initially in 40.0 mL; $\dfrac{10.0 \text{ g } H_2O}{18.015 \text{ g/mol}} =$ H_2O initially in 40.0 mL

At equilibrium $[(CH_3)_3SnCl] = 0.375$ M, $[H_2O] = 11.8$ M, $[(CH_3)_3SnOH] = 2.13$ M, and $[HCl] = 2.13$ M

$$K = \frac{[(CH_3)_3SnOH][HCl]}{[(CH_3)_3SnCl][H_2O]} = \frac{2.13 \times 2.13}{0.375 \times 11.8} = 1.03$$

c. $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol-K})(298\ K) \ln 1.03 = -73.2$ J

d. $\Delta H^\circ = (323 + 459) - (356 + 428) = -2$ kJ

33. $CH_4 + CO_2 \rightleftharpoons 2\,CO + 2\,H_2$
$\Delta H^\circ = 2(-110) - (-74.9) - (-393.5) = 248$ kJ
$\Delta S^\circ = 2(198) + 2(131) - 186 - 214 = 258$ J/K
$\Delta G^\circ = 2(-137) - (-50.6) - (-395) = 172$ kJ
at 1000 K, $\Delta G^\circ = 248 - 1000(0.258) = -10$ kJ
$CH_4 + CO_2 \rightleftharpoons CH_3CO_2H$
$\Delta H^\circ = -434.7 - (-74.9) - (-393.5) = 33.7$ kJ
$\Delta S^\circ = 282 - 186 - 214 = -118$ J/K
$\Delta G^\circ = -377 - (-50.6) - (-395) = 68.6$ kJ
at 1000 K, $\Delta G^\circ = 33.7 - 1000\,(-0.118) = 152$ kJ

At 298 K, neither reaction is spontaneous; however, the second reaction has the less positive change in free energy, so it is more likely to occur. At 1000 K, the first reaction has a negative free-energy change so it is spontaneous while the second reaction is still not spontaneous.

34. (a) $\Delta H^\circ = [3(410) + 358 + 460] + 1071 - [3(410) + 347 + 799 + 358 + 460] = -75$ kJ from bond energies

$\Delta H^\circ = -764.0 + (-283.3) - (-923.8) = -123.5$ kJ from heats of combustion

$\Delta H^\circ = -434.7 - (-201) - (-110) = -123.7$ kJ from ΔH_f°

(b) $282 - 240 - 198 = -156$ J/K

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -123.7 \text{ kJ} - 298\ K\,(-0.156 \text{ J/K}) = -77.2$ kJ

$$\ln K = -\frac{(-77{,}200 \text{ J/mol})}{8.314 \text{ J/K-mol})(298\ K)} = 31.2$$

$K = 3.4 \times 10^{13}$ or $K_p = 1.4 \times 10^{12}$

(d) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -123.7 - 473(-0.156) = -49.9$ kJ

$$\ln K = -\frac{(-49{,}900 \text{ J/mol})}{8.314 \text{ J/K-mol})(473\ K)} = 12.7$$

$K = 3.3 \times 10^5$ or $K_p = 8.4 \times 10^3$

35. (a)

$$\begin{array}{rll} HCl(g) \longrightarrow & H(g) + Cl(g) & \Delta H^\circ = 428.0 \text{ kJ} \\ H(g) \longrightarrow & H^+(g) + e^- & \Delta H^\circ = 1312 \text{ kJ} \\ Cl(g) + e^- \longrightarrow & Cl^-(g) & \Delta H^\circ = -347 \text{ kJ} \\ \hline HCl(g) \longrightarrow & H^+(g) + Cl^-(g) & \Delta H^\circ = 1393 \text{ kJ} \end{array}$$

(b) The entropy change should be favorable because one mole of gaseous particles will be converted into two moles of particles. The reaction will not occur to an appreciable extent because ΔH° is positive and has a large magnitude. Using the date in Table 14.2 one might estimate ΔS° to be 150 J/K-mol. With this estimated value, $\Delta G^\circ = 1393$ kJ/mol − 298 K(0.150 kJ/K-mol) = +1348 kJ and thus the reaction is not spontaneous.

(c) The entropy change is negative because the ionization of the HCl causes water molecules to associate with the two ions; i.e., the order associated with the water molecules increases. The reaction has a high extent because the negative enthalpy change has a large magnitude due to strong charge-dipole interactions between the water molecules and the ions and therefore $\Delta G^\circ < 0$.

36.

$$\begin{array}{r} Na(s) + 1/2\,O_2(g) + 1/2\,H_2(g) \longrightarrow NaOH(s) \\ \Delta H^\circ = -426.8 \text{ kJ} \\ NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq) \\ \Delta H^\circ = -44.8 \text{ kJ} \\ H_2O(l) \longrightarrow 1/2\,O_2(g) + H_2(g) \\ \Delta H^\circ = -241.8 \text{ kJ} \\ \hline Na(s) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + 1/2\,H_2 \\ \Delta H^\circ = -229.8 \text{ kJ} \end{array}$$

37. (a) $\Delta H_{\text{vap}} = 95.4 - 50.6 = 44.8$ kJ

$$\Delta S_f(g) = \frac{\Delta H_f{}^\circ - \Delta G_f{}^\circ}{T} = \frac{95.4\text{ kJ} - 159.4\text{ kJ}}{298\ K} =$$

-0.215 kJ/K

$$\Delta S_f(l) = \frac{\Delta H_f{}^\circ - \Delta G_f{}^\circ}{T} = \frac{50.6\text{ kJ} - 149.4\text{ kJ}}{298\ K} =$$

$-\ 0.332$ kJ/K

$\Delta S_{\text{vap}} = \Delta S_f(g) - \Delta S_f(l) = 0.117$ kJ/K $= 117$ J/K

(b) Although the entropy change associated with vaporization is favorable, the enthalpy change is not favorable. That is, the vaporization of hydrazine is not a spontaneous process at 298 K ($\Delta G^\circ > 0$), but condensation of the hydrazine (i.e., the reverse process) is spontaneous.

(c) The comparison must be made by considering the formation of these two compounds from the elements in their standard states. The conversion of the triple bond in nitrogen to a single N—N bond in hydrazine costs approximately 790 kJ/mol (as based on average bond energies). Conversion of the double bond in oxygen to a single bond costs about 260 kJ/mol. Although some energy is regained by the formation of O—H or N—H bonds in these two compounds, there is not sufficient bond formation in the hydrazine to compensate for the energy cost so the process is endothermic. In the formation of hydrogen peroxide, the formation of two O—H bonds is more than adequate to offset the energy costs for breaking the bonds in diatomic oxygen and hydrogen.

38. $\Delta H^\circ = 2(-286\text{ kJ}) - 95.4\text{ kJ} = -667$ kJ for gaseous hydrazine

Conversion of liquid hydrazine to gaseous hydrazine ($\Delta H_{\text{vap}} = 44.8$ kJ) requires enthalpy, so the reaction,

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\ H_2O(l)$$

will have a heat of combustion of

$$\Delta H^\circ = -667\text{ kJ} + 44.8\text{ kJ} = -622\text{ kJ}$$

39. 1723.8 kJ/mol = Bond energy for N—N + 4(382 kJ/mol) Thus, the N—N bond energy is 196 kJ/mol. This value is much greater than the N—N bond energy in N_2O_4 because the electronegative oxygen atoms in N_2O_4 decrease the electron density between the nitrogen atoms and thereby weaken the bond.

40. (a) $3\ H_2(g) + CO(g) \rightarrow CH_4(g) + H_2O(g)$

$\Delta H^\circ = -242 + (-74.9) - (-110) = -207$ kJ

(b) $\Delta H^\circ = 3(432\text{ kJ}) + 1071\text{ kJ} - 4(410\text{ kJ}) - 2(460\text{ kJ}) = -193$ kJ

(c) Because the reaction yields a decrease in the number of moles of gaseous species, the change in entropy can be estimated by comparison of processes in Table 14.3 to fall between -150 J/K and -200 J/K.

$\Delta S^\circ = 186 + 189 - 3(131) - 198 = -216$ J/K

(d) $\Delta G^\circ = -\ 207\text{ kJ} - (298\ K)(-\ 0.216\text{ kJ/K}) = -143$ kJ

(e) $K = 1.17 \times 10^{25}$ at 25 °C

41. $\Delta H^\circ = 941\text{ kJ} + 2(494\text{ kJ}) - 4(464\text{ kJ}) = 73$ kJ

42. $\Delta G^\circ = 2(-237\text{ kJ}) - 2(-114\text{ kJ}) = -246$ kJ

43. $\Delta G^\circ = 2\Delta G_f^\circ = 2[(-45.6) - 298(-0.0992)] = -32.1$ kJ

$$\ln K = -\frac{-32100\text{ J/mol}}{(8.314\text{ J/mol-K})(298\ K)} = 13.0$$

$K = 4.4 \times 105$

44. (a) $\Delta H^\circ = 3(1305) - 3273 = -\ 642$ kJ

(b) $\Delta S^\circ = 173 - 3(201) = -430$ J/K

(c) $\Delta G^\circ = -\ 642 - 298(-0.430) = -\ 514$ kJ

(d) Even though the reaction has a high equilibrium constant, the rate of the reaction may be too slow to make the process viable.

45. (a) $\Delta H^\circ = 432 + 149 - 2(294.6) = -8.2$ kJ

(b) $\Delta S^\circ = 2(206) - 261 - 131 = 20$ J/K

(c) $\Delta G^\circ = -\ 8.2\text{ kJ} - 298\text{ K }(0.020\text{ kJ/K}) = -\ 14.2$ kJ

$$\ln K = \frac{-14200\text{ J/mol}}{(8.314\text{ J/mol-K})(298\ K)} = 5.7$$

$K = 3.0 \times 10^2$

(d) It would decrease K.

(e) It would not affect the extent of reaction.

(f) $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g) \quad \Delta H^\circ = -8.2$

$I_2(s) \rightleftharpoons I_2(g) \quad \Delta H^\circ = 63$

$H_2(g) + I_2(s) \rightleftharpoons 2\ HI(s) \quad \Delta H^\circ = 55$ kJ

(g) $\Delta G^\circ = 2\ \Delta G_f^\circ[HI(g)]$ (from Appendix 2, $\Delta G_f^\circ[HI(g)] = 1.3$ kJ/mol)

$\Delta G^\circ\ 2\ (1.3\text{ kJ}) = 2.6$ kJ

46. (a) Using standard heats of formation

$\Delta H^\circ = 2\ \Delta H_f^\circ(PCl_3(g)) + 6\ \Delta H_f^\circ(HCl(g)) - 2\ \Delta H_f^\circ(PH_3(g)) - 3\ \Delta H_f^\circ(Cl_2(g)) = 2(-279) + 6(-93) - 2(9) - 3(0) = -1134$ kJ

Using bond energies

$\Delta H^\circ = 6(\text{P—H}) + 3(\text{Cl—Cl}) - 6(\text{P—Cl}) - 6(\text{H—Cl}) = 6(322) + 3(240) - 6(326) - 6(428) = -1872$ kJ

(The two values differ because bond energies are average values.)

(b) $\Delta S^\circ = 2\ S^\circ(PCl_3(g)) + 6\ S^\circ(HCl(g)) - 2\ S^\circ(PH_3(g)) - 3S^\circ(Cl_2(g)) = 2(312) + 6(187) - 2(210) - 3(223) = 657$ J/K

(c) The product of the reaction has three more moles of gas than the reactants. Each mole of gas contributes another set of very closely spaced translational energy levels to the system. The more the molecules are spread out over different energy levels, the greater the disorder and the greater the entropy.

(d) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -1{,}134{,}000\text{ J} - 298\ K(657\text{ J/K}) = -1330$ kJ

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{1330\text{ kJ/mol}}{(0.008314\text{ J/mol-K})(298\ K)} = 537$$

$K = e^{537}$

$\log e^{537} = \log 10^x$

$537 \log e = \times \log 10$

$233.22 = x$

$K = 10^{233.22} = 1.7 \times 10^{233}$

(e) The large negative enthalpy change is due to the fact that the H—Cl bond is stronger than the Cl—Cl bond. This is a result of the greater ionic character in the H—Cl bond and the shorter bond distance. The P—Cl is similar to the P—H bond in strength.

47. Nitrogen gas (N_2) appears as a reactant in the equation for the heat of formation of compounds containing nitrogen. Because of the triple bond and the small size of the nitrogen atoms, the bond energy in N_2 is very high. Hence, most nitrogen compounds are unstable relative to the elements.

Fluorine gas (F_2) appears as a reactant in the equation for the heat of formation of compounds containing fluorine. Because of the weak F—F single bond (partly a result of the repulsion of the lone pairs of electrons on the fluorines), little energy is necessary to break this bond. Moreover, because of its small size and high electronegativity (which gives rise to a high ionic character) fluorine forms strong bonds with most elements.

48. (a) $\Delta H^\circ = \Sigma\text{BE}$ for bonds broken $- \Sigma\text{BE}$ for bonds formed

Bonds broken		Bonds formed	
C—H	411 kJ/mole	C—F	485 kJ/mole
C—H	411 kJ/mole	C—F	485 kJ/mole
F—F	155 kJ/mole	H—F	565 kJ/mole
F—F	155 kJ/mole	H—F	565 kJ/mole
	1132 kJ/mole		2100 kJ/mole

$\Delta H^\circ = 1132\text{ kJ} - 2100\text{ kJ} = -968\text{ kJ/mol}$

(b) The bond energies used to determine ΔH° are only average bond energies, and they will not be the same as the actual bond energies associated with the reactants and products. Thus, enthalpy changes determined by using bond energies are less accurate.

49. $\Delta H^\circ = -623\text{kJ}$ is determined by applying Hess' Law to the problem.

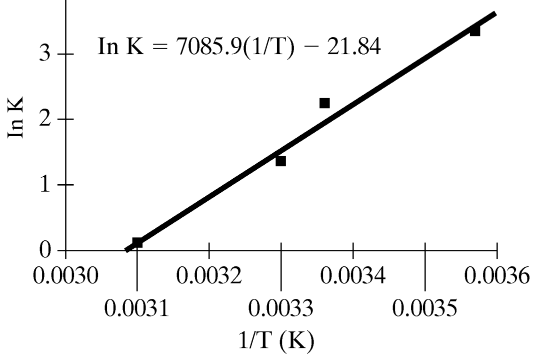
$$2[CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g)] \qquad \Delta H^\circ = 2(-802\text{kJ})$$

$$2\ CO_2(g) + H_2O(g) \longrightarrow CH_2CO(g) + 2\ O_2(g) \qquad \Delta H^\circ = 981\text{ kJ}$$

$$2\ CH_4(g) + 2\ O_2(g) \longrightarrow CH_2CO(g) + H_2O(g) \qquad \Delta H^\circ = -623\text{ kJ}$$

50. (a) From the slope of the plot of ln K versus $1/T$ (in K) $\Delta H^\circ = -58.9\text{ kJ}$

From the intercept of the line $\Delta S^\circ = -181.6\text{ J/K}$



(b) $\Delta H^\circ = \Delta H_f^\circ(N_2O_4) - 2\ \Delta H_f^\circ(NO_2) = 9.6\text{ kJ/mol} - 2(33.9\text{ kJ/mol}) = -58.2\text{ kJ}$

Thus, the ΔH° value from part (a) agrees within 0.7 kJ/mol or 1.2%

$\Delta S^\circ = \Delta S^\circ(N_2O_4) - 2\ \Delta S^\circ(NO_2) = 304.2\text{ J/K mol} - 2(240.2\text{ J/K mol}) = -176.2\text{ J/K}$

Thus, the ΔS° value from part (a) agrees within 3.3%

51. 1 (c) 2 (b)

CHAPTER 15

1. $Mg^{2+}(aq) + 2\ {}^-OH(aq) \rightarrow Mg(OH)_2(s)$

2. (a) $ClO^- + H^+ \rightarrow HClO$
(b) $2F^- + Pb^{2+} \rightarrow \underline{PbF_2}$
(c) no reaction
(d) $Pb^{2+} + C_2O_4^{2-} \rightarrow \underline{PbC_2O_4}$
(e) $Ni^{2+} + S^{2-} \rightarrow \underline{NiS}$

3. (a) $KNO_3 + PbCO_3$ extent high because $PbCO_3$ is insoluble
(b) $MgCl_2 + H_2O$ extent high because H_2O is weak electrolyte
(c) $BaCl_2 + H_2S$ extent high because H_2S is a gas and is a weak electrolyte
(d) $BaS + Ag_2SO_4$ extent low because reactants are more insoluble

4. (a) $K > 1$; (b) $K < 1$; (c) $K > 1$; (d) $K > 1$

5. (b), (c), (e), (f), (i), (j)

6. lead chloride, barium sulfate and copper(II) hydroxide.

7. $3\ Mg^{2+} + 2\ PO_4^{3-} \rightleftharpoons Mg_3(PO_4)_2(s)$

$$0.20\ M\ Mg^{2+} \times 50\text{ mL} \times \frac{2\text{ mol }PO_4^{3-}}{3\text{ mol }Mg^{2+}} \times \frac{1.00\text{ L}}{0.20\text{ mol }S^{2-}} = 33\text{ mL}$$

8. $\dfrac{1\text{ mol }Sb_2S_3}{3\text{ mol }S^{2-}} \times (0.0400\text{ L} \times 0.50\text{ mol }S^{2-}/\text{L}) \times 339.68\text{ g/mol} = 2.26\text{ g }Sb_2S_3$

9. $K_{sp} = [Ag^+][Cl^-]$ $\quad K_{sp} = [Ag^+]^2[CO_3^{2-}]$
$K_{sp} = [Al^{3+}][OH^-]^3$

10. Molar concentration of LiF = (1.8 g/L) /(25.939 g/mol) = 0.069 mol/L
$K_{sp} = [Li^+][F^-] = (0.069)(0.069) = 4.8 \times 10^{-3}$

11. $= \dfrac{1.35\text{ g/L}}{413\text{ g/mol}} = 3.27 \times 10^{-3}\text{ mol/L}$

$[Cu^{2+}] = 3.27 \times 10^{-3}\text{ mol/L}$
$[IO_3^-] = 6.54 \times 10^{-3}\text{ mol/L}$
$K_{sp} = (3.27 \times 10^{-3})(6.54 \times 10^{-3})^2 = 1.40 \times 10^{-7} = 1 \times 10^{-7}$

12. $\dfrac{1.040\text{ g/L}}{112.33\text{ g/mol}} = 9.26 \times 10^{-3}\text{mol/L}$

$[Mg^{2+}] = [C_2O_4^{2-}] = 9.26 \times 10^{-3}$
$K_{sp} = (9.26 \times 10^{-3})(9.26 \times 10^{-3}) = 8.57 \times 10^{-5} = 9 \times 10^{-5}$

13. $\dfrac{0.4655\text{ g/L}}{245.2\text{ g/mol}} = 1.899 \times 10^{-3}\text{mol/L}$

$[Pb^{2+}] = 1.899 \times 10^{-3}$

$[F^-] = 2[Pb^{2+}] = 3.798 \times 10^{-3}$
$K_{sp} = (1.899 \times 10^{-3})\ (3.798 \times 10^{-3})^2 = 2.739 \times 10^{-8} = 3 \times 10^{-8}$

14. $[Pb^{2+}] = 3(1.29 \times 10^{-7}) = 3.87 \times 10^{-7}$
$[PO_4^{3-}] = 2(1.29 \times 10^{-7}) = 2.58 \times 10^{-7}$
$K_{sp} = (3.87 \times 10^{-7})^3\ (2.58 \times 10^{-7})^2 = 3.86 \times 10^{-33} = 4 \times 10^{-33}$

15. $Ca_3(PO_4)_2(_s) \rightarrow 3\ Ca^{2+} + 2\ PO_4^{3-}$
$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (1.2 \times 10^{-5})^3(0.80 \times 10^{-5})^2 = 1.1 \times 10^{-25}$

16. $K_{sp} = 6 \times 10^{-5} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3$
$x = 0.025$; therefore, $[Ag^+] = 0.5\ M$

17.

	$PbCl_2(s) \longrightarrow$	Pb^{2+}	$+\ 2\ Cl^-$
Start	——	0	0
Change	——	x	$2x$
Equilibrium	——	x	$2x$

$K_{sp} = 1.0 \times 10^{-4} = (x)(2x)^2$
$1.0 \times 10^{-4} = 4x^3$
$x = 2.9 \times 10^{-2}$

Because x is the number of moles of $PbCl_2$ that dissolve in each liter of solution, the molar solubility is 2.9×10^{-2}.

18. (a) $s = [Ag^+] = [Br^-]$
$s = \sqrt{7.7 \times 10^{-13}} = 9 \times 10^{-7}\ M$
(b) $[Mg^{2+}] = s;\ [OH^-] = 2s$
$$s = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 2 \times 10^{-4}\ M$$
(c) $s = [Zn^{2+}]=[S^{2-}]$
$s = \sqrt{1 \times 10^{-23}} = 3 \times 10^{-12}\ M$
(d) $[CO_3^{2-}] = s;\ [Li^+] = 2s$
$$s = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 8 \times 10^{-2}\ M$$

19. $[Mg^{2+}] = 3s;\ [PO_4^{3-}] = 2s$
$(3s)^3(2s)^2 = 4 \times 10^{-13}$
$$s = \sqrt[3]{\frac{4 \times 10^{-13}}{108}} = 1.3 \times 10^{-3}$$
$[Mg^{2+}] = 3(1.3 \times 10^{-3}) = 4 \times 10^{-3}\ M$
$[PO_4^{3-}] = 2(1.3 \times 10^{-3}) = 3 \times 10^{-3}\ M$

20. $MgNH_4PO_4 \rightarrow Mg^{2+} + NH_4^+ + PO_4^{3-}$
$s = [Mg^{2+}] = [NH_4^+] = [PO_4^{3-}]$
$s = \sqrt[3]{3 \times 10^{-13}}$
$s = 7 \times 10^{-5}$
$7 \times 10^{-5}\ \text{mol/L} \times 137.3\ \text{g/mol} = 1 \times 10^{-2}\ \text{g/L}$

21. In $Fe(OH)_2$: $[OH^-] = 2[Fe^{2+}]$
$[Fe^{2+}]\ (2[Fe^{2+}])^2 = 2 \times 10^{-15}$
$$[Fe^{2+}] = \sqrt[3]{\frac{2 \times 10^{-15}}{4}} = 8 \times 10^{-6}\ \text{mol/L}$$
In FeS: $[S^{2-}] = [Fe^{2+}]$
$[Fe^{2+}][Fe^{2+}] = 1 \times 10^{-18}$
$[Fe^{2+}] = \sqrt{1 \times 10^{-18}} = 1 \times 10^{-9}\ \text{mol/L}$
Thus, the $Fe(OH)_2$ solution contains more iron.

22. For $Al(OH)_3$: $[Al^{3+}] = s;\ [OH^-] = 3s$
$s(3s)^3 = 5 \times 10^{-33}$
$$s = \sqrt[4]{\frac{5 \times 10^{-33}}{27}} = 4 \times 10^{-9}\ \text{mol/L}$$
For $Mn(OH)_2$: $[Mn^{2+}] = s;\ [OH^-] = 2s$
$s(2s)^2 = 2 \times 10^{-13}$
$$s = \sqrt[3]{\frac{2 \times 10^{-13}}{4}} = 4 \times 10^{-5}\ \text{mol/L}$$
The $Mn(OH)_2$ is more soluble.

23. $s = [Hg^{2+}] = [S^{2-}]$
$s^2 = 1 \times 10^{-54}$
$s = 1 \times 10^{-27}\ \text{mol/L}$
$$\frac{1\ \text{mol}}{1 \times 10^{-27}\ \text{mol/L}} = 1 \times 10^{27}\ \text{L}$$

24. (a) $s = [Ba^{2+}] = [CrO_4^{2-}]$
$s = \sqrt{2.3 \times 10^{-10}} = 1 \times 10^{-5}\ M$
(b) $[CrO_4^{2-}] = s;\ [Ba^{2+}] = s + 0.050 \cong 0.050$
$$s = \frac{2 \times 10^{-10}}{0.050} = 4.6 \times 10^{-9}\ M$$
(c) $[Ba^{2+}] = s;\ [CrO_4^{2-}] = s + 0.050 \cong 0.050$
$$s = \frac{2.3 \times 10^{-10}}{0.050} = 4.6 \times 10^{-9}\ M$$

25. (a) $[Mg^{2+}] = s;\ [OH^-] = 2s$
$s(2s)^2 = 1.8 \times 10^{-11}$
$$s = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 2 \times 10^{-4}\ \text{mol/L}$$
(b) $[OH^-] = 2s;\ [Mg^{2+}] = s + 0.020 \cong 0.020$
$(0.020)(2s)^2 = 1.8 \times 10^{-11}$
$s = 1.5 \times 10^{-5}\ M$
(c) $[Mg^{2+}] = s;\ [OH^-] = 2s + 0.020 \cong 0.020$
$s(0.020)^2 = 1.8 \times 10^{-11}$
$s = 5 \times 10^{-8}\ M$

26. (a) $6 \times 10^{-38} = x(3x)^3$; $x = [Fe^{3+}] = 2 \times 10^{-10}\ M$
(b) $6 \times 10^{-38} = x(1.0 + 3x)^3$; $x = [Fe^{3+}] = 6 \times 10^{-38}\ M$

27. (a) $Ag_3PO_4 \rightleftharpoons 3\ Ag^+ + PO_4^{3-}$
$K_{sp} = 1.4 \times 10^{-16} = [Ag^+]^3[PO_4^{3-}] = (3x)^3(x) = 27x^4$
$x = 4.8 \times 10^{-5}$
$[Ag^+] = 3x = 1.4 \times 10^{-4}\ M$
(b) Less soluble; common ion effect
or
$1.4 \times 10^{-16} = (x)^3(0.05\ M + x)$
$[Ag^+] = x = 1.4 \times 10^{-5}$
(c) More soluble; acid effect
$Ag_3PO_4 + 3\ HNO_3 \rightarrow 3\ Ag^+ + 3\ NO_3^- + H_3PO_4$ weak acid

28. AgCl. The K_{sp} for AgCl is 1.8×10^{-10}, which is so much greater than the K_{sp} of Ag_2S that we do not need a calculation to tell us that AgCl is more soluble.

29. CuS is more insoluble than CoS and therefore the reaction will go toward the side that ties up the ions more effectively; that is, to the right.

$BaSO_4$ is more insoluble and therefore the extent will be low.

30. (a) The third equation because it is the net ionic form of equation (2). Equation (1) implies that $NaNO_3$ is insoluble.

(b) All three

(c) In the mixture of the two solutions, the concentrations of the ions are $1 \times 10^{-5}\,M\,\mathrm{Ag^+}$ and $1 \times 10^{-6}\,M\,\mathrm{Cl^-}$. Inserting these into the expression $[\mathrm{Ag^+}][\mathrm{Cl^-}]$ results in 1×10^{-11}, which is less than the solubility product constant of 1.8×10^{-10}. Therefore, AgCl will not precipitate.

31. (a) No, this is not balanced and will lead to an incorrect K_{sp} expression.

(b) 2

(c) Yes, because $[\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 > 1.8 \times 10^{-11}$.

32. Before: $[\mathrm{Pb^{2+}}] = [\mathrm{SO_4^{2-}}]$

$$[\mathrm{Pb^{2+}}] = \sqrt{1.6 \times 10^{-8}} = 1.3 \times 10^{-4}$$

After: $[\mathrm{SO_4^{2-}}] = [\mathrm{Pb^{2+}}] + 1.3 \times 10^{-3} \cong 1 \times 10^{-3}$

$$[\mathrm{Pb^{2+}}] = \frac{1.6 \times 10^{-8}}{1.0 \times 10^{-3}} = 1.6 \times 10^{-5}$$

33. $$\frac{1.00\ \mathrm{g}}{42.0\ \mathrm{g/mol}} \times \frac{1000\ \mathrm{mL/L}}{100\ \mathrm{m/L}} = 0.0238\ \mathrm{mol/L}$$

$[\mathrm{F^-}] = 2[\mathrm{Ca^{2+}}] + 0.0238 \cong 0.0238$

$[\mathrm{Ca^{2+}}]\,(0.0238)^2 = 4 \times 10^{-11}$

$[\mathrm{Ca^{2+}}] = 7 \times 10^{-8}$

34. $\mathrm{Ca_3(PO_4)^2 \rightleftharpoons 3Ca^{2+} + 2\,PO_4^{3-}}$

$K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 = (1 \times 10^{-5})^3(2/3 \times 10^{-5})^2 = 4 \times 10^{-26}$

3×10^{-11} g.

35. $$[\mathrm{Ag^+}] = \frac{1.0\ \mathrm{mL} \times 0.100\ M}{16\ \mathrm{mL}} = 6.3 \times 10^{-4}\ M$$

$$[\mathrm{SO_4^{2-}}] = \frac{15.0\ \mathrm{mL} \times 0.100\ M}{16.0\ \mathrm{mL}} = 9.4 \times 10^{-3}\ M$$

$\underline{\mathrm{Ag_2SO_4}} \rightleftharpoons \mathrm{2\,Ag^+ + SO_4^{2-}}$

$(6.3 \times 10^{-4})^2(9.4 \times 10^{-3}) = 3.7 \times 10^{-9}$

$3.7 \times 10^{-9} < K_{\mathrm{sp}}\ (6 \times 10^{-5})$

Therefore, no precipitate will form.

36. $$[\mathrm{S^{2-}}] = \frac{s}{[\mathrm{Mn^{2+}}]} = \frac{1 \times 10^{-11}}{5 \times 10^{-3}} = 2 \times 10^{-9}\ M$$

37. $[\mathrm{Ba^{2+}}] = s$; $[\mathrm{SO_4^{2-}}] = s + 0.025 \cong 0.025$

$$s = \frac{1 \times 10^{-10}}{0.025} = 4.0 \times 10^{-9}\ \mathrm{mol/L}$$

$(4.0 \times 10^{-9}\ \mathrm{mol/L})\,(0.25\ \mathrm{L})\,(233\ \mathrm{g/mol}) = 2.3 \times 10^{-7}$ g

38. AgI (yellow) is much less soluble than AgCl.

39. In $0.10\ M\ \mathrm{Ag^+}$:

$s = [\mathrm{CrO_4^{2-}}]$; $[\mathrm{Ag^+}] = 2s + 0.010 \cong 0.010$

$$s = \frac{1.9 \times 10^{-12}}{(0.10)^2} = 1.9 \times 10^{-10}\ M$$

In $0.10\ M\ \mathrm{CrO_4^{2-}}$:

$[\mathrm{Ag^+}] = 2s$; $[\mathrm{CrO_4^{2-}}] = s + 0.10 \cong 0.10$

$$s = \sqrt{\frac{1.9 \times 10^{-12}}{0.40}} = 2.2 \times 10^{-6}$$

$\mathrm{Ag_2CrO_4}$ is more soluble in 0.10 M chromate.

40. $$[\mathrm{Br^-}] = \frac{7.7 \times 10^{-13}}{5.0 \times 10^{-3}} = 1.5 \times 10^{-10}\ \mathrm{mol/L}$$

$(1.5 \times 10^{-10}\ \mathrm{mol/L})\,(0.450\ \mathrm{L})\,(79.9\ \mathrm{g/mol}) = 5 \times 10^{-9}$ g

41. $\mathrm{Pb^{2+} + 2\,Cl^- \rightleftharpoons PbCl_2}$ $\quad K_{sp} = 1.0 \times 10^{-4}$

$\mathrm{Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4}$ $\quad K_{sp} = 1.6 \times 10^{-8}$

After $\mathrm{PbCl_2}$ is precipitated, $[\mathrm{Pb^{2+}}] = 1.0 \times 10^{-2}\ M$. When sulfuric acid is added, there is sufficient $\mathrm{Pb^{2+}}$ present to cause the product of $[\mathrm{Pb^{2+}}][\mathrm{SO_4^{2-}}]$ to exceed the K_{sp} of lead sulfate; i.e.; $[\mathrm{Pb^{2+}}][\mathrm{SO_4^{2-}}] > K_{sp}$. Therefore, $\mathrm{PbSO_4}$ precipitates.

42. After mixing, the silver ion concentration is $1.0 \times 10^{-5}\ M$ and the concentration of the chloride ion is $1.0 \times 10^{-6}\ M$. Inserting these into the expression $[\mathrm{Ag^+}][\mathrm{Cl^-}]$ results in 1.0×10^{-11}, which is less than the solubility product constant of 1.8×10^{-10}. Therefore, AgCl will not precipitate.

43. Yes, because $[\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 > 1.8 \times 10^{-11}$.

44. $K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = 1.8 \times 10^{-11}$

$1.8 \times 10^{-11} = (0.01)[\mathrm{OH^-}]^2$; $[\mathrm{OH^-}] = 4 \times 10^{-5}\ M$

45. (a) $$[\mathrm{SO_4^{2-}}] = \frac{1 \times 10^{-10}}{[\mathrm{Ba^{2+}}]} = \frac{1 \times 10^{-10}}{1.0 \times 10^{-3}} = 1 \times 10^{-7}\ M$$

(b) $$[\mathrm{SO_4^{2-}}] = \frac{2 \times 10^{-5}}{[\mathrm{Ca^{2+}}]} = \frac{2 \times 10^{-5}}{1.0 \times 10^{-3}} = 2 \times 10^{-2}\ M$$

(c) $$[\mathrm{SO_4^{2-}}] = \frac{1.6 \times 10^{-8}}{[\mathrm{Pb^{2+}}]} = \frac{1.6 \times 10^{-8}}{1.0 \times 10^{-3}} = 1.6 \times 10^{-5}\ M$$

46. (a) $$[\mathrm{Mg^{2+}}] = \frac{1.0 \times 10^{-3}}{2} = 5.0 \times 10^{-4}$$

$$[\mathrm{CO_3^{2-}}] = \frac{1.0 \times 10^{-3}}{2} = 5.0 \times 10^{-4}$$

$(5.0 \times 10^{-4})\,(5.0 \times 10^{-4}) > 8 \times 10^{-11}$

Thus, a precipitate of $\mathrm{MgCO_3}$ will form.

(b) $[\mathrm{Ca^{2+}}]\,[\mathrm{F^-}]^2$

$(5.0 \times 10^{-4})\,(5.0 \times 10^{-5})^2 < 4 \times 10^{-11}$

No precipitate will form.

(c) $(5.0 \times 10^{-6})\,(5.0 \times 10^{-6}) > 1 \times 10^{-28}$

Thus, PbS will precipitate.

(d) $(5.0 \times 10^{-3})\,(5.0 \times 10^{-6}) > 1 \times 10^{-22}$

Thus, a precipitate of NiS will form.

47. (a) Potential Precipitate: $\mathrm{Ag_2SO_4}$: $K_{sp} = 6 \times 10^{-5}$

$$[\mathrm{Ag^+}] = \frac{0.001\ \mathrm{L} \times 0.1\ \mathrm{mol/L}}{1.001\ \mathrm{L}} = 1 \times 10^{-4}\ M$$

$$[\mathrm{SO_4^{2-}}] = \frac{1\ \mathrm{L} \times 0.01\ \mathrm{mol/L}}{1.001\ \mathrm{L}} = 0.01\ M$$

$Q = [\mathrm{Ag^+}]^2[\mathrm{SO_4^{2-}}] = (1 \times 10^{-4})^2\,(0.01) = 1 \times 10^{-10}$

$Q < K_{sp}$, the reaction will shift to the right to form more ions, so no precipitate will form

(b) Potential Precipitate: $\mathrm{PbCl_2}$: $K_{sp} = 1 \times 10^{-4}$

$$[\mathrm{Pb^{2+}}] = \frac{1\ \mathrm{g\ Pb(NO_3)_2/279\ g/mol}}{0.1\ \mathrm{L}} = 0.04\ M$$

$[\mathrm{Cl^-}] = 0.01\ M$

$Q = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 = (0.04)\,(0.01)^2 = 4 \times 10^{-6}$

$Q < K_{sp}$, the reaction will shift to the right to form more ions, so no precipitate will form

(c) Potential Precipitate: $\mathrm{Mg(OH)_2}$: $K_{sp} = 2 \times 10^{-11}$

$[\mathrm{Mg^{2+}}] = 1 \times 10^{-4}\ M$

$$[\mathrm{OH^-}] = \frac{0.001\ \mathrm{L} \times 1\ \mathrm{mol/L}}{1.001\ \mathrm{L}} = 0.001\ M$$

$Q = [Mg^{2+}][OH^-]^2 = (1 \times 10^{-4})(0.001)^2 = 1 \times 10^{-10}$
$Q > K_{sp}$, the reaction will shift to the left to form the precipitate

(d) Potential Precipitate: $Mg(OH)_2$: $K_{sp} = 2 \times 10^{-11}$
$[Mg^{2+}] = 1 \times 10^{-4}\ M$

$$[OH^-] = \frac{0.001\ L \times 1\ mol/L}{1.001\ L} = 0.001\ M$$

$Q = [Mg^{2+}][OH^-]^2 = (1 \times 10^{-4})(0.001)^2 = 1 \times 10^{-10}$
$Q > K_{sp}$, the reaction will shift to the left to form the precipitate

(e) Potential Precipitate: SrF_2: $K_{sp} = 3 \times 10^{-9}$

$$[Sr^{2+}] = \frac{0.001\ L \times 0.1\ mol/L}{1.001\ L} = 1 \times 10^{-4}\ M$$

$$[F^-] = \frac{1\ L \times 0.01\ mol/L}{1.001\ L} = 0.01\ M$$

$Q = [Sr^{2+}]\,[F^-]^2 = (1 \times 10^{-4})(0.01)^2 = 1 \times 10^{-8}$
$Q > K_{sp}$, the reaction will shift to the left to form the precipitate

(f) Potential Precipitate: BaC_2O_4: $K_{sp} = 2 \times 10^{-7}$

$$[Ba^{2+}] = \frac{0.001\ L \times 0.01\ mol/L}{1.001\ L} = 1 \times 10^{-5}\ M$$

$$[C_2O_4^{\ 2-}] = \frac{1\ L \times 0.1\ mol/L}{1.001\ L} = 0.1\ M$$

$Q = [Ag^+]^2[SO_4^{\ 2-}] = (1 \times 10^{-5})2\ (0.1) = 1 \times 10^{-11}$
$Q < K_{sp}$, the reaction will shift to the right to form more ions, so no precipitate will form

(g) Potential Precipitate: CaC_2O_4: $K_{sp} = 2 \times 10^{-9}$

$$[Ca^{2+}] = \frac{0.001\ g\ CaCl_2/111\ g/mol}{1\ L} = 9 \times 10^{-6}\ M$$

$$[C_2O_4^{\ 2-}] = \frac{0.001\ g\ Na_2C_2O_4/134\ g/mol}{1\ L} = 7 \times 10^{-6}\ M$$

$Q = [Ca^{2+}][C_2O_4^{\ 2-}] = (9 \times 10^{-6})\,(7 \times 10^{-6}) = 6 \times 10^{-11}$
$Q < K_{sp}$, the reaction will shift to the right to form more ions, so no precipitate will form

48. $[Pb^{2+}]\,[Cl^-]^2 = 6.0 \times 10^{-3}$

$$[Cl^-] = \sqrt{\frac{6.9 \times 10^{-3}}{0.10}} = 0.26\ M$$

$$[Ag^+] = \frac{5 \times 10^{-8}}{0.26} = 2 \times 10^{-7}\ M$$

$$[Hg_2^{\ 2+}] = \frac{1 \times 10^{-14}}{(0.26)^2} = 1 \times 10^{-13}\ M$$

49. Ag_2CrO_4 is less soluble and therefore silver ion will tie up more of the chromate than the dichromate. The equilibrium will be shifted to the left to compensate for the decrease in chromate concentration.

50. (a) $[Pb^{2+}] = \dfrac{1.6 \times 10^{-8}}{0.10} = 1.6 \times 10^{-7}$

(b) $[Pb^{2+}] = \dfrac{1.7 \times 10^{-14}}{0.10} = 1.7 \times 10^{-13}$

(c) $PbCrO_4$ precipitates first.

(d) $[CrO_4^{\ 2-}] = \dfrac{1.7 \times 10^{-14}}{1.6 \times 10^{-7}} = 1.1 \times 10^{-7}$

51. (a) This compound is not affected by acid because the anion is the anion of a strong acid (remember that the strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, and $HClO_4$). That is, because H_2SO_4 is a strong acid it is completely dissociated in water and therefore the H^+ ions do not "tie-up" the sulfate ions.

(b) This compound dissolves in acid because the sulfite ion is the anion of a weak acid (H_2SO_3). Thus, H^+ ions will react with $SO_3^{\ 2-}$ ions to form H_2SO_3 molecules (thereby providing a driving force for the reaction). Moreover, H_2SO_3 decomposes to the gas SO_2 which leaves the solution and drives the reaction

$$\underline{BaSO_3} + 2\,H^+ \rightleftharpoons Ba^{2+} + H_2SO_3$$

farther to the right.

(c) This compound dissolves in acid because the sulfide ion reacts with H^+ to form the weak electrolyte and gas H_2S.

52. (a) $Ag_2SO_4 \rightarrow 2Ag^+ + SO_4^{\ 2-}$
$K_{sp} = [Ag^+]^2[SO_4^{\ 2-}] = 6 \times 10^{-5} = (2x)^2(x)$
$4x^3 = 6 \times 10^{-5}$
$x = 0.025$ mol/L
7.8 g/L

(b) $Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^{\ +}$

53. (a), (c), (d) all contain anions of weak acids, and will therefore react with H^+ to form a weak electrolyte.

54. (a) $s = [C_2O_4^{\ 2-}]$; $[Ag^+] = 2s$
$(2s)^2(s) = 8.9 \times 10^{-12}$

$$s = \sqrt[3]{\frac{8.9 \times 10^{-12}}{4}} = 1.3 \times 10^{-4}\ mol/L$$

(b) $[C_2O_4^{\ 2-}] = 1.3 \times 10^{-4}$
$[Ag^+] = 2(1.3 \times 10^{-4}) = 2.6 \times 10^{-4}$ mol/L

(c) $s = [C_2O_4^{\ 2-}]$; $[Ag^+] = 2s + 0.010 \cong 0.010$

$$s = \frac{8.9 \times 10^{-12}}{1 \times 10^{-4}} = 8.9 \times 10^{-8}\ mol/L$$

55. $[Ni^{2+}][OH^-]^2 = 2 \times 10^{-16}$
Assuming that $x \ll 1$, $(1)(2x)^2 = 2 \times 10^{-16}$
$4x^2 = 2 \times 10^{-16}$; $\times = 7 \times 10^{-9}$
Molar solubility if $Ni(OH)_2 = x/2 = 4 \times 10^{-9}$ mol/L

56.

	$Ca_3(PO_4)_2$	Ca^{2+}	$PO_4^{\ 3-}$
Start	0	1	0
Change	$-x$	$3x$	$2x$
Equilibrium satd		$1 + 3x$	$2x$

x will be small enough so that $1 + 3x = 1$
$K_{sp} = [Ca^{2+}]^3[PO_4^{\ 3-}]^2 = 1 \times 10^{-25}$
$(1)^3(2x)^2 = 1 \times 10^{-25}$
$x = 2 \times 10^{-13}\ M$

57. (a) $\dfrac{6.7\ g}{84\ g}$/mol = 0.080 mol

$\underline{AlF_3} \rightleftharpoons Al^{3+} + 3F^-$
$K_{sp} = [Al^{3+}][F^-]^3 = (8 \times 10^{-2})(3 \times 8 \times 10^{-2})^3 = 1.1 \times 10^{-3}$

(b) $\underline{AlF_3} \rightleftharpoons Al^{3+} + 3F^-$ let x = molar sol
$K_{sp} = (1)\,(3x)^3 = 1.1 \times 10^{-3}$; $x = 0.034\ M$

58. c < b < d < a < e (c) and (b) common ion effect; (d) salt effect; (e) effect of acid

59. $c < b < a < d < e$

60. (a), (c), (d), (f), (h), and (j) contain anions of weak acids

61. The carbonate in the marble reacts with the acid in acid rain to form the weak electrolyte carbonic acid. This increases the solubility of the calcium carbonate and therefore the marble will dissolve and weather more readily in the acidic rainfall. The minerals that make up granite have very low solubilities, and the anions in these minerals do not form weak electrolytes upon reaction with acid.

62. (a) To find weight percent silver, we need to know the weight of silver in the original sample. The weight of silver may be obtained provided we know the number of moles of silver in the original sample. If the reaction goes to completion, all of the silver in the original sample should be converted into the AgCl solid, which we have weighed.

$$\frac{0.3544\text{ g AgCl}}{143.32\text{ g/mol AgCl}} = 1.433 \times 10^{-3}\text{ mol AgCl which}$$

equal moles Ag

1.433×10^{-3} mol Ag × 107.87 g/mol Ag = 0.1546 g Ag

$$\frac{0.1456\text{ g Ag}}{1.2398\text{-g sample}} \times 100\% = 12.48\%\text{ silver}$$

(b) The loss due to solubility will originate from two sources, the solution in which the silver is precipitated and from the wash step.

Precipitation step: The Ag^+ concentration will be controlled by the K_{sp} of AgCl and the solution in which the silver was precipitated. Here we will use a K_{sp} with two significant figures.

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+]\,[Cl^-]$$

Excess chloride was added in the precipitation step and so will act as a common ion. We need to calculate how much excess Cl^- is present in the precipitation solution.

amount of Cl^- added: $0.080\ M \times 0.200\text{ L} = 0.016$ mol Cl^-

The amount of silver originally present (from part A) = 0.001433 mol, which would be the amount of Cl^- which will react since there is a 1:1 reaction stoichiometry.

Excess Cl^- is then, $0.016 - 0.001433 = 0.015$ mol Cl^-, in a total volume of 400 mL

$$[Cl^-] = \frac{0.015\text{ mol}}{0.400\text{ L}} = 0.0375\ M\text{ acting as a common ion,}$$

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+]\,[0.0375]$$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.0375} = 4.8 \times 10^{-9}\ M$$

Moles Ag lost in 400 mL of solution: $\dfrac{4.8 \times 10^{-9}\text{ mol}}{\text{L}} \times 0.400\text{ L} = 1.9 \times 10^{-9}$ mol, which is

1.9×10^{-9} mol × 107.87 g/mol = 2.07×10^{-7} g Ag lost

In the wash step, there are no common ions present so the $[Ag^+]$ is determined from the K_{sp} expression, $K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$, based on the dissociation stoichiometry, $[Ag^+] = [Cl^-]$

$$1.8 \times 10^{-10} = [Ag^+][Ag^+],\ [Ag^+] = 1.3 \times 10^{-5}\ M$$

Moles Ag lost in 400 mL of solution: × 0.400 L = 5.2×10^{-6} mol, which is 5.2×10^{-6} mol × 107.87 g/mol = 5.6×10^{-4} g Ag lost.

The total silver lost would be $2.07 \times 10^{-7}\text{ g} + 5.6 \times 10^{-4}\text{ g} = 5.6 \times 10^{-4}$ g

The error would then be:

$$\frac{(\text{amount Ag lost})}{(\text{total Ag})} \times 100\%$$

$$= \frac{5.6 \times 10^{-4}\text{ g}}{(5.6 \times 10^{-4}\text{ g} + 0.1456\text{ g})} \times 100\% = 0.38\%$$

(c) The white-to-purple film found on the glassware is AgCl solid. Although the silver ion will not be effectively removed by water, it is known to effectively form a complex with ammonia. Formation of the $Ag(NH_3)_2{}^+$ complex will shift the dissolution equilibria to the right, causing more AgCl to dissolve, removing the film.

63. (a) $\dfrac{5.6291\text{ g ore} \times 0.216\text{ g Ag}}{1.00\text{ g ore}} = 1.22\text{ g Ag}$

$$\frac{1.22\text{ g Ag}}{107.87\text{ g/mol Ag}} = 1.13 \times 10^{-2}\text{ mol Ag}$$

$$\frac{1.13\ \times 10^{-2}\text{ mol Ag} \times 1\ Ag_3PO_4}{3\text{ Ag}} = 0.377 \times 10^{-2}\text{ mol}$$

0.00377 mol Ag_3PO_4 × 418.6 g/mol Ag_3PO_4 = 1.58 g Ag_3PO_4

(b) Silver will be lost in two steps: precipitation and washing.

Precipitation Step: $[Ag^+]$ determined from the K_{sp} expression with the excess phosphate at 0.12 M,

$K_{sp} = 1.4 \times 10^{-16} = [Ag^+]^3\,[PO_4{}^{3-}] = [Ag^+]^3\,[0.12]$

$[Ag^+] = 1.1 \times 10^{-5}\ M.$

Silver lost in 2.5 L of solution would be:

1.1×10^{-5} mol/L × 2.5 L = 2.8×10^{-5} mol Ag

2.8×10^{-5} mol Ag × 107.87 g/mol Ag = 3.0×10^{-3} g Ag lost

Wash Step: No common ion, 0.5 L of wash water. $3[PO_4{}^{-3}] = [Ag^+]$

$K_{sp} = 1.4 \times 10^{-16} = [Ag^+]^3\,[PO_4{}^{-3}] = [3[PO_4{}^{-3}]]^3\,[PO_4{}^{-3}]$

$[PO_4^{3-}] = 4.8 \times 10^{-5}\ M$, so $[Ag^+] = 3(4.8 \times 10^{-5}\ M) = 1.4 \times 10^{-4}\ M$

Silver lost in 0.5 L of solution would be:

1.4×10^{-4} mol/L × 0.5 L = 7.0×10^{-5} mol Ag

7.0×10^{-5} mol Ag × 107.87 g/mol Ag = 7.6×10^{-3} g Ag lost in wash step

Total silver lost: $3.0 \times 10^{-3}\text{ g} + 7.6 \times 10^{-3}\text{ g} = 1.1 \times 10^{-2}$ g

(c) If we lost 1.1×10^{-2} g when we used 5.6921 g of ore, we can set up a ratio to find the amount we would lose in 5000 kg of ore.

$$\frac{0.011\text{ g}}{5.6921\text{ g}} = \frac{X\text{ g}}{5000 \times 10^3\text{ g}}$$

X g = 9.7×10^3 g Ag lost.

(d) $\dfrac{9.7 \times 10^3 \text{ g Ag}}{28.35 \text{ g/ounce}} \times \$5.00/\text{ounce} = \$1700$

(e) 1. Phosphate anion can form a weak electrolyte by reacting with H^+ making the treatment solution more acidic, resulting in an enhanced solubility of the compound and increased silver loss.
   2. Increase, for the same reason as 1.
   3. Excess phosphate anion will act as a common ion, shifting the equilibrium to the left, which results in the formation of more silver phosphate precipitate. This would reduce the silver ion concentration in solution and reduce silver ion losses.
   4. Reducing the volume of solutions will not change the concentration of silver ion (will not affect the equilibrium position), but lower volumes will reduce the number of moles of silver lost.

(f) By looking at the table of K_{sp} values, we can see that calcium and magnesium also form insoluble phosphate compounds and may precipitate along with the Ag_3PO_4.

64. Assuming no excess of chloride ion, the K_{sp} expression will provide the concentrations of Pb^{2+} and Cl^-.

$K_{sp} = 1.0 \times 10^{-4} = [Pb^{2+}][Cl^-]^2$

Based on the dissociation reaction, there will be two Cl^- for every one Pb^{2+} so $2[Pb^{2+}] = [Cl^-]$ and the K_{sp} expression may be written,

$1.0 \times 10^{-4} = [Pb^{+2}](2[Pb^{+2}])^2 = 4\,[Pb^{+2}]^3$

and the concentration of Pb^{+2} will be 2.9×10^{-2} *M* which is far in excess of the acceptable limit.

In theory we can reduce the lead ion to a nonhazardous level ($<10^{-7}$ *M*) by using a sufficient excess of the common ion Cl^- and shifting the dissociation equilibrium to the left, precipitating more $PbCl_2$ and reducing the Pb^{2+} level. We can calculate the necessary Cl^- concentration by setting the $[Pb^{2+}] = 1.0 \times 10^{-7}$ and substituting into the K_{sp} expression, and solving for $[Cl^-]$

$K_{sp} = 1.0 \times 10^{-4} = [Pb^{+2+}][Cl^-]^2 = [1.0 \times 10^{-7}][Cl^-]^2$

$[Cl^-] = 32\ M$

If the chloride ion were to originate from soluble NaCl, we would need 32 mol NaCl per liter of water which corresponds to ≈1800 g NaCl per liter of water. NaCl has a solubility of about 360 g per liter of water and therefore a 32 *M* solution is impossible to obtain.

CHAPTER 16

1. (a) PH_3, (b) $H_2C_2O_4$, (c) PH_3, (d) H_2O, (e) HBr, (f) hydroxyacetic acid, (g) 3-chloropropanoic acid, (h) $P(OH)_3$, (i) ClOH, (j) H_2SO_3, (k) NH_4^+, (l) H_2S

2. (a) $Al(OH)_3$ (b) BaO (c) CH_3^- (d) NH_2^- (e) F^- (f) O^{2-} (g) PO_4^{3-} (h) O^{2-} (I) $ClNH_2$ (j) $NaNH_2$ (k) PH_3 (l) HCO_3^-

3. (a) $HClO_3$ is the stronger acid because the additional oxygen atom removes more electron density from the oxygen of the O—H bond and thereby increases its electron affinity. In other words, the negative charge on ClO_3^- is better stabilized than the charge on ClO_2^-.

(b) H_2S is the stronger acid because the S—H bond is weaker than the O—H bond in water.

(c) Even though nitrogen has a stronger affinity for electrons than phosphorus, ammonia is the stronger base because the N—H bond in the conjugate acid (NH_4^+) is stronger than the P—H bond in PH_4^+.

(d) The electronegativity difference between Li and O is so large that the Li—O bond is essentially totally ionic, so LiOH is a source of hydroxide ions. In ClOH the Cl—O bond is polar and the Cl atom attracts electron density from the O—H bond and makes the compound acidic.

(e) The chlorine is more electronegative than iodine and therefore exerts a stronger effect on the O—H bond of the acid.

4. (a) CH_3^-; (b) NH_2^-; (c) F^-; (d) O^{2-}; (e) PO_4^{3-}; (f) O^{2-}; (g) CH_3NH_2; (h) CH_3NH_2; (i) $NaNH_2$; (j) aniline; (k) aniline

5. (a) HIO_3, (b) $ClCH_2CO_2H$, (c) H_3AsO_4, (d) H_2SO_3 (e) HClO

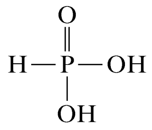
6. (a) PO_4^{3-} (b) NO_2^- (c) NH_3 (d) S^{2-} (e) $Ba(OH)_2$

6. (a) PO_4^{3-} (b) NO_2^- (c) NH_3 (d) S^{2-} (e) $Ba(OH)_2$

7. (a) $CH_3CHFCOOH$ (b) HOCl (c) PH_3 (d) trifluoroacetic acid

8. Ammonia is basic because the lone pair of electrons on the nitrogen may be shared with a proton; i.e., the availability of the nonbonding electrons allows ammonia to act as a proton acceptor. When the nitrogen atom of ammonia is substituted with electron-withdrawing groups, the electron density on the nitrogen atom is reduced, and therefore, substituted ammonia is a poorer base. The trend above reflects the electronegativity trend N < O < F; the more electronegative group has a greater effect on the lone pair electron density.

9. (a)



$$H{-}\overset{\overset{\large O}{\|}}{\underset{\underset{\large OH}{|}}{P}}{-}OH$$

(b) The acid dissociation constant for the second ionization of H_3PO_3 must be compared with K_b for the monosodium salt, which is $K_w/K_{a1} = 6.3 \times 10^{-13}$. The solution is acidic because $K_{a2} > (K_w/K_{a1})$.

10. (a) greater (b) less (c) less (d) greater (e) less

11. (a) $K = 1$ (b) $K > 1$ (c) $K > 1$ (d) $K > 1$ (e) $K > 1$ (f) $K > 1$

12. (a) less (b) greater (c) less (d) greater (e) greater (f) less (g) less (h) less

13. (a) $K < 1$. The hydronium ion is a stronger acid than $CH_3CH_2CO_2H$ and $CH_3CH_2CO_2^-$ is a stronger base than H_2O. Therefore, because the better proton donor and better proton acceptor are on the product side of the expression, the reaction as written will favor the reactants.

(b) The stronger acid and stronger base are on the reactant side and therefore $K > 1$.

(c) The stronger acid and stronger base are on the product side, the reaction as written will favor the reactants. $K < 1$.

(d) HSO_3^- is a stronger acid than water as can be seen from the K_{a2} for H_2SO_3 (6×10^{-8} as compared to that for water (about 10^{-16}). Therefore $K < 1$.

(f) $K < 1$. H_3O^+ is a stronger acid than HSO_3^-.

(g) $K < 1$ because OH^- is a stronger base than HSO_3^-.

14. Formula weight $Na_2CO_3 = 106$ g/mol

$$\frac{0.5110}{106} = 4.82 \times 10^{-3}\ \text{mol} \times 2 = 9.64 \times 10^{-3}\ \text{mol HCl}$$

$$\frac{9.64 \times 10^{-3}\ \text{mol}}{0.035\ \text{L}} = 0.3161\ M$$

15. No. Although the pH is a measure of hydrogen ion (or hydronium ion) concentration in an aqueous solution, it does not give the molar concentration of weak acids because these acids do not completely dissociate. For example, a pH 3.0 solution of HCl is 0.0010 *M* in HCl, but a pH 3.0 solution of acetic acid is 0.057 *M* in acetic acid.

16. (a) $\text{pH} = -\log[H_3O^+] = -\log(1.5 \times 10^{-4}) = 3.82$

17. (a) $\text{pH} + \text{pOH} = 14.00$

$\text{pH} = 14 - \text{pOH}$

$\text{pH} = 14.00 - (-\log 1.0) = 14.00$

18. (a) $[H_3O^+] = \text{antilog}(-\text{pH}) = 3.0 \times 10^{-2}$

19. (a) $$\text{moles NaOH} = \frac{0.980\ \text{g}}{39.9971\ \text{g/mol}} = 0.0245\ \text{mol}$$

$$[OH^-] = \frac{0.0245\ \text{mol}}{0.250\ \text{L}} = 0.0980\ M$$

$\text{pOH} = -\log[OH^-] = -\log(0.0980) = 1.009$

$\text{pH} = 14.000 - 1.009 = 12.991$

(b) $\dfrac{2.5\ \text{mL} \times 12\ M}{200\ \text{mL}} = 0.15\ M$; pH = 0.82 and pOH = 13.17

(c) millimoles KOH = 10.0 mL × 0.1 *M* = 1.0 millimole

millimoles HCl = 5.0 mL × 0.2 *M* = 1.0 millimole

Acid and base neutralize each other, therefore pH = pOH = 7.0.

(d) millimoles KOH = 150.0 mL × 0.10 *M* = 15 millimoles

millimoles HCl = 250.0 mL × 0.10 *M* = 25 millimoles

After mixing the solution contains 10 millimoles of HCl in 400.0 mL, Thus,

$$[H_3O^+] = \frac{0.010\ \text{mol HCl}}{0.4001\ \text{L}} = 0.025\ M$$

Therefore, pH = 1.60 and pOH = 12.40

(e) $[OH^-] = 0.10\ M$ pOH = 1.00 pH = 13.00

20. $CH_3CH_2CO_2H + H_2O \rightleftharpoons CH_3CH_2CO_2^- + H_3O^+$

$[H_3O^+] = \text{antilog}(-3.0) = 1 \times 10^{-3}\ M = [CH_3CH_2CO_2^-]$

$[CH_3CH_2CO_2H] = 0.10 - 1 \times 10^{-3} = 0.10\ M$

$$K_a = \frac{[H_3O^+][CH_3CH_2CO_2^-]}{[CH_3CH_2CO_2H]} = \frac{(1 \times 10^{-3})^2}{(0.10)} = 1.0 \times 10^{-5}$$

21. $(CH_3)_3C_2O_2H + H_2O \rightleftharpoons (CH_3)_3C_2O_2^- + H_3O^+$

$[H_3O^+] = 6.3 \times 10^{-4}\ M = [(CH_3)_3C_2O_2^-]$

$$\frac{\dfrac{5.1\ \text{g}}{102\ \text{g/mol}}}{1.0\ \text{L}} = 5.0 \times 10^{-2}\ M$$

$[(CH_3)_3C_2O_2H] = 5.0 \times 10^{-2} - 6.3 \times 10^{-4}$

$$K_a = \frac{(6.3 \times 10^{-4})^2}{5.0 \times 10^{-2}} = 8 \times 10^{-6}$$

22. $\text{pOH} = 14.00 - 9.35 = 4.65$

$[OH^-] = 2.24 \times 10^{-5}\ M$

$$K_b = \frac{(2.24 \times 10^{-5})^2}{1.0} = 5.0 \times 10^{-10}$$

23.

	NH_3	NH_4^+	OH^-
Start	0.0033	0.0	0.0
Change	$-x$	$+x$	$+x$
Equilibrium 0.0033	$-x$	x	x

$$K_b = 1.8 \times 10^{-5} = \frac{x^2}{0.0033} - x$$

$x = 0.00025$

$[OH^-] = 0.00025\ M$ and pOH = 3.60 Thus, pH = 10.40

24. $$K_a = 1.4 \times 10^{-4} = \frac{x^2}{0.16 - x}$$

$x = 4.7 \times 10^{-3} = [H_3O^+]$ Therefore, pH = 2.33

25. (a) $HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$

$$K_a = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = 1.8 \times 10^{-4}$$

$[H_3O^+] = x = [HCO_2^-]$

$[HCO_2H] = 0.10 - x$

$$K_a = \frac{x^2}{0.1 - x}$$

$[H_3O^+] = [HCO_2^-] = 4.2 \times 10^{-3}\ M$

$[HCO_2H] = 0.10\ M$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-3}} = 2.4 \times 10^{-12}\ M$$

(b) $Cl_2CHCO_2H + H_2O \rightleftharpoons Cl_2CHCO_2^- + H_3O^+$

$[Cl_2CHCO_2^-] = x = [H_3O^+]$

$[Cl_2CHCO_2H] = 1.0 - x$

$$K_a = \frac{x^2}{1.0 - x} = 3.3 \times 10^{-2}$$

$x = 0.17\ M$

$[H_3O^+] = [Cl_2CHCO_2^-] = 0.17\ M$

$[Cl_2CHCO_2H] = 0.83\ M$

$[OH^-] = 5.9 \times 10^{-14}\ M$

(c) $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$

$[OH^-] = [(C_2H_5)_3NH^+] = x$

$[(C_2H_5)_3N] = 0.010 - x$

$$K_b = \frac{x^2}{0.010 - x} = 4.0 \times 10^{-4}$$

$x = 1.8 \times 10^{-3}\ M$

$[(C_2H_5)_3NH^+] = [OH^-] = 1.8 \times 10^{-3}\ M$

$[(C_2H_5)_3N] = 8 \times 10^{-3}\ M$; $[H_3O^+] = 5.6 \times 10^{-12}\ M$

(d) $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$[OH^-] = [C_6H_5NH_3^+] = x$; $[C_6H_5NH_2] = 0.15 - x$

$$K_b = \frac{x^2}{0.15 - x} = 3.8 \times 10^{-10}$$

$x = 7.5 \times 10^{-6}\ M$
$[C_6H_5NH_3^+] = [OH^-] = 7.5 \times 10^{-6}\ M$
$[C_6H_5NH_2] = 0.15\ M$; $[H_3O^+] = 1.3 \times 10^{-9}\ M$

26. $K_a = 1.8 \times 10^{-5} = \dfrac{(1.00 \times 10^{-4})^2}{0.100 - (1.00 \times 10^{-4})} = 1.00 \times 10^{-7}$

27. $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{(1.0 \times 10^{-5})(1.0 \times 10^{-5})}{(1.00 \times 10^{-2} - 1.0 \times 10^{-5})} =$
1.0×10^{-8}

28. $M + H_2O \rightarrow MH^+ + OH^-$

$$K_b = [MH^+]\frac{[OH^-]}{[M]}$$

$[OH^-] = \text{antilog}[-(14 - 10.43)] = 2.7 \times 10^{-4}$

$$K_b = \frac{(2.7 \times 10^{-4})^2}{0.10} = 7.3 \times 10^{-7}$$

29. (a) $HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$
$[H_3O^+] = [NO_2^-] = x$; $[HNO_2] = 0.010 - x$

$$\frac{x^2}{0.010 - x} = 4.6 \times 10^{-4}$$

$x = 1.9 \times 10^{-3}\ M$; pH = 2.72

(b) $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$
$[HS^-] = [H_3O^+] = x$; $[H_2S] = 0.10 - x$

$$\frac{x^2}{0.10 - x} = 1.0 \times 10^{-7}$$

$x = 1.0 \times 10^{-4}$; pH = 4.00

(c) $H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$
$[H_3NOH^+] = [OH^-] = x$; $[H_2NOH] = 0.010 - x$

$$\frac{x^2}{0.010 - x} = 1.1 \times 10^{-8}$$

$x = 1.05 \times 10^{-5}$; pH = 9.02

30. $K_b = 1.8 \times 10^{-5} = \dfrac{(7.4 \times 10^{-3})(7.4 \times 10^{-3})}{(x - 7.4 \times 10^{-3})}$

Assuming $x \gg 7.4 \times 10^{-3}$, then $x = 3.0$
$[NH_3] = 3.0\ M$

$$\frac{3.0\ \text{mol/L} \times 1\ \text{L} \times 17.030\ \text{g/mol}}{1.00\ \text{g/mL} \times 1000\ \text{mL}} \times 100 = 5.1\%\ NH_3$$

31. $\dfrac{1.004\ \text{g/mL} \times 1000\ \text{gmL/L} \times 0.04}{60\ \text{g/mol}} = 0.67$ mol/L acetic acid

$\dfrac{x^2}{0.67 - x} = 1.8 \times 10^{-5}$; $x = 3.5 \times 10^{-3}\ M$; pH = 2.5

Therefore, the vinegar is acceptable.

32. (a) When a polyprotic acid loses its first proton, the conjugate base produced possesses a negative charge. The second ionization does not occur to as great an extent as the first one (i.e., $K_{a1} > K_{a2}$) because the loss of the second proton would generate another negative charge on the conjugate, which is unfavorable given the presence of an existing negative charge. This same argument is applicable for the explanation of the difference between K_{a2} and K_{a3}. Alternatively, after a polyprotic acid has lost a proton, the negative charge that remains on the conjugate base significantly reduces the electron-withdrawing ability of the group and the acidity associated with protons 2, 3 and so on is decreased.

(b) Barium carbonate reacts with HCl to produce carbonic acid, a weak electrolyte, and barium chloride, a salt. The carbonic acid subsequently decomposes irreversibly to carbon dioxide and water. The sulfate ion in barium sulfate is the conjugate base of a strong acid; therefore, the sulfate ion will not react with HCl to produce a weak electrolyte.
$BaCO_3(s) + 2\ HCl(aq) \rightarrow BaCl_2(aq) + H_2CO_3(aq)$
$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O$

(c) Copper(II) carbonate reacts with HCl to produce carbonic acid, which subsequently decomposes to carbon dioxide and water. Although HCl will convert sulfide ion to hydrogen sulfide, the concentration of the sulfide in the acidic solution is sufficiently great that the K_{sp} for CuS is exceeded; i.e., copper (II) sulfide will not dissolve.
Because $[H^+]^2[S^{2-}] = 1.3 \times 10^{-21}$ and $[H^+] = 1\ M$, $[S^{2-}] = 1.3 \times 10^{-21}$
Now for CuS, $K_{sp} = 1 \times 10^{-45}$, therefore the maximum cupric ion concentration would be about 7×10^{-25}; i.e., it is not soluble.

(d) Vapor from the bottle of hydrochloric acid contains $HCl(g)$ and vapor from the bottle of aqueous ammonia contains $NH_3(g)$. When these two vapors mix, the HCl and NH_3 react to produce microscopic particles of ammonium chloride, which is a salt.

33. (a) The concentration of the carbonate ion in the saturated solution of $CaCO_3$ is too low to force the precipitation of ferric carbonate. However, in aqueous solution the carbonate ion reacts with water to produce hydroxide ion, and the hydroxide ion concentration is sufficiently great to cause the precipitation of ferric hydroxide, $Fe(OH)_3$, which has a very small K_{sp} value (on the order of 10^{-38}).

When the solid $CaCO_3$ is mixed with water, a saturated solution of calcium carbonate is produced. From the K_{sp} for this carbonate (8.7×10^{-9}), the concentration of the carbonate ion would be $9.3 \times 10^{-5}\ M$.
$K_{sp} = 8.7 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] = x^2$; $x = 9.3 \times 10^{-5}$
However, K_{a2} for carbonic acid is 4.8×10^{-11}, therefore, this solution will be basic.
$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$
$K_b = 2.1 \times 10^{-4}$ from $K_b = K_w/K_{a2}$
Thus, the overall equilibrium is
$CaCO_3(s) + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^-$
The equilibrium constant, K, for this process is
$K = K_{sp}K_b = (8.7 \times 10^{-9})(2.1 \times 10^{-4}) = 1.8 \times 10^{-12}$
$K = 1.8 \times 10^{-12} = [Ca^{2+}][HCO_3^-][OH^-]$
$1.8 \times 10^{-12} = x^3$
$x = 1.2 \times 10^{-4} = [OH^-]$
Because the K_{sp} for $Fe(OH)_3$ is small, ferric hydroxide will precipitate.
$Fe(OH)_3 \rightleftharpoons Fe^{3+}1 + 3\ OH^-$
K_{sp} for $Fe(OH)_3 = 6 \times 10^{-38} = [Fe^{3+}][OH^-]^3$
Therefore, for the conditions given in the problem
$[Fe^{3+}][OH^-]^3 = (1.0 \times 10^{-3})(1.2 \times 10^{-4})^3 > 6 \times 10^{-38}$
so ferric ion precipitates as the hydroxide. Ferric car-

bonate does not precipitate because the carbonate ion concentration is too low; indeed, virtually all of the carbonate ions are gain a proton from water to become bicarbonate ions.

(b) In summary, the relevant reaction equations are:
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$
$CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^{1-}(aq) + OH^-(aq)$
$Fe^{3+}(aq) + 3\ OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

34. $Na_2O(s) + H_2O \rightleftharpoons 2\ Na^+ + 2\ OH^-$

$$\frac{0.155\ \text{g}\ Na_2O}{100\ \text{mL}} \times 1000\ \text{mL/L} \times 1\ \frac{\text{mol}}{62\ \text{g}} \times \frac{2\ \text{mol}\ OH^-}{1\ \text{mol}\ Na_2O} =$$

$0.050\ \text{M}\ OH^-$
$\text{pH} = 12.7$

35. The first ionization of H_2S is the more important contribution to $[H_3O^+]$.

$H_2S + H_2O \rightleftharpoons H_3O^+ + SH^- \qquad K_a = 5.7 \times 10^{-8}$

$$5.7 \times 10^{-8} = \frac{[H_3O^+][SH^-]}{[H_2S]} = \frac{x^2}{0.010 - x} \qquad x = 2.4 \times 10^{-5}$$

The second ionization is less important.

$SH^- + H_2O \rightleftharpoons H_3O^+ + S^{2-} \qquad K_a = 1.2 \times 10^{-15}$

$$1.2 \times 10^{-15} = \frac{[H_3O^+][S^{2-}]}{[SH^-]} = \frac{(2.4 \times 10^{-5} + x)x}{(2.4 \times 10^{-5} - x)}$$

$x = 1.2 \times 10^{-15}$

Thus, $[H_3O^+] = [SH^-] = 2.4 \times 10^{-5}\ M\ [S^{2-}] = 1.2 \times 10^{-15}\ M$

36. $[S^{2-}] = 1 \times 10^{-13}\ M$ for a saturated solution of H_2S
$[M^{2+}][S^{2-}] = (1.0 \times 10^{-1})(1 \times 10^{-13}) = 1 \times 10^{-14}$
K_{sp} is exceeded for each sulfide

37. $[H^+]^2[S^{2-}] = 1 \times 10^{-21} \qquad [H^+] = 5.0 \times 10^{-2}\ M$

$$\text{Therefore: } [S^{2-}] = \frac{1 \times 10^{-21}}{[H^+]^2} = \frac{1 \times 10^{-21}}{(5.0 \times 10^{-2})^2} = 5 \times 10^{-19}$$

$CuS(s) \rightleftharpoons Cu^{2+} + S^{2-}$
Therefore: $[Cu^{2+}] = s$ and $[S^{2-}] = s + 5 \times 10^{-19}$
$K_{sp} = [Cu^{2+}][S^{2-}] = 1 \times 10^{-45}$
$(s)(s + 5 \times 10^{-19}) = 1 \times 10^{-45}$

$$s = \frac{1 \times 10^{-41}}{5 \times 10^{-19}} = 2 \times 10^{-27}\ M$$

Therefore $2 \times 10^{-27}\ M$ or $2 \times 10^{-25}\ g$ of CuS will dissolve.

38. $K_{sp} = [Zn^{2+}][S^{2-}] = 1 \times 10^{-23}$

In order to prevent Zn^{2+} from precipitating, the sulfide ion concentration cannot exceed $2 \times 10^{-22}\ M$

$$[S^{2-}] = \frac{1 \times 10^{-23}}{5.0 \times 10^{-2}} = 2 \times 10^{-22}\ M$$

Using this sulfide ion concentration and the following equation

$$[H^+]^2[S^{2-}] = 1 \times 10^{-21}$$

gives
$[H^+] = 2.2\ M$ in order to prevent precipitation of ZnS
$[Cd^{2+}][S^{2-}] = 1 \times 10^{-28}$

At this point the sulfide ion concentration is 2×10^{-22}, therefore

$$[Cd^{2+}] = \frac{1 \times 10^{-41}}{5 \times 10^{-19}} = 2 \times 10^{-27}\ M$$

39. a. $$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(1.6 \times 10^{-3})^2}{0.010 - 1.6 \times 10^{-3}} = 3.0 \times 10^{-4}$$

b. $$K_b = 3.3 \times 10^{-11} = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{1.0 - x} = 5.7 \times 10^{-6}$$

$[HA] = [OH^-] = 5.7 \times 10^{-6}\ M\ [A^-] = 1.0\ M$; pH = 8.76

40. (a) $OBr^- + H_2O \rightleftharpoons HOBr + OH^-$
$\text{pOH} = 14.00 - 10.84 = 3.16$
$[OH^-] = HOBr = 6.92 \times 10^{-4}\ M$; $[OBr^-] = 0.10\ M$

$$K_b = \frac{[HOBr][OH^-]}{[OBr^-]} = \frac{(6.92 \times 10^{-4})(6.92 \times 10^{-4})}{0.10} = 4.8 \times 10^{-6}$$

(b) $$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-6}} = 2.1 \times 10^{-9}$$

41. propanoic acid: $CH_3CH_2CO_2H$
conjugate base of propanoic acid: $CH_3CH_2CO_2^-$
$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.3 \times 10^{-5} = 7.7 \times 10^{-10}$

42. ethyl amine: $C_2H_5NH_2$
conjugate acid: $C_2H_5NH_3^+$
$K_a = K_w/K_b = 1.0 \times 10^{-14}/5.6 \times 10^{-4}$

43. (a) $$3 \times 10^{-4} = \frac{[H_3O^+][Asp^-]}{[HAsp]} = \frac{x^2}{0.1 - x}$$

$[H_3O^+] = 0.005\ M$; pH = 2.3

(b) $$K_b = 3 \times 10^{-11} = \frac{[HAsp^-][OH^-]}{[Asp^-]} = \frac{x^2}{0.1 - x}$$

$[OH^-] = 2 \times 10^{-6}\ M$
$\text{pH} = 14.0 - 5.7 = 8.3$

44. $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$
$[H_3O^+] = 1.58 \times 10^{-6}\ M = [CH_3NH_2]$
$[CH_3NH_3^+] = 0.10\ M$

(a) $$K_a = \frac{(1.58 \times 10^{-6})(1.58 \times 10^{-6})}{0.10} = 2.5 \times 10^{-12}$$

(b) $$K_b = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-11}} = 4.0 \times 10^{-4}$$

45. (a) $(C_6H_5)_3SiCl \rightarrow (C_6H_5)_3Si^+ + Cl^-$ slow step
$(C_6H_5)_3Si^+ + OH^- \rightarrow (C_6H_5)_3SiOH$ fast step
(b) rate $= k[\phi_3SiCl]$
(c) $\phi_3SiOH + H_2O \rightleftharpoons \phi_3SiO^+ + H_3O^+$
(d) $H_3O^+ = 10^{-6}$

$$K_a = \frac{(10^{-6})^2}{1} = 10^{-12}$$

(e) $\phi_3SiO^- + H_2O \rightleftharpoons \phi_3SiOH + OH^-$

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

46. (a) $$\frac{1.0 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8}$$

(b) $$K_a = 1.0 \times 10^{-6} = \frac{x^2}{0.1 - x}$$

$x = 4.5 \times 10^{-4}$
$[OH^-] = 4.5 \times 10^{-4}$, therefore, pH = 10.65

47. $K_{sp} = 4 \times 10^{-11} = [Ca^{2+}][F^-]^2 = x(2x)^2; x = 2 \times 10^{-4}$
Thus, 2×10^{-4} mol of CaF_2 or 0.02 g will dissolve in one liter of water.

48. (a) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
$x = [NH_3] = [H_3O^+]$ and $[NH_4^+] = 1.0 - x$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\frac{x^2}{1 - x} = 5.6 \times 10^{-10}$$

$x = 2.4 \times 10^{-5}\ M$
$[NH_3] = [H_3O^+] = 2.4 \times 10^{-5}\ M$; $[NH_4^+] = 1.0\ M = [Cl^-]$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{2.4 \times 10^{-5}} = 4.2 \times 10^{-10}\ M$$

(b) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$
$x = [HNO_2] = [OH^-]$ and $[NO_2^-] = 0.010 - x$

$$K_h = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11}$$

$$\frac{x^2}{0.010 - x} = 2.2 \times 10^{-11}$$

$x = 4.7 \times 10^{-7}\ M$
$[HNO_2] = [OH^-] = 4.7 \times 10^{-7}\ M$; $[NO_2^-] = 0.01\ M = [Na^+]$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-7}} = 2.1 \times 10^{-8}$$

(c) $F^- + H_2O \rightleftharpoons HF + OH^-$
$x = [HF] = [OH^-]$ and $[F^-] = 0.10 - x$

$$K_h = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.9 \times 10^{-11}$$

$$\frac{x^2}{0.10 - x} = 2.9 \times 10^{-11}$$

$x = 1.7 \times 10^{-6}\ M$
$[HF] = [OH^-] = 1.7 \times 10^{-6}\ M$; $[F^-] = [K^+] = 0.10\ M$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-6}} = 5.9 \times 10^{-9}\ M$$

49. (a) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{x^2}{0.50 - x} = 1.8 \times 10^{-5}$$

$x = 3.0 \times 10^{-3}$
pOH = 2.52
pH = 11.48

(b) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$$[NH_4^+] = \frac{535\ g}{(53.5\ g/mol)(0.5\ L)} = 0.200\ M$$

$$K_h = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.200 - x}$$

$x = 1.10 \times 10^{-5}$
pH = 4.98

(c) Mixing results in a solution $0.20_3\ M$ in NH_3 and 0.12 M NH_4Cl.

$$K_h = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(0.20)x}{(0.12)}$$

$x = 3.30 \times 10^{-1o}$
pH = 9.48

50. (a) neutral (b) acidic (c) basic (d) basic
Cesium hydrogen sulfide contains the cesium ion and the hydrogen sulfide ion, HS^-. Cesium does not react with water, but the hydrogen sulfide ion can react in two ways:

$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$ (1)
$HS^- + H_2O \rightleftharpoons H_2S + OH^-$ (2)

The first reaction is the second dissociation of the acid H_2S; the K for (1) is therefore K_{a2}. In reaction 2, HS^- acts as a base, and this $K_b = K_w/K_{a1}$.

$K_{a2} = 1 \times 10^{-13}$
$K_b = 1.0 \times 10^{-14}/1 \times 10^{-7} = 1 \times 10^{-7}$

Thus, K_b is larger than K_{a2}, the extent of (2) is greater than that of (1), and since (2) produces OH^-, the solution has more OH^- than H_3O^+.

(e) basic
Two reactions occur in this solution:

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (1)
$CN^- + H_2O \rightleftharpoons HCN + OH^-$ (2)

The K for (1) is 5.6×10^{-10} while the K for (2) is 2.0×10^{-5}. Thus, (2) has the greater extent and the concentration of OH^- will be greater than that of H_3O^+.

51. (a) $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$$K_{a2} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11}$$

acidic

(b) $HS^- + H_2O \rightleftharpoons H_2S + OH^-$

$$K = \frac{1.0 \times 10^{-14}}{1 \times 10^{-7}} = 1 \times 10^{-7}$$

$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$
$K = 1 \times 10^{-13}$
basic

52. (a) acidic, (b) acidic, (c) basic, (d) basic, (e) neutral, (f) basic, (g) basic, (h) basic, (i) acidic, (j) acidic, (k) acidic, (l) acidic, (m) neutral

53. Ka: 7.5×10^{-3}
6.2×10^{-8}
2.2×10^{-13}
$Na^+ + H_2O$ nr
$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \quad K_{a2} = 6.2 \times 10^{-8}$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \quad \frac{K_w}{K_{a1}} = \frac{10^{-14}}{7.5 \times 10^{-3}} =$$

1×10^{-12}
Therefore, solution is acidic.

54. $$K_a = 6.8 \times 10^{-4} = \frac{(0.10 + x)(x)}{(0.20 - x)}$$

Assuming $x \ll 0.10$, then $x = 1.4 \times 10^{-3}$
$[F^-] = 1.4 \times 10^{-3}\ M$; pH $= -\log(0.10 + 1.4 \times 10^{-3}) = 0.99$

55. $K_a(HNO_2) = 4.6 \times 10^{-4}$; therefore, $K_b(NO_2^-) = 2.2 \times 10^{-11}$
$K_b(NH_3) = 1.8 \times 10^{-5}$; therefore, $K_a(NH_4^+) = 5.6 \times 10^{-10}$
In solution two processes are occurring:

$H_2O + NO_2^- \rightleftharpoons HNO_2 + {}^-OH$
$H_2O + NH_4^+ \rightleftharpoons H_3O^+ + NH_3$

The solution will be acidic because the second equilibrium has the larger K value.

56. (a) $K_a = 1.8 \times 10^{-5} = \dfrac{x(0.050 + x)}{0.17 - x}$

$x = [H_3O^+] = 6.1 \times 10^{-5}$; pH = 4.21

(b) The concentration of acetic acid is decreased from 0.17 to 0.16 M and the concentration of the acetate ion is increased from 0.050 M to 0.060 M.

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.060 + x)}{0.16 - x}$$

$x = [H_3O^+] = 4.8 \times 10^{-5}$; pH = 4.32

(c) In pure water the pH = 7.00. In a 0.01 M OH^- solution, the pH = 12.00, thus the addition of 0.01 mol of hydroxide ion to a liter of water would change the pH by 5 full units.

57. (a) $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$

$0.100\ L \times 0.10\ M = 0.010$ mol $CH_3CO_2H = 0.010$ mol OH^-

$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$

$x = [CH_3CO_2H] = [OH^-]$; $[CH_3CO_2^-] = 0.010 - x$

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\frac{x^2}{0.05 - x} = 5.6 \times 10^{-10} = 5.6 \times 10^{-10}$$

$x = 5.3 \times 10^{-6}\ M = [OH^-]$

pH = 8.72

(b) $\dfrac{100\ \text{mL} \times 0.10\ M}{(1860 + 100)\ \text{mL}} = 5.1 \times 10^{-3}\ M$ acetic acid; solution would be acidic with pH less than (a).

(c) $\dfrac{100\ \text{mL} \times 0.10\ M\ CH_3CO_2H}{100\ \text{mL} + 50\ \text{mL}} = 0.067\ M\ CH_3CO_2H$

$$\frac{50\ \text{mL} \times 0.10\ M\ CH_3CO_2^-}{100\ \text{mL} + 50\ \text{mL}} = 3.3 \times 10^{-2}\ M\ CH_3CO_2^-$$

The acetic acid solution buffered with acetate ion would still be acidic with a pH less than (a). Therefore (a) would increase the pH to the greatest extent.

58. $CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$

$K_a = \dfrac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H^-]} = 1.8 \times 10^{-5}$; $[H_3O^+] = 1 \times 10^{-5}\ M$

$$\frac{[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{[H_3O^+]}{K_a} = \frac{10^{-5}}{1.8 \times 10^{-5}} = \frac{0.56}{1}$$

acid-to-salt ratio of 0.56 to 1.0

59. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

pOH = 14.00 − 8.2 = 5.8

$[OH^-] = 1.6 \times 10^{-6}\ M$

$[NH_3] = 0.25 - 1.6 \times 10^{-6}$

Let x = mol/L of NH_4Cl added; then $[NH_4^+] = x + 1.6 \times 10^{-6}$

Therefore: $\dfrac{x(1.6 \times 10^{-6})}{0.25} = 1.8 \times 10^{-5}$

$$x = \frac{(1.8 \times 10^{-5})(0.25)}{1.6 \times 10^{-6}} = 2.8\ M$$

$$2.8\ M \times 0.100\ L \times \frac{53.45\ g\ NH_4Cl}{1\ mol} = 15\ g\ NH_4Cl$$

60. (a) $ClCH_2CO_2H + H_2O \rightleftharpoons H_3O^+ + ClCH_2CO_2^-$

$x = [H_3O^+]$; therefore $[ClCHCO_2^-] = x + 0.20$

$[ClCH_2CO_2H] = 0.10 - x$

$$\frac{(x)(x + 0.20)}{0.10 - x} = 1.4 \times 10^{-3}$$

$x = 7.0 \times 10^{-4}\ M$

pH = −log (7 × 10^{-4}) = 3.15

(b) $ClCH_2CO_2^- + H^+ \rightarrow ClCH_2CO_2H$

0.010 mol HCl forms 0.010 mol of $ClCH_2CO_2H$

$[ClCH_2CO_2H] = 0.10 + 0.01 = 0.11\ M$

$[ClCH_2CO_2^-] = 0.20 - 0.01 = 0.19\ M$

$$[H_3O^+] = \frac{K_a[ClCH_2CO_2H]}{[ClCH_2CO_2^-]} = \frac{(0.11)(1.4 \times 10^{-3})}{0.19} =$$

$8.1 \times 10^{-4}\ M$

pH = −log (8.1 × 10^{-4}) = 3.09

$ClCH_2CO_2H + OH^- \rightarrow ClCH_2CO_2^- + H_2O$

0.010 mol of NaOH forms 0.010 mol of $ClCH_2CO_2^-$

$[ClCH_2CO_2H] = 0.10 - 0.010 = 0.09\ M$

$[ClCH_2CO_2^-] = 0.20 + 0.01 = 0.21\ M$

$$[H_3O^+] = \frac{K_a[ClCH_2CO_2H]}{[ClCH_2CO_2^-]} = \frac{(0.09)(1.4 \times 10^{-3})}{0.21} =$$

$6 \times 10^{-4}\ M$

pH = −log (6 × 10^{-4}) = 3.2

61. (a) # moles NH_3 = 0.10 M × 0.1000 L − 1.0 M × 0.0050 = L = 0.0050 mol

moles NH_4^+ = 0.10 M × 0.1000 L + 1.0 M × 0.0050 L = 0.015 mol

$[NH_3] = 0.0050\ \text{mol}/0.1050\ L = 0.048\ M$

$[NH_4^+] = 0.015\ \text{mol}/0.1050\ L = 0.14\ M$

$$K_a = 5.6 \times 10^{-10} = \frac{(0.048 \times x)(x)}{(0.14 - x)}$$

Assuming $x \ll 0.048$, then $x = 1.6 \times 10^{-9}$ and $[H^+] = 1.6 \times 10^{-9}\ M$. Therefore, the resulting pH = 8.80

(b) # moles NH_3 = 0.10 M × 0.1000 L + 1.0 M × 0.0050 L = 0.015 mol

moles NH_4^+ = 0.10 M × 0.1000 L − 1.0 M × 0.0050 L = 0.005 mol

$[NH_3] = 0.015\ \text{mol}/0.1050\ L = 0.14\ M$

$[NH_4^+] = 0.015\ \text{mol}/0.1050\ L = 0.048\ M$

$$K_a = 5.6 \times 10^{-10} = \frac{(0.14 \times x)(x)}{(0.048 - x)}$$

Assuming $x \ll 0.048$, then $x = 1.9 \times 10^{-10}$ and $[H^+] = 1.9 \times 10^{-10}\ M$. Therefore, the resulting pH = 9.72

62. pOH = 14 − 9.25 = 4.75; $[OH^-] = 1.8 \times 10^{-5}$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\frac{[OH^-]}{K_b} = \frac{[NH_4^+]}{[NH_3]} = \frac{1.8 \times 10^{-5}}{1.8 \times 10^{-5}} = 1$$

0.1 L × 0.1 mol/L = 0.01 mol NH

Need 0.01 mol NH_4Cl

0.01 × 53.5 = 0.53 g NH_4Cl

63. $K_a = 1.8 \times 10^{-5} = \dfrac{(1.5 \times 10^{-5}\ M)(x)}{(0.75\ M)}$

$[CH_3CO_2Na] = 0.90\ M$

64. $$\frac{3.2 \times 10^{-8}\,[\mathrm{OCl^-}]}{[\mathrm{HOCl}]} = 3.0 \times 10^{-8}$$

$$\frac{[\mathrm{HOCl}]}{[\mathrm{OCl^-}]} = 1.1$$

65. Because one mole of $Al(OH)_3$ will react with three moles of HCl ("stomach acid"), while $Mg(OH)_2$ will react with two moles, and $NaHCO_3$ with only one mole, $Al(OH)_3$ neutralizes more acid per gram than the other two. Sodium bicarbonate has two disadvantages: it contains sodium, which appears to contribute to higher blood pressure, and the reaction with acid produces carbonic acid. The carbonic acid decomposes to CO_2 which increases the "gas" in the stomach (some people probably consider this a benefit).

66. (a) 50 mL × 0.20 *M* HCl = 10 millimoles of HCl
50 mL × 0.20 M NaOH = 10 millimoles of NaOH
$H^+ + OH^- \rightleftharpoons H_2O$
same as a solution of KCl; pH = 7.0
(b) 30 mL × 0.10 *M* HCl = 3 millimoles of HCl
30 mL × 0.10 *M* NH3 = 3 millimoles of NH_3
$NH_3 + H^+ \rightarrow NH_4{}^+$ produces 3 millimoles of NH_4Cl in 60 mL of solution, or 0.050 *M* NH_4Cl
$NH_4{}^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$
$[H_3O^+] = [NH_3] = x$ and $[NH_4{}^+] = 0.050 = x$

$$\frac{x^2}{0.050 - x} = \frac{K_w}{K_b} = 5.6 \times 10^{-1o}$$

$x = 5.3 \times 10^{-6}$
$pH = -\log(5.3 \times 10^{-6}) = 5.28$
(c) $HCN + OH^- \rightarrow CN^- + H_2O$
25 mL × 0.20 *M* HCN = 5 millimoles of HCN
25 mL × 0.20 *M* NaOH = 5 millimoles of NaOH
$[CN^-] = 0.10\ M$
$CN^- + H_2O \rightleftharpoons HCN + OH^-$
$x = [HCN] = [OH^-];\ [CN^-] = 0.10 - x$

$$K_h = \frac{x^2}{0.10 - x} = \frac{K_w}{K_a} = 2.0 \times 10^{-5}$$

$x = 1.4 \times 10^{-3}$; $pH = 14 - (-\log 1.4 \times 10^{-3}) = 11.15$

67. (a) When 0.0016 mol of ammonia, NH_3, are mixed with water to give a total volume of 60 mL, the $[NH_3] = 0.027\ M$.

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = \frac{x^2}{0.027 - x}$$

$x = [OH^-] = 7.0 \times 10^{-4}$
$[H_3O^+] = 1.0 \times 10^{-14}/7.0 \times 10^{-4} = 1.4 \times 10^{-11}$
pH = 10.85
(b) $[NH_3] = 0.027\ M$ and $[NH_4{}^+] = 0.020\ M$

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4O^+][OH^-]}{[NH_3]} = \frac{(0.020 + x)x}{0.027 - x}$$

$x = [OH^-] = 2.4 \times 10^{-5}$
$[H_3O^+] = 1.0 \times 10^{-14}/2.4 \times 10^{-5} = 4.2 \times 10^{-10}$
pH = 9.38
(c) $K_a = K_w/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

$$K_a = 5.6 \times 10^{-10} = \frac{[H_3][OH^-]}{[NH_3]} = \frac{x^2}{0.027 - x}$$

$x = [H_3O^+] = 3.9 \times 10^{-6}$
pH = 5.41

(d) A strong base, NaOH, is added to a weak base, NH_3. They will not react and the pH will be determined by the amount of strong base present. The concentration of NaOH is 0.027 *M*, so the pH is 12.43.

68. $\underline{Mg(OH)_2} \rightleftharpoons Mg^{2+} + 2\,OH^-$
$[OH^-] = 1.0 \times 10^{-2} + 2x;\ [Mg^{2+}] = x$
$[Mg^{2+}]\,[OH^-]^2 = 1.8 \times 10^{-11}$
$(x)\,(1.0 \times 10^{-2} + 2x)^2 = 1.8 \times 10^{-11}$
$x = 1.8 \times 10^{-7}\ M$

69. $$\frac{10\ \mathrm{mL} \times 20\ M\ NH_3}{20\ \mathrm{mL}} = 1.0\ M\ NH_3;$$

$$\frac{10\ \mathrm{mL} \times 1.0\ M\ NH_4Cl}{20\ \mathrm{mL}} = 0.50\ M\ NH_4Cl$$

$$\frac{10\ \mathrm{mL} \times 0.10\ M\ Mn(NO_3)_2}{20\ \mathrm{mL}} = 0.050\ M\ Mn(NO_3)_2$$

$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$
$x = [OH^-];\ [NH_4{}^+] = 0.50 + x;\ [NH_3] = 1.0 - x$

$$\frac{(0.50 + x)(x)}{(1.0 - x)} = 1.8 \times 10^{-5}$$

$x = 3.6 \times 10^{-5}\ M = [OH^-]$
$\underline{Mn(OH)_2} \rightleftharpoons Mn^{2+} + 2\,OH^-$
$K_{sp} = [Mn^{2+}]\,[OH^-]^2 = 2 \times 10^{-13}$
$(5.0 \times 10^{-2})\,(3.6 \times 10^{-5})^2 = 6.5 \times 10^{-11}$
$6.5 \times 10^{-11} > 2 \times 10^{-13}$
Therefore manganese(II) hydroxide will precipitate.

70. (a) $$0.04522\ \mathrm{L} \times 0.1054\ N\ \mathrm{NaOH} = \frac{\text{grams of acid}}{\text{equivalent weight}}$$

$$\text{Equivalent weight} = \frac{0.2145\ \mathrm{g}}{0.04522\ \mathrm{L} \times 0.1054\ N} =$$

45.00 g/equivalent

(b) $$\frac{3.15\ \text{g acid}}{100\ \mathrm{g}\ C_6H_6} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} = \frac{31.5\ \text{g acid}}{\text{kilograms of } C_6H_6}$$

$$m = \frac{31.5}{\text{kilograms} \times \text{molecular weight}};$$

$$\Delta T = K_b m = \frac{\text{grams of acid}}{\text{kilograms} \times \text{molecular weight}}$$

$$\text{Molecular weight} = \frac{2.53 \times 31.5}{0.886} = 89.9\ \mathrm{g}$$

$$0.9817\ \mathrm{g}\ CO_2 \times \frac{\dfrac{12.01\ \mathrm{g\ C}}{44.01\ \mathrm{g}\ CO_2}}{1.004\text{-g sample}} \times 100\% = 26.68\%\ \mathrm{C}$$

$$\frac{0.2007\ \mathrm{g}\ H_2O \times \dfrac{2.016\ \mathrm{gH}}{18.02\ \mathrm{g}\ H_2O}}{1.004\text{-g sample}} \times 100\% = 2.236\%\ \mathrm{H}$$

$$\frac{26.68\ \mathrm{g\ C}}{12.01\ \mathrm{g/mol}} = 2.22\ \mathrm{mol\ C};\ \frac{2.24\ \mathrm{g\ H}}{1.008\ \mathrm{g/mol}} = 2.22\ \mathrm{mol\ H};$$

$$\frac{71.08\ \mathrm{g\ O}}{16\ \mathrm{g/mol}} = 4.44$$

Empirical formula = CHO_2; molecular formula = $C_2H_2O_4$

71. $$0.5955\ \mathrm{g}\ CO_2 \times \frac{\dfrac{12.01\ \mathrm{g\ C}}{44.01\ \mathrm{g}\ CO_2}}{0.3045\text{-g sample}} \times 100\% = 53.37\%\ \mathrm{C}$$

$$0.4263\text{ g H}_2\text{O} \times \frac{\dfrac{2.016\text{ g H}}{18.02\text{ g H}_2\text{O}}}{0.3045\text{ g}} \times 100\% = 15.67\%\text{ H}$$

$$PV = nRT = \frac{g}{MW};\ g = \frac{PV(MW)}{RT}$$

$$\frac{\frac{750}{760} \times 0.043\text{ L} \times 28.02\text{ g/mol}}{0.0821\text{ L-atm/K-mol} \times 298\ K} \times \frac{1}{0.1562\text{ g}} \times 100\% =$$

31.11% N

$$\frac{53.37\text{ g C}}{12.01\text{ g/mol}} = 4.44 - \text{C} \qquad \frac{15.67\text{ g H}}{1.008\text{ g/mol}} = 15.55 - \text{H}$$

$$\frac{31.11\text{ g N}}{14.01\text{ g/mol}} = 2.22 - \text{N}$$

$$\frac{4.44}{2.22} = 2 - \text{C} \qquad \frac{15.55}{2.22} = 7 - \text{H} \qquad \frac{2.22}{2.22} = 1 - \text{N}$$

$$0.03806\text{ L} \times 0.1104\ M = \frac{0.1891\text{ g}}{\text{molecular weight}}$$

$$\text{or: molecular weight} = \frac{0.18912}{0.03806\text{ L} \times 0.1104\text{ M}} = 45\text{ g/mol}$$

molecular formula = C_2H_7N

72. (a) $\frac{x^2}{1.0 - x} = 1.8 \times 10^{-5}$ Thus, $x = 4.2 \times 10^{-3} = [OH^-]$

$pH = 14.00 - 2.37 = 11.63$

(b) $1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.44 + x)x}{0.11 - x}$

$x = 4.5 \times 10^{-6} = [OH^-]$; $pH = 14.00 - 5.35 = 8.65$

(c) $5.6 \times 10^{-10} = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{x^2}{0.5 - x}$

$x = 1.7 \times 10^{-5} = [H^+]$; Therefore, pH = 4.77

(d) pKa = pH + 1.00

Therefore, K_a for the indicator was between 2.2×10^{-8} and 2.2×10^{-10}

73. (a) $HA_c + H_2O \rightleftharpoons H_3O^+ + A_c^- \qquad K_a = 1.8 \times 10^{-5}$

$\frac{x^2}{0.1 - x} = 1.8 \times 10^{-5}$

$x = 1.3 \times 10^{-3}$

pH = 2.9

(b) mole HAc = 0.050 mol

after addition 0.010 mol HA
0.040 mol Ac^-

$\frac{[H_3O^+][Ac^-]}{[HAc]} = 1.8 \times 10^{-5}$

$\frac{[H_3O^+][0.04]}{[0.01]} = 1.8 \times 10^{-1}$

$[H_3O^+] = 4.5 \times 10^{-5}$

pH = 5.3

(c) At equivalence point there are 0.05 L × 0.1 mol/L = 0.005 mol of acetate ion in 0.10 L. Thus, $[Ac^-] = 0.005$ mol/0.1L = 0.05 M

$Ac^- + H_2O \rightleftharpoons HAc + OH^-$

$K_h = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

$\frac{x^2}{0.05} = 5.6 \times 10^{-10}$

$x = 5.3 \times 10^{-6}$

pOH = 5.3

pH = 8.7

(d) thymol blue or phenolphthalein

74. (a) 0.05 L × 0.1 mol/L =$\underline{0.005\text{ mol}}$

(b) $HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = 1.4 \times 10^{-4}$

$\frac{x^2}{0.1 - x} = 1.4 \times 10^{-4}$; $x = 3.74 \times 10^{-3}$

solve with quadratic formula because of significant figures and relatively high K_a

$x^2 + 1.4 \times 10^{-4} \times -1.4 \times 10^{-5} = 0$

$$x = \frac{-1.4 \times 10^{-4} \pm \sqrt{(1.4 + 10^{-4})2 + 4(1.4 + 10^{-5})}}{2}$$

$$= \frac{-1.4 \times 10^{-4} \pm 7.48 \times 10^{-3}}{2}$$

$= 3.67 \times 10^{-3}$

pH = 2.44

(c) at midpoint $[HA] = [A^-]$

$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$

$[H_3O^+] = K_a \frac{[HA]}{[A^-]} = K_a(1) = 1.4 \times 10^{-4}$

pH = 3.85

(d) 35 mL of 0.1 M OH^- = 0.035 × 0.1 mol/L = 0.0035 mol

$HA + OH^- \rightarrow A^- + H_2O$

So, 0.0035 mol A^- formed, leaving 0.0015 mol HA

Thus $[H_3O^+] = K_a \frac{[0.0015]}{[0.0035]} = 6 \times 10^{-5}$

pH = 4.22

(e) $A^- + H_2O \rightleftharpoons HA + OH^-$

$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.4 \times 10^{-4}} = 7.1 \times 10^{-11}$

$[A^-] = 0.05\ M$

$\frac{x^2}{0.05 - x} = 7.1 \times 10^{-11}$

$x = 1.9 \times 10^{-6} = [OH^-]$

pOH = 5.72

pH = 8.28

(f) pH = pK_a (HIn)

phenol red or thymol blue

(g) pH = pK_a (HIn) = 4.7; $[H_3O^+] = 2.0 \times 10^{-5}$

$\frac{[HA]}{[A^-]} = \frac{[H_3O^+]}{K_a}$ from before $= \frac{2.0 \times 10^{-5}}{1.4 \times 10^{-4}} = 0.143$

let x = moles A^-, moles HA at beginning = 0.005

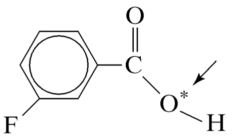
$\frac{0.005 - x}{x} = 0.143$; $x = 0.00437$ mol

$\frac{0.00437\text{ mol}}{0.1000\text{ mol/L}} = 0.0437\text{ L} = 43.7\text{ mL}$

(h) Two factors influence acidity: Bond energy and electron affinity

BE is the same in both molecules; therefore m is stronger than p due to EA.

EA in m is greater



because electronegative F is closer to oxygen.

75. 0.04090 $M \times$ 0.02562 L = 1.048×10^{-3} mol NaOH
1.048×10^{-3} mol NaOH $\times$ (1 mol acid/2 mol NaOH) = 5.240×10^{-4} mol
5.240×10^{-4} mol $\times$ 150.088 g/mol = 7.865×10^{-2} g tartaric acid
Acidity = (7.865×10^{-2} g tartaric acid/ 10.00 mL) $\times$ 100 mL = 0.7865 g per 100 mL of wine

76. (a) (50.0 mL)(0.125 M) = (x mL)(0.0250 M); $x = 250$
(b) $[NH_4^+]$ = 0.00625 mol/0.300 L = 0.0208 M

$$K_a = 5.6 \times 10^{-10} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{x^2}{0.0208 - x}$$

$x = [H_3O^+] = 3.4 \times 10^{-6}$
pH = 5.47
(c) An indicator that changes color at a pH of 5.5 is required. Methyl red changes over a range of 4.4 to 6.2, so it would be a suitable indicator.

77. # moles HA = 0.020 $M \times$ 0.1000 L $-$ 0.050 $M \times$ 0.0200 L = 0.0010 mol
moles NaA = # moles A^- = 0.050 $M \times$ 0.0200 L = 0.0010 mol
$[H^+] = 1.0 \times 10^{-6}$

$$K_h = \frac{(1.0 \times 10^{-6})(0.0010)}{(0.0010)} = 1.0 \times 10^{-6}$$

78. $NaAl(OH)_2CO_3 + 4\,H^+ \rightarrow Na^+ + Al^{3+} + 3\,H_2O + CO_2$
(0.25 M $-$ 0.10 M) $\times$ 0.0950 L = 0.014 mol of acid

$$\frac{1\ \text{mol NaAl(OH)}_2\text{CO}_3}{4\ \text{mol H}^+} \times 0.014\ \text{mol H}^+ \times 143.995\ \text{g/mol} =$$

0.50 g

79. $$\frac{3.5\ \text{g HCl}}{36.461\ \text{g/mol}} = 0.096\ \text{mol HCl}$$

$KOH(aq) + HCl(aq) \rightarrow H_2O(l) + NaCl(aq)$

$$\frac{0.096\ \text{mol KOH}}{0.125\ \text{mol/L}} = 0.77\ \text{L or 770 mL}$$

80. (a) The volume of 0.10 M HCl added to reach the equivalence point is

$$\frac{0.080\ M \times 25.0\ \text{mL}}{0.10\ M} = 20\ \text{mL}$$

The concentration of NH_4Cl at the equivalence point is

$$\frac{0.080\ M \times 25.0\ \text{mL}}{25\ \text{mL} + 20\ \text{mL}} = 0.044\ M$$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$$\frac{[NH_3][H_3O^+]}{[NH_4^+]} = K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$[H_3O^+]^2 = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} \times 4.4 \times 10^{-2}$$

$$= \frac{4.4 \times 10^{-16}}{1.8 \times 10^{-5}}$$

$[H_3O^+]^2 = 2.4 \times 10^{-11}$
$[H_3O^+] = 4.9 \times 10^{-6}$
pH = 6 $-$log 4.9 = 6 $-$ 0.69 = 5.31 methyl red

(b) The volume of 0.20 M KOH added to reach the equivalence point is

$$\frac{4.0 \times 0.10}{0.20} = 20.0\ \text{mL}$$

The concentration of KNO_2 at the equivalence point is

$$\frac{40.0 \times 0.10}{60} = 0.067\ M$$

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$$\frac{[HNO_2][OH^-]}{[NO_2^-]} = K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{4.6 \times 10^{-4}}$$

$$[OH^-]^2 = \frac{1 \times 10^{-14}}{4.6 \times 10^{-4}} \times 6.7 \times 10^{-2}$$

$$= \frac{6.7 \times 10^{-16}}{4.6 \times 10^{-4}}$$

$[OH^-]^2 = 1.46 \times 10^{-12}$
$[OH^-] = 1.2 \times 10^{-6}$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{1.2 \times 10^{-6}} \times 8.3 \times 10^{-9}$$

pH = 9 $-$ log 8.3 = 9 $-$ 0.92 = 8.08 cresol purple
(c) 7.0; phenol red

81. (a) At equivalency point solution contains $NH_2NH_3^+\ Cl^-$ salt:

$$[NH_2NH_3^+] = \frac{0.002500\ \text{mol}}{0.04500\ \text{L}} = 0.05556\ M$$

$NH_2NH_3^+ + H_2O \rightleftharpoons NH_2NH_2 + H_3O^+$

$$K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8} =$$

$$\frac{[NH_2NH_2][H_3O^+]}{[NH_2NH_3^+]} = \frac{x^2}{0.05556 - x}$$

assume $x \ll 0.05556$
$x = 2.36 \times 10^{-5}$ $[H_3O^+] = 2.36 \times 10^{-5}$
pH = 4.63

(b) $$1.0 \times 10^{-6} = \frac{[NH_2NH_3^+][^-OH]}{[NH_2NH_2]} = \frac{x^2}{0.1250 - x}$$

assume $x < 0.1250$
$x = 3.54 \times 10^{-4}$
$[^-OH] = 3.54 \times 10^{-4}$ pOH = 3.45 pH = 10.55
(c) $pK_a = -\log(1 \times 10^{-7}) = 7.0$
Range = 6–8
Not a useful indicator for this titration.

82. (a) $$\frac{0.4929\ \text{g KHSO}_4}{136.2\ \text{g/mol}} = 0.03513\ \text{L}$$

$M = 0.1029$

(b) $\dfrac{0.4929 \text{ g KHSO}_4}{136.2 \text{ g/mol}} \times = 0.07231 \text{ M}$

(c) Potassium sulfate produces a neutral solution, therefore the pH = 7.0.

83. $NaOH + \; HNO_3 \rightarrow NaNO_3 + H_2O$
$0.0050\ M\ NaNO_3 \quad pH = 7$; phenol red
$ClCH_2CO_2^- + H_2O = ClCH_2CO_2H + OH^-$
$x = [OH^-] = [ClCH_2CO_2H]; 0.0050 - x = [ClCH_2CO_2^-]$

$$\frac{x^2}{(0.0050 - x)} = \frac{K_w}{K_a} = 7.1 \times 10^{-12}$$

$x = 1.9 \times 10^{-7}\ M = [OH^-]$
$pOH = -\log(1.9 \times 10^{-7}) = 6.72; pH = 7.28$
Use phenol red
$O_2NC_6H_4O^- + H_2O \rightarrow O_2NC_6H_4OH + OH^-$
$x = [OH^-] = [O_2NC_6H_4OH]$ and $[O_2NC_6H_4O^-] = 0.0050 - x$

$$\frac{x^2}{0.0050 - x} = \frac{K_w}{K_a} = 1.4 \times 10^{-7}$$

$x = 2.6 \times 10^{-5}\ M$
$pOH = -\log(2.6 \times 10^{-5}) = 4.58; pH = 9.42$
Use phenolphthalein

84. (a) $ClC_6H_4CO_2H + \; H_2O \rightleftharpoons ClC_6H_4CO_2^- + H_3O^+$
$[H_3O^+] = 9.55 \times 10^{-4}\ M = [ClC_6H_4CO_2^-]$
$[ClC_6H_4CO_2H] = 1.00 \times 10^{-2} - 9.55 \times 10^{-4} = 9.0 \times 10^{-3}\ M$

$$K_a = \frac{(9.55 \times 10^{-4})(9.55 \times 10^{-4})}{9.0 \times 10^{-3}} = 1.0 \times 10^{-4}$$

(b) $x = [H_3O^+] = [ClC_6H_4CO_2^-]; \quad 1.0 - x = [ClC_6H_4CO_2H]$

$$\frac{x^2}{(1.0 - x)} = 1.0 \times 10^{-4}$$

$x = 1.0 \times 10^{-2}$
$pH = -\log(1.0 \times 10^{-2}) = 2.00$

(c) $ClC_6H_4CO_2^- + H_2O \rightleftharpoons ClC_6H_4CO_2H + OH^-$
$x = [ClC_6H_4CO_2^-] = [OH^-]; \quad 0.10 - x = [ClC_6H_4CO_2^-]$

$$\frac{x^2}{(0.10 - x)} = 1.0 \times 10^{-10}$$

$x = 3.2 \times 10^{-6}\ M = [OH^-]$
$pOH = -\log(3.2 \times 10^{-6}) = 5.49; pH = 8.51$

(d) $x = [H_3O^+]; [ClC_6H_4CO_2H] = 1.0 - x;$
$[ClC_6H_4CO_2^-] = 0.10 + x$

$$\frac{(x)(0.10 + x)}{(1.0 - x)} = 1.0 \times 10^{-4}$$

$x = 1.0 \times 10^{-3}\ M = [H_3O^+]$
$[ClC_6H_4CO_2H] = 1.0\ M; [ClC_6H_4CO_2^-] = 0.10\ M = [Na^+]$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} \times 1.0 \times 10^{-11}\ M; \quad [H_3O^+] = 1.0 \times 10^{-3}$$

85. (a) $ClC_6H_4CO_2^- + H_2O \rightleftharpoons ClC_6H_4CO_2H + OH^-$
$x = [OH^-] = [ClC_6H_4CO_2H]$ and $[ClC_6H_4CO_2^-] = 0.050 - x$

$$\frac{x^2}{(0.050 - x)} = 1.0 \times 10^{-10}$$

$x = 2.2 \times 10^{-6}\ M$
$[OH^-] = 2.2 \times 10^{-6}\ M = [ClC_6H_4CO_2H]$
$[ClC_6H_4CO_2^-] = 0.050\ M = [Na^+]$
$[H_3O^+] = = 4.5 \times 10^{-9}\ M$

(b) $pH = 14.00 - (-\log 2.2 \times 10^{-6}) = 8.34$

(c) cresol purple

(d) Middle of methyl orange endpoint = 3.75
$[H_3O^+] = 1.8 \times 10^{-4}$ at endpoint

$$K_a = \frac{[H_3O^+][ClC_6H_4CO_2^-]}{[ClC_6H_4CO_2H]} = 1.0 \times 10^{-4}$$

$$\text{and} = \frac{[ClC_6H_4CO_2^-]}{[ClC_6H_4CO_2H]} = \frac{1.0 \times 10^{-4}}{1.8 \times 10^{-4}} = 0.56$$

$$\frac{x}{0.1 - x} = 0.56$$

$x = 0.036\ M$
0.064 mol/L of $ClC_6H_4CO_2H$ remains

$$50 \text{ mL} \times \frac{0.036}{0.10} = 18 \text{ mL used;}$$

$$\frac{32}{50} \times 100\% = 64\% \text{ error}$$

86. (a) $2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^-; K = [NH_4^+]\,[NH_2^-]$

(b) $K_a = K_b = 2 \times 10^{-16}; K_b(NH_3) = 1.8 \times 10^{-5}$

$$K_a(NH_3) = \frac{K_w}{K_b(NH_2^-)} = \frac{10^{-14}}{10^{21}} = 10^{-35}$$

Thus, NH_3 is a stronger base by 10^{11} but a weaker acid by 10^{19}. Acidity of H_2O relative to NH_3 makes $K(NH_3) < K_w$.

(c) $NH_4^+; NH_2^-$
$pH(NH_3) = -\log[NH_4^+]; pOH(NH_3) = -\log[NH_2^-]$
$pH(NH_3)$ liquid $NH_3 = 16.35$
$[NH_4^+] = [NH_2^-]$
$[NH_4^+] = [NH_2^-] = 2 \times 10^{-33}$
$[NH_4^+] = 4.5 \times 10^{-17}; -\log[NH_4^+] = 16.35$

(d) less than 16.35

(e) With 1×10^{-3} M $NaNH_2$:

$$[NH_4^+] = \frac{2 \times 10^{-33}}{[NH_2^-]} = \frac{2 \times 10^{-33}}{1 \times 10^{-3}} = 2 \times 10^{-30}$$

$-\log[NH_4^+] = 29.7$
With $1 \times 10^{-3}\ M\ NH_4Cl$:
$[NH_4^+] = 1.0 \times 10^{-3}\ M$
$-\log(NH_4^+) = -\log(1 \times 10^{-3}) = 3.0$

(f) $NH_4Cl + NaNH_2 \rightarrow NaCl + 2\,NH_3$

87. (a) $CH_3CONH_2 + \; NH_3(l) \rightarrow CH_3CONH^- + NH_4^+$

$$K_a = \frac{[CH_3CONH^-][NH_4^+]}{[CH_3CONH_2]}$$

$pH(NH_3) = 3$

$$\frac{x^2}{0.1 - x} = 10^{-5}$$

$x = 10^{-3} = [NH_4^+]$

(b) $CH_3CONH^- + NH_3(l) \rightarrow CH_3CONH_2 + NH_2^-$

$$K_b = \frac{K(NH_3)}{K_a} = \frac{2 \times 10^{-33}}{1 \times 10^{-5}} = 2 \times 10^{-28}$$

$$\frac{x^2}{0.1 - x} = 2 \times 10^{-28}$$

$x^2 = 20 \times 10^{-30}$; $\times = 4.5 \times 10^{-15} = [NH_2^-]$

$pOH(NH_3) = 14.35$

$pH(NH_3) = 32.70 = 14.35 = 18.35$

88. 1. d 2. d 3. a 4. d 5. d 6. c 7. a 8. d

89. (a) FCH_2COOH
(b) KH_2PO_4
(c) $KHCO_3$
(d) $K_a\ 3 \times 10^{-8}$

$$K_w = \frac{10^{-14}}{10^{-8}} = 10^{-6}$$

(e) $K_{a_1} = 1 \times 10^{-2}$
$x \cong 1 \times 10^{-1}$
(f) $pOH = 2$; $OH^- = 10^{-2}$
$(10^{-2})(10^{-2}) = 10^{-4}$
(g) $K_a\ HF = 3 \times 10^{-4}$
$K_a\ HNO_2 = 5 \times 10^{-4}$
$K_b\ F^- > NO_2^-$
(h) $K_a\ HF = 3 \times 10^{-4}$
$K_a\ HNO_2 = 5 \times 10^{-4}$
$K_a\ HCN = 5 \times 10^{-10}$
Thus, CN^- is strongest base (the weaker the acid the stronger the conjugate base)
(i) NH_3/NH_4Cl
(j) 100 mL

CHAPTER 17

1. The reaction
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$
is also an electron-sharing reaction. More specifically, it is a base displacement reaction in which the hydroxide ion displaces ammonia from the adduct NH_4^+. Notice that in this analysis we think of the ammonium ion as an adduct ot NH_3 and H^+ and water as an adduct of OH^- and H^+.

2. (a) $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$
(b) $Cd^{2+} + 4\,NH_3 \rightleftharpoons Cd(NH_3)_4^{2+}$
(c) $Al(OH)_3 + 3\,H_3O^+ \rightleftharpoons Al^{3+} + 6\,H_2O$
(d) $Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-$
(e) $Zn^{2+} + 4\,OH^- \rightleftharpoons Zn(OH)_4^-$
(f) $Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+$

3. (a) $Sn^{2+}(aq) + 3\,HCl(aq) \leftrightharpoons SnCl_3^- + 3\,H^+$
geometry: trigonal pyramid
(b) $SnCl_4 + 2\,Cl^- \rightleftharpoons SnCl_6^{2-}$
geometry: octahedral
(c) $B(OH)_3 + 2\,H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$
geometry: tetrahedral
(d) $AlF_3 + F^- \rightleftharpoons AlF_4^-$
geometry: tetrahedral

4. Beryllium has only *s* and *p* orbitals in its valence shell and therefore can form bonds to only four oxygens. Aluminum also has *d* orbitals in its valence shell and can expand the octet.

5. Your electron-dot formulas should show formal charges of −1 on tin in $SnCl_5^-$ and 2− on tin in $SnCl_6^{2-}$. Generally, structures with lower formal charges are more stable.

6. (a) This result is an example of the salt effect. The mercuric nitrate in solution is an inert electrolyte.
(b) The ammonia reacts with the silver ions to form a complex in an equilibrium process that has a relatively large value for K (2×10^7).
$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+$
(c) Aluminum hydroxide is amphoteric and can accept another hydroxide ion to form a water-soluble anion. Magnesium hydroxide is not amphoteric.
(d) Sulfide is a "soft base" and therefore will bind more tightly with "soft cations" than with "hard cations." Zn^{2+} is the hardest of the three cations, therefore the sulfide will be bound least tightly and the salt will more readily dissociate in water. Cd^{2+} and Hg^{2+} are softer than Zn^{2+} and will bind more strongly with the sulfide and reduce the solubility. Because Hg^{2+} is the largest of the three cations, it is the softest and therefore binds sulfide most tightly.
(e) The central atom of both compounds is able to accept another pair of electrons to complete an octet so both are Lewis acids. Boron is a harder acid than aluminum; e.g., if one contrasts B^{3+} and Al^{3+}. Thus, if a proton is added to an oxygen atom of $B(OH)_3$ the water molecule formed is more tightly bound than a similar water molecule formed by the addition of a proton to $Al(OH)_3$.

7. $Cu(OH_2)_6^{2+} + 4\,Cl^- \rightleftharpoons CuCl_4^{2-} + 6\,H_2O$
When concentrated HCl is added to the aqueous solution of cupric ions, the equilibrium is shifted in favor of the copper chloride complex, which is yellow-green in color. When the solution is diluted with water, the equilibrium is shifted back in favor of the hydrated cupric ion, which is blue.
$Co(OH_2)_6^{2+} + 4\,Cl^- \rightleftharpoons CoCl_4^{2-} + 6\,H_2O$
Similarly, when concentrated HCl is added to the aqueous Co^{2+}, the equilibrium is shifted in favor of the tetrahedral cobalt chloride complex, which is blue. When this solution is diluted with water, the equilibrium is shifted back in favor of the aquo cobaltous ion, which is pink.

8. (a) $B(OH)_3 + 2\,H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$

(b) $$K_a = \frac{[B(OH)_4^-][H_3O^+]}{[B(OH)_3]} = 1.0 \times 10^{-9}$$

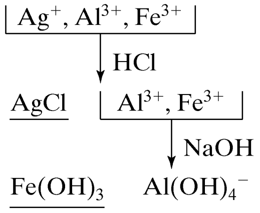
$[H_3O^+] = [B(OH)_4^-] = x$; $[B(OH)_3] = 0.010 - x$

$$\frac{x^2}{(0.010 - x)} = 1.0 \times 10^{-9}$$

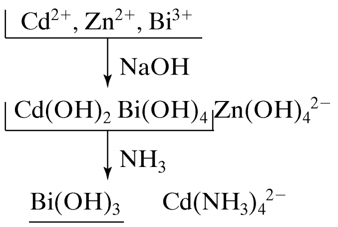
$x = 3.2 \times 10^{-6}$; pH = 5.49

9. (a) OH^-; $Al(OH)_3(s) + OH^- \rightarrow Al(OH)_4^-$
(b) NH_3; $AgCl(s) + 2\,NH_3 \rightarrow Ag(NH_3)_2^+(aq) + Cl^-$
(c) NH_3; $Ni(OH)_2 + 6NH_3 \rightarrow Ni(NH_3)_6^{2+}(aq) + 2\,OH^-$
(d) OH^-; $Zn(OH)_2 + 2\,OH^- \rightarrow Zn(OH)_4^{2-}(aq)$
(e) OH^-; $Mg^{2+}(aq) + 2\,OH^- \rightarrow Mg(OH)_2(s)$
$Sb^{3+}(aq) + 4OH^- \rightarrow Sb(OH)_4^{2-}(aq)$

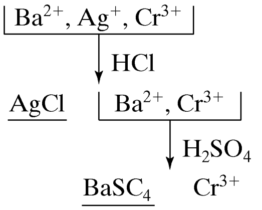
10. (a)



(b)



(c)



11. (a) Step 1: Add dilute NH_3 to precipitate $Cr(OH)_3$, $Fe(OH)_3$ and $Co(OH)_2$.
Step 2: Add excess concentrated NH_3 to dissolve Co^{2+} as $Co(NH_3)_6^{2+}$ and separate the solution from solid $Cr(OH)_3$ and $Fe(OH)_3$.
Step 3: Add excess 6 *M* NaOH to dissolve Cr^{3+} as $Cr(OH)_4^-$ and then separate it from the solid $Fe(OH)_3$.
(b) Step 1: Add $H_2SO_4(aq)$ in order to precipitate $SrSO_4$ from solution, and then separate the solution from this solid.
Step 2: Add excess $NH_3(aq)$ in order to precipitate $Al(OH)_3$ and form
$Zn(OH)_4^{2-}$ which will remain in solution. Next, separate the solution from the solid aluminum hydroxide.
(c) Step 1: Add $HCl(aq)$ to precipitate AgCl, and separate the solution from this solid salt.
Step 2: Add excess $NH_3(aq)$ to precipitate $Fe(OH)_3$ and to form $Cu(NH_3)_4^{2+}$ which will remain in solution. Separate the solution from the solid ferric hydroxide.
(d) Step 1: Add $HCl(aq)$ to precipitate AgCl, and separate the solution from this solid salt.
Step 2: Add excess 6 *M* NaOH to precipitate $Bi(OH)_3$ and $Ni(OH)_2$ and to form $Cr(OH)_4^-$ which will remain in solution. Separate the solution from the solid hydroxides.
Step 3: Add excess concentrated $NH_3(aq)$ to dissolve the Ni^{2+} as the complex $Ni(NH_3)_6^{2+}$ and leave the $Bi(OH)_3$ as the solid. Separate the solution, which contains the nickel, from the solid bismuth hydroxide.

12. The reaction is a base displacement. Trimethylamine (one base) is displacing the iodide in the adduct CH_3I. The product is the tetramethyl ammonium ion and because it is ionic it may be soluble in water.

13. $Pb^{2+} + 2\,I^- \rightarrow PbI_2$ $\quad Hg^{2+} + 2\,I^- \rightarrow HgI_2$
$PbI_2 + 2\,I^- \rightarrow PbI_4^{2-}$ $\quad HgI_2 + 2\,I^- \rightarrow HgI_4^{2-}$

14. $PbI_2(s) \rightarrow Pb^{2+} + 2\,I^-\ K_{sp} = 1 \times 10^{-8}$
$Pb^{2+} + 4\,I^- \rightarrow PbI_4^{2-}\ K_f = 2 \times 10^6$
add the two equation and multiply $K_{sp} \times K_f$
Thus, *K* for the reaction is 2×10^{-2}

15. $Cd^{2+} + 4\,CN^- \rightleftharpoons Cd(CN)_4^{2-}$

$$K = \frac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4} = 5.9 \times 10^{18}$$

$[Cd(CN)_4^{2-}] = 0.0010\ M$
$[CN^-] = x$
$[Cd^{2+}] = 1.0 \times 10^{-8}\ M$

$$K = \frac{[1.0 \times 10^{-3}]}{[1.0 \times 10^{-8}][x]^4}$$

$x = 3.\,6 \times 10^{-4}$
However, $4(1.0 \times 10^{-3})$ mol/L CN^- ions are needed to form the complex.
$4.0 \times 10^{-3} + 3.6 \times 10^{-4} = 4.4 \times 10^{-3}$ mol/L cyanide ion

16. $AgI + 2\,CN^- \rightleftharpoons Ag(CN)_2^- +^-$

$$K = \frac{[Ag(CN)_2^-][I^-]}{[CN^-]^2} = K_f K_{sp}$$

$$[I^-] = \frac{0.10\text{ mol}}{0.100\text{ L}} = 1.0\ M$$

$[Ag(CN)_2^-] = 1.0\ M$

$$\frac{(1)^2}{[CN^-]^2} = (1.0 \times 10^{20})(8 \times 10^{-17})$$

$[CN^-] = 1.1 \times 10^{-2}\ M$

$$\frac{0.2\text{ mol}}{100\text{ mL}} + \frac{0.0011\text{ mol}}{100\text{ mL}} = 0.20\text{ mol}$$

17. $Ni^{2+} + 6\,NH_3 \rightleftharpoons Ni(NH_3)^{2+}{}_6$

$$\text{moles of }Ni^{2+} = \frac{6.50\text{ g}}{129.61\text{ g/mol}} = 5.02 \times 10^{-2}\text{ mol}$$

$$K_{\text{formation}} = 2.0 \times 10^8 = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6}$$

K_f is large so assume all Ni^{2+} is complexed.
$[NH_3] = 5\text{ mol} - 6(5.02 \times 10^{-2}) = 4.7$

$$2.0 \times 10^8 = \frac{5.02 \times 10^{-2} - x}{(x)(4.7 + 6x)^6}$$

Assume $x \ll 5 \times 10^{-2}$
Then $x = 2.3 \times 10^{-14}$
$[Ni^{2+}] = 2.3 \times 10^{-14}\ M$

18. (a) $AgCl + 2\,NH_3 \rightleftharpoons Ag(NH_3)_{2-} + Cl^-$

$$\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]} = K_f K_{sp}$$

$$[Cl^-] = \frac{0.010\text{ mol}}{0.100\text{ L}} = 0.10\ M = [Ag(NH_3)_{2+}]$$

$$\left(\frac{(0.10)^2}{(1.8 \times 10^{-10})(1.6 \times 10^7)}\right)^{1/2} = [NH_3] = 1.9\ M$$

Need 0.19 mol + 2(0.010 mol) = 0.21 mol/100 mL; have 0.32 mol/100 mL
Yes, the AgCl will dissolve.

(b) $AgBr + 2\,NH_3 \rightleftharpoons Ag(NH_3)_{2+} + Br^-$

$$K_f K_{sp}\ \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2}$$

$$[Br^-] = \frac{0.010\text{ mol}}{0.100\text{ L}} = 0.10\ M = [Ag(NH_3)_{2+}]$$

$$\left(\frac{(0.10)^2}{(7.7 \times 10^{-13})(1.6 \times 10^7)}\right)^{1/2} = [NH_3] = 28.5\ M$$

No, AgBr will not be dissolved.

19. $\underline{AgCl} \rightleftharpoons Ag^+ + Cl^-$ $\quad K_{sp} = [Ag^+][Cl^-]$

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3 \quad K_{inst} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

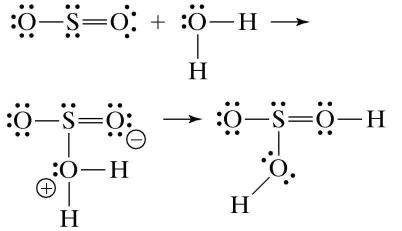
$$K = \frac{K_{sp}}{K_{inst}} = \frac{1.8 \times 10^{-10}}{6.2 \times 10^{-8}} = 2.9 \times 10^{-3}$$

20. (a) The mechanism of the S_N2 reaction involves a concerted (i.e., one step) process between the attacking nucleophile and the substrate that bears the leaving group. The S_N1 reaction involves a step-wise mechanism in which the substrate bearing the leaving group loses the leaving group to form a carbocation, a reactive intermediate, that subsequently is attacked by the nucleophile in the second step of the S_N1 reaction.

(b) Lewis acids and bases may be categorized into groups based upon their structures. Hard acids have small acceptor atoms or relatively high positive charge, whereas soft acids have large acceptor atoms or relatively low positive charge. Similarly, hard bases have donor atoms that are highly electronegative and are not easily polarized, whereas soft bases have donor atoms that are less negative and more polarizable. Generally, hard acids prefer to bind to hard bases, and soft acids prefer to bind to hard bases.

21. (a) addition (b) base-displacement
(c) addition (d) acid-displacement

22. (a) $Al(OH)_3 + 3\,H_3O^+ \rightleftharpoons Al^{3+} + 6\,H_2O$
$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-$
(b) $Pb^{2+} + 2\,Cl^- \rightleftharpoons PbCl_2$
$\underline{PbCl_2} + 2\,Cl^- \rightleftharpoons PbCl_4^{2-}$
(c) $CF_4 + F^- \rightarrow$ no reaction
$SiF_4 + 2\,F^- \rightarrow SiF_6^{2-}$
(d)



23. The equilibrium constant is large because hydroxide ion is a harder base than ammonia and displaces ammonia from the adduct ammonium ion and bonds to the hard acid H^+.

24. Yes, the zinc ion is smaller than the cadmium ion and therefore harder. The hard base, hydroxide ion, is more likely to react with the harder acid.

25. HgS because Hg^{2+} is the softest acid (all three cations are in the same group) and S^{2-} is a soft base.

26. This is an acid displacement reaction with H^+ displacing Zn^{2+} in the adduct containing the hard base NH_3. Because H^+ is very hard it is safe to conclude that NH_3 prefers to combine with H^+ in the ammonium ion. Thus, the equilibrium constant should be large.

27. (a) less than 1 (b) greater than 1
(c) greater than 1 (d) less than 1
(e) greater than 1

28. (a) $K < 1$; boron trifluoride, a hard acid, will react to a greater extent with the trimethylamine, which is a harder base than trimethylphosphine.

(b) $K > 1$; trimethylamine is a stronger base than dimethyl ether, which is less willing to share electrons because oxygen is more electronegative than nitrogen.

(c) $K < 1$; boron trifluoride is a stronger acid than trimethylborane and will react to a greater extent with the trimethylamine to form an adduct. Boron trifluoride is a stronger acid than trimethylborane because the fluorine atoms withdraw more electron density from the boron atom.

(d) $K < 1$; the proton is a hard acid and will therefore react to a greater extent with the harder base, which is water.

(e) $K > 1$; ammonia is a stronger base than water.

(f) $K > 1$; the cadmium ion is a soft Lewis acid and should react to a greater extent with the softer base, the iodide ion. (The formation constant for the chloride complex is about 10^3, but the formation constant for the iodide complex is about 10^6.)

(g) $K < 1$; boron and fluoride are both small and hard, but the iodide ion is larger and soft.

(h) $K < 1$; cadmium does not form an amphoteric hydroxide, but zinc does form such a complex.

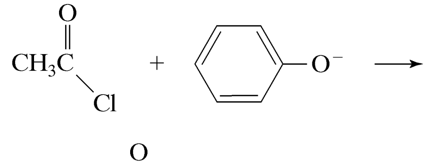
29. The equilibrium constant should be less than unity because the formation of LiF from lithium, a hard Lewis acid, and fluoride, is favorable. Also, the soft Lewis acid and base, the cesium ion and iodide ion, respectively, should favor the formation of CsI. $\Delta H° \sim 147$ kJ and because $\Delta H°$ is a good approximation for $\Delta G°$, $K \sim 10^{-26}$.

30. The enthalpy changes suggest that the second reaction is less favorable than the first reaction. Therefore, the trimethylcarbonium ion is less reactive than the methyl cation towards H_2S, which is a softer base than water, and this result indicates that the trimethylcarbonium ion is harder than the methyl cation.

31. Because the proton is a hard acid, hydrogen-bonding should be better with hard bases. This conclusion is supported by the fact that water, alcohols, ammonia, and amines all participate in hydrogen-bonding. Conversely, thiols (RSH) and phosphines (R_3P), which are soft bases, do not form hydrogen bonds.

32. (a) oxide (b) oxide (c) oxide (d) sulfide
(e) oxide (f) sulfide

33. (a) Products:
$CH_3OCH_3 + {}^-I$
(b) Products:
$CH_3CH_2NH_2 + Br^-$
(c)



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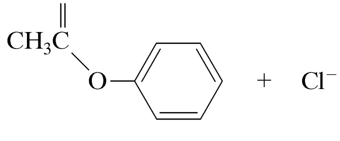
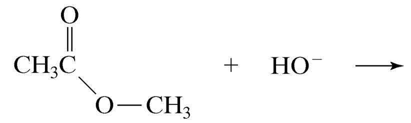


(d)



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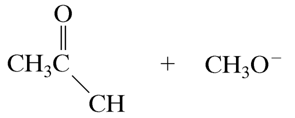
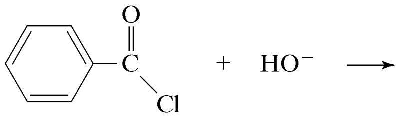


(e)



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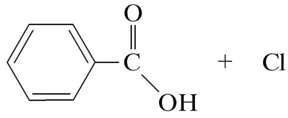
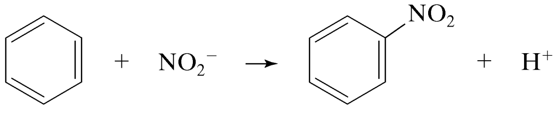


34. (a) $Pb(H_2O)_4^{2+} + H_2O \rightleftharpoons Pb(H_2O)_3(OH)^+ + H_3O^+$
(b) $Pb(H_2O)_4^{2+} + 2\,CH_3CO_2^- \rightleftharpoons Pb(CH_3CO_2)_2 + 4\,H_2O$
(c) $Zn^{2+} + 4\,H_2O \rightleftharpoons Zn(H_2O)_4^{2+}$
(d) $Zn(OH)_2 + 2\,H_3O^+ \rightleftharpoons Zn^{2+} + 4\,H_2O$
(e) $Zn(OH)_2 + 2\,OH^- \rightleftharpoons Zn(OH)_4^{2-}$
(f) $NH_3 + BF_3 \rightleftharpoons F_3B{-}NH_3$
(g) $4\,NH_3 + Cu(H_2O)_4^{2+} \rightleftharpoons 4\,H_2O + Cu(NH_3)_4^{2+}$
(h) $Cd(NH_3)_4^{2+} + 4\,H^+ \rightleftharpoons Cd^{2+} + 4\,NH_4^+$
(i) $CO_2 + OH^- \rightleftharpoons HCO_3^-$
(j) $H_2C{=}O + CH_3^- \rightarrow CH_3CH_2O^-$
(k) $SO_2 + OH^- \rightleftharpoons HSO_3^-$
(l) $CH_3Br + CH_3O^- \rightarrow CH_3OCH_3 + Br^-$
(m) $CH_3CO_2CH_3 + OH^- \rightleftharpoons CH_3CO_2H + CH_3O^-$
(n)

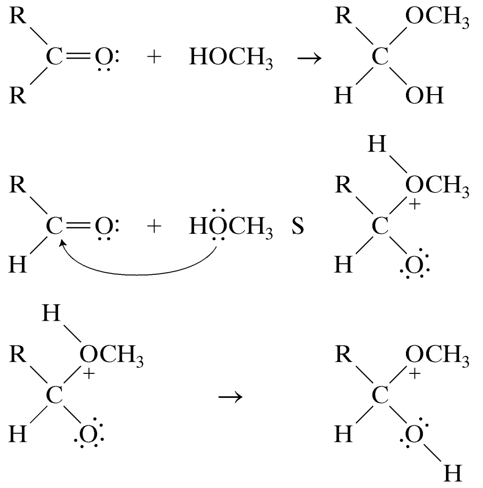


36. (a) In an addition reaction a Lewis acid adds directly to a base to form an adduct, but in a displacement reaction an acid or base reacts with a substrate (an adduct) only as it displaces a "leaving group" originally bonded to the substrate structure.
(b) In a base-displacement reaction a Lewis base reacts with an acid-base adduct to liberate the base of the adduct and to form a new adduct with the acid. In an acid-displacement a Lewis acid reacts with an adduct to form a bond with the base of the adduct and to liberate the acid that was originally part of adduct.
(c) Amphiprotic compounds may act as a Brønsted-Lowry acid and base, but an amphoteric compound acts as Lewis acid and a Brønsted-Lowry acid.
(d) As an acid: $Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-$
As a base: $Al(OH)_3 + 3\,H_3O^+ \rightleftharpoons Al^{3+} + 6\,H_2O$
(e) Basicity refers to the extent of an acid-base reaction, but nucleophilicity refers to the rate of the acid-base reaction.
(f) A hard acid has high charge and small size (low polarizability) whereas a soft acid has relatively low charge and a large size (great polarizability).
(g) A nucleophile is a "nucleus loving" species whereas an electrophile is an "electron loving" species.
(h) An S_N1 mechanism is one that requires two or more steps for a nucleophile to attack a substrate and accomplish a substitution, whereas an S_N2 mechanism is one that requires a single (concerted) step to accomplish the substitution of the nucleophile for the "leaving group."

37. (a) F^-, (b) OH^-, (c) NH_2^-

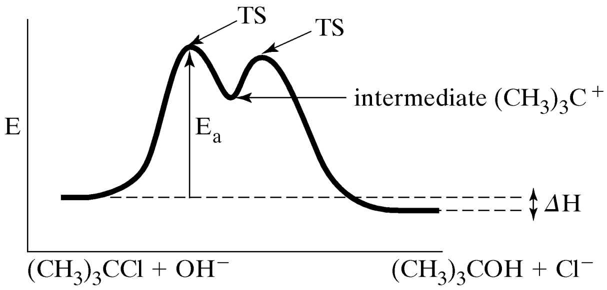
38. (1), (a); (2), (b); (3), (b); (4), (a)

39.

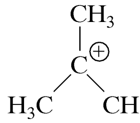


40. (a) A (b) B (c) B (d) A (e) B

41.



42.



trigonal plane
sp^2 hybrid
< = 120°

43.

(a) 6	(b) 5×10^{-9}
(c) hard	(d) adduct
(e) base	(f) amphoteric
(g) Cl^- Pb^{2+}	(h) low large
(i) electrophilic	(j) CH_4

CHAPTER 18

1. (a) −2 (b) +7 (c) +4 (d) +4
(e) +8 (f) +7 (g) +2 (h) +6

2.

(a) Ag^{+1}; N^{+5}; O^{-2}	(b) Cs^{+1}; F^{-1}
(c) S^{+6}; O^{-2}	(d) C^{-3}; H^{+1}
(e) S^{+6}; O^{-2}	(f) C°; H^{+1}; O^{-2}
(g) Mg^{+2}; P^{+5}; O^{-2}	(h) As°
(i) K^{+1}; Br^{+5}; O^{-2}	(j) Hg^{+1}; Cl^{-1}
(k) Cr^{+3}; O^{-2}; H^{+1}	(l) Ca^{+2}; H^{-1}
(m) U^{+6}; O^{-2}	(n) H^{+1}; As^{+3}; O^{-2}

(o) Na^{+1}; S^{+2}; O^{-2} (p) S^{+7}; O^{-2}
(q) Ce^{+3}; N^{+5}; O^{-2} (r) Sb^{+3}; S^{-2}

3. (a) oxidant SO_2; reductant S
(b) oxidant CuO; reductant NH_3
(c) oxidant NO_2; reductant NO_2
(d) oxidant $Hg_2{}^{2+}$; reductant $Hg_2{}^{2+}$
(e) oxidant $Ca_3(PO_4)_2$; reductant C

4.

oxidant	reductant	oxidant	reductant
(a) HNO_3	CuS	(e) none	none
(b) $K_2Cr_2O_7$	$SnCl_2$	(f) $BaSO_4$	C
(c) $CuSO_4$	KI	(g) $KClO_3$	$KClO_3$
(d) Cl_2	Cl_2		

5. (a)

$$\begin{array}{r} C_3H_6O + 5\,H_2O \longrightarrow 3\,CO_2 + 16\,H^+ + 16\,e^- \\ Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \\ \hline 3\,C_3H_6O + 64\,H^+ + 8\,Cr_2O_7{}^{2-} \longrightarrow \\ 9\,CO_2 + 16\,Cr^{3+} + 41\,H_2O \end{array}$$

(b)

$$\begin{array}{r} 2\,IO_3{}^- + 12\,H^+ + 10\,e^- \longrightarrow I_2 + 6\,H_2O \\ 2\,I^- \longrightarrow I_2 + 2\,e^- \\ \hline IO_3{}^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O \end{array}$$

(c)

$$\begin{array}{r} Br_2 + 12\,OH^- \longrightarrow 2\,BrO_3{}^- + 6\,H_2O + 10\,e^- \\ Br_2 + 2\,e^- \longrightarrow 2\,Br^- \\ \hline 3\,Br_2 + 6\,OH^- \longrightarrow 5\,Br^- + BrO_3{}^- + 3\,H_2O \end{array}$$

(d)

$$\begin{array}{r} Zn \longrightarrow Zn^{2+} + 2\,e^- \\ NO_3{}^- + 10\,H^+ + 8\,e^- \longrightarrow NH_4{}^+ + 3\,H_2O \\ \hline 4\,Zn + 10\,H^+ + NO_3{}^- \longrightarrow 4\,Zn^{2+} + NH_4{}^+ + 3\,H_2O \end{array}$$

(e)

$$\begin{array}{r} \underline{FeS_2} + 8\,H_2O \longrightarrow Fe^{3+} + 2\,SO_4{}^{2-} + 16\,H^+ + 15\,e^- \\ NO_3{}^- + 2\,H^+ + e^- \longrightarrow NO_2 + H_2O \\ \hline \underline{FeS_2} + 14\,H^+ + 15\,NO_3{}^- \longrightarrow \\ Fe^{3+} + 2\,SO_4{}^{2-} + 15\,NO_2 + 7\,H_2O \end{array}$$

6. (a)

$$\begin{array}{r} C_2H_4 + 4\,H_2O \longrightarrow 2\,CO_2 + 12\,H^+ + 12\,e^- \\ MnO_4{}^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O \\ \hline 5\,C_2H_4 + 12\,MnO_4{}^- + 36\,H^+ \longrightarrow \\ 12\,Mn^{2+} + 10\,CO_2 + 28\,H_2O \end{array}$$

(b)

$$\begin{array}{r} ClO_3{}^- + 6\,H^+ + 6\,e^- \longrightarrow Cl^- + 3\,H_2O \\ HNO_2 + H_2O \longrightarrow NO_3{}^- + 3\,H^+ + 2\,e^- \\ \hline ClO_3{}^- + 3\,HNO_2 \longrightarrow Cl^- + 3\,NO_3{}^- + 3\,H^+ \end{array}$$

7. (a)

$$\begin{array}{r} Zn + 4\,OH^- \longrightarrow Zn(OH)_4{}^{2-} + 2\,e^- \\ NO_3{}^- + 6\,H_2O + 8\,e^- \longrightarrow NH_3 + 9\,OH^- \\ \hline 4\,Zn + NO_3{}^- + 6\,H_2O + 7\,OH^- \longrightarrow 4\,Zn(OH)_4{}^{2-} + NH_3 \end{array}$$

(b)

$$\begin{array}{r} CrO_4{}^{2-} + 4\,H_2O + 3\,e^- \longrightarrow \underline{Cr(OH)_3} + 5\,OH^- \\ S^{2-} \longrightarrow \underline{S + 2\,e^-} \\ \hline 2\,CrO_4{}^{2-} + 3\,S^{2-} + 8\,H_2O \longrightarrow \underline{Cr(OH)_3} + 3\,S + 10\,OH^- \end{array}$$

8. (a) $2\,KNO_3 \rightarrow 2\,KNO_2 + O_2$
(b) $2\,Na + 2\,H_2O \rightarrow 2\,NaOH + H_2$
(c) $3\,Fe + 4\,H_2O \rightarrow Fe_3O_4 + 4\,H_2$
(d) $C_2H_5OH + 3\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$
(e) $Fe_3O_4 + 4\,H_2 \rightarrow 3\,Fe + 4\,H_2O$
(f) $CO_2 + NaOH \rightarrow NaHCO_3$
(g) $MnO_2 + 4\,HCl \rightarrow 2\,H_2O + MnCl_2 + Cl_2$
(h) $Zn + 2\,KOH \rightarrow K_2ZnO_2 + H_2$
(i) $Cu + 2\,H_2SO_4 \rightarrow 2\,H_2O + SO_2 + CuSO_4$
(j) $Al(NO_3)_3 + 3\,NH_3 + 3\,H_2O \rightarrow Al(OH)_3 + 3\,NH_4NO_3$
(k) $Al(NO_3)_3 + 4\,NaOH \rightarrow NaAlO_2 + 3\,NaNO_3 + 2\,H_2O$

9. (a) oxidation: $2\,S_2O_3{}^{2-} \rightarrow S_4O_6{}^{2-} + 2\,e^-$
reduction: $I_2 + 2\,e^- \rightarrow 2\,I^-$
balanced: $2\,S_2O_3{}^{2-} + I_2 \rightarrow S_4O_6{}^{2-} + 2\,I^-$
(b) oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$
reduction: $Ce^{4+} + e^- \rightarrow Ce^{3+}$
balanced: $Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$
(c) oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$
reduction: $NO_3{}^- + 4\,H^+ + 3\,e^- \rightarrow NO + 2\,H_2O$
balanced: $3\,Fe^{2+} + NO_3{}^- + 4\,H^+ \rightarrow 3\,Fe^{3+} + NO + 2\,H_2O$
(d) oxidation: $\underline{Ag_2S} \rightarrow 2\,Ag^+ + S + 2\,e^-$
reduction: $NO_3{}^- + 4\,H^+ + 3\,e^- \rightarrow NO + 2\,H_2O$
balanced: $3\,\underline{Ag_2S} + 2\,NO_3{}^- + 8\,H^+ \rightarrow 6\,Ag^+ + 3\,S + 2NO + 4H_2O$
(e) oxidation: $H_2S \rightarrow 2\,H^+ + S + 2\,e^-$
reduction: $Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$
balanced: $3\,H_2S + Cr_2O_7{}^{2-} + 8\,H^+ \rightarrow 3\,S + 2\,Cr^{3+} + 7\,H_2O$
(f) oxidation: $Cl_2 + 12\,OH^- \rightarrow 2\,ClO_3{}^- + 6\,H_2O + 10\,e^-$
reduction: $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$
balanced: $6\,Cl_2 + 12\,OH^- \rightarrow 10\,Cl^- + 2\,ClO_3{}^- + 6\,H_2O$
(g) oxidation: $\underline{Fe(OH)_2} + OH^- \rightarrow \underline{Fe(OH)_3} + e^-$
reduction: $O_2{}^{2-} + 2\,H_2O + 2\,e^- \rightarrow 4\,OH^-$
balanced: $2\,\underline{Fe(OH)_2} + O_2{}^{2-} + 2\,H_2O \rightarrow 2\,\underline{Fe(OH)_3} + 2\,OH^-$
(h) oxidation: $\underline{Bi_2S_3} \rightarrow 2\,Bi^{3+} + 3\,S + 6\,e^-$
reduction: $NO_3{}^- + 4\,H^+ + 3\,e^- \rightarrow NO + 2\,H_2O$
balanced: $\underline{Bi_2S_3} + 2\,NO_3{}^- + 8\,H^+ \rightarrow 2\,Bi^{3+} + 3\,S + 2\,NO + 4\,H_2O$
(i) oxidation: $Zn \rightarrow Zn^{2+} + 2\,e^-$
reduction: $H_3AsO_4 + 8\,H^+ + 8\,e^- \rightarrow AsH_3 + 4\,H_2O$
balanced: $4\,Zn + H_3AsO_4 + 8\,H^+ \rightarrow 4\,Zn^{2+} + AsH_3 + 4\,H_2O$
(j) oxidation: $\underline{CrI_3} + 32\,OH^- \rightarrow CrO_4{}^{2-} + 3\,IO_4{}^- + 16\,H_2O + 27\,e^-$
reduction: $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$
balanced: $2\,\underline{CrI_3} + 64\,OH^- + 27\,Cl_2 \rightarrow 2\,CrO_4{}^{2-} + 6\,IO_4{}^- + 32\,H_2O + 54\,Cl^-$

10. (a) $3\,Fe^{2+} + NO_3{}^- + 4\,H^+ \rightarrow 3\,Fe^{3+} + NO + 2\,H_2O$
(b) $2\,Cr^{3+} + 6\,ClO_3{}^- + H_2O \rightarrow Cr_2O_7{}^{2-} + 6\,ClO_2 + 2\,H^+$
(c) $2\,MnO_4{}^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$
(d) $2\,IO_3{}^- + 10\,I^- + 12\,H^+ \rightarrow 6\,I_2 + 6\,H_2O$
(e) $2\,Fe^{3+} + SO_3{}^{2-} + H_2O \rightarrow 2\,Fe^{2+} + SO_4{}^{2-} + 2\,H^+$
(f) $3\,\underline{Sb_2S_3} + 10\,NO_3{}^- + 10\,H^+ \rightarrow 3\,\underline{Sb_2O_5} + 9\,S + 10\,NO + 5\,H_2O$
(g) $3\,\underline{As_2S_3} + 28\,NO_3{}^- + 10\,H^+ + 4\,H_2O \rightarrow 9\,SO_4{}^{2-} + 6\,H_3AsO_4 + 28\,NO$

11. (a) $Cl_2 + 2\,OH^- \rightarrow Cl^- + ClO^- + H_2O$
(b) $4\,\underline{Co(OH)_2} + O_2 + 2\,H_2O \rightarrow 4\,\underline{Co(OH)_3}$
(c) $2\,Al + 2\,OH^- + 6\,H_2O \rightarrow 2\,Al(OH)_4{}^- + 3\,H_2$
(d) $2\,MnO_4{}^- + 7\,S^{2-} + 8\,H_2O \rightarrow 2\,\underline{MnS} + 5\,S + 16\,OH^-$
(e) $NO_2{}^- + 2\,Al + H_2O + OH^- \rightarrow NH_3 + 2\,AlO_2{}^-$

12. (a) $14\,H^+ + Cr_2O_7{}^{2-} + 6\,Cl^- \rightarrow 2\,Cr^{3+} + 3\,Cl_2 + 7\,H_2O$
(b) Na^+ and $NO_3{}^-$
(c) $0.575\text{ L} \times 6.00\text{ mol/L} = 3.45\text{ mol }H^+$

$$\frac{13\text{ g}}{261.967\text{ g/mol}} = 0.519\text{ mol }Na_2Cr_2O_7$$

$$\frac{3.45 \text{ mol}}{0.519 \text{ mol}} = 6.65 < 14$$

Therefore, HNO_3 is the limiting reagent for this reaction.

(d) $\dfrac{3 \text{ mol } Cl_2}{14 \text{ mol } HNO_3} \times 3.45 \text{ mol } HNO_3 \times 0.800 = 0.591$ mol Cl_2

$$\frac{591 \text{ mol } Cl_2 \times 0.08205 \text{ L-atm/mol-K} \times 318\ K}{0.980 \text{ atm}} =$$

15.7 L of Cl_2

13. (a) $6\,HCl(aq) + 2\,KMnO_4(aq) + 5\,H_2O_2(l) \rightarrow$
$2\,MnCl_2(aq) + 5\,O_2(g) + 8\,H_2O(g) + 2\,KCl(aq)$
(b) $6\,H^+ + 2\,MnO_4^- + 5\,H_2O_2 \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$
(c) $0.100 \text{ L} \times 6.0 \text{ mol/L} = 0.60 \text{ mol HCl}$

$$\frac{36.0 \text{ g}}{158.034 \text{ g/mol}} = 0.228 \text{ mol } KMnO_4$$

$$\frac{0.60 \text{ mol}}{0.228 \text{ mol}} = 2.6 < 3$$

Therefore, HCl is the limiting reagent for this reaction.

$$\frac{5 \text{ mol } O_2}{6 \text{ mol HCl}} \times 0.60 \text{ mol HCl} = 0.50 \text{ mol } O_2$$

$$\frac{0.50 \text{ mol } O_2 \times 0.08205 \text{ L-atm/mol-K} \times 298\ K}{1.00 \text{ atm}} =$$

12.1 L of O_2

14. (a) $PbO_2(s) + Pb(s) + 2\,H_2SO_4(aq) \rightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$
(b) $\dfrac{5.30 \text{ L} \times 15.5\ M}{18.0\ M} = 4.56 \text{ L}$

15. $6\,Mn^{2+} + 5\,O_3 + 9\,H_2O \rightarrow 6\,MnO_4^- + 18\,H^+$

16. $2\,CrO_4^{2-} + 2\,H_2O + 3\,H_2S \rightarrow 2\,\underline{Cr(OH)_3} + 4\,OH^- + 3\,S$

17. $N_2H_4 + 2\,O_2 \rightarrow N_2 + 2\,H_2O_2$

18. (a) $Pt / Br^-, Br_2 // H_2O_2, H^+ / Pt$
(b) $Cd / Cd^{2+} // Pb^{2+} / Pb$
(c) $Cu / Cu^{2+} // Fe^{2+}, Fe^{3+} / Pt$
(d) $Zn / Zn^{2+} // H_2, H^+ / Pt$
(e) $Hg / Hg^{2+} // Ce^{4+}, Ce^{3+} / Pt$
(f) $Pt / I^-, I_2 // ClO_3^-, Cl^-, H^+ / Pt$

19. (a) $Cd / Cd^{2+} // Ni^{2+} / Ni$
anode: $Cd \rightarrow Cd^{2+} + 2\,e^-$
cathode: $Ni^{2+} + 2\,e^- \rightarrow Ni$
overall: $Cd + Ni^{2+} \rightarrow Cd^{2+} + Ni$
(b) $Cu / Cu^{2+} // NO_3^-, H^+, NO / Pt$
anode: $Cu \rightarrow Cu^{2+} + 2\,e^-$
cathode: $NO_3^- + 4\,H^+ + 3\,e^- \rightarrow NO + 2\,H_2O$
overall: $3\,Cu + 2\,NO_3^- + 8\,H^+ \rightarrow Cu^{2+} + 2\,NO + 4\,H_2O$
(c) $Pt / I^-, I_2 // Fe^{3+}, Fe^{2+} / Pt$
anode: $2\,I^- \rightarrow I_2 + 2\,e^-$
cathode: $Fe^{3+} + e^- \rightarrow Fe^{2+}$
overall: $2\,I^- + 2\,Fe^{3+} \rightarrow I_2 + 2\,Fe^{2+}$
(d) Co / Co^{2+} (0.01 M) $// Co^{2+} / Co$
anode: $Co \rightarrow Co^{2+} + 2\,e^-$
cathode: $Co^{2+} + 2\,e^- \rightarrow Co$
overall: $Co^{2+} + Co \rightarrow Co + Co^{2+}$
(e) $Pt / H_3PO_3, H_3PO_4, H^+ // ClO_3^-, Cl^-, H^+ / Pt$
anode: $H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2\,H^+ + 2\,e^-$
cathode: $ClO_3^- + 6\,H^+ + 6\,e^- \rightarrow Cl^- + 3\,H_2O$
overall: $3\,H_3PO_3 + ClO_3^- \rightarrow 3\,H_3PO_4 + Cl^-$

20. $Li^+, Ni^{2+}, Sn^{2+}, Co^{3+}$

21. $Ca^\circ, Sn^{2+}, Cu^\circ, Fe^{2+}$

22. (a) No reaction
(b) $3\,NO_3^- + 2\,Bi^\circ + 5\,H^+ \rightarrow 3\,HNO_2 + 2\,BiO^+ + H_2$
(c) No reaction

23. (a) Ag° must be oxidized and Fe^{3+} reduced. The overall reaction would be:
$Ag^\circ + Fe^{3+} \rightarrow Ag^+ + Fe^{2+}$
$E^\circ_{rx} = E^\circ_{Fe} - E^\circ_{ox} = 0.77\text{ V} - 0.80\text{ V} = -0.03\text{ V}$
The negative E°_{rx} indicates the reaction as written is not spontaneous.
(b) $3\,Co^{3+} + Al^\circ \rightarrow 3\,Co^{2+} + Al^{3+}$

24. (a) $0.34 - (-0.41) = 0.75$ V
(b) $1.06 - (-0.44) = 1.50$ V
(c) $1.33 - 0.80 = 0.53$ V
(d) $1.82 - (-0.28) = 2.10$ V

26. <u>Spontaneous Reaction</u>
$Cl_2 + 2\,I^- \rightarrow 2\,Cl^- + I_2$
$2\,H^+ + Zn \rightarrow H_2 + Zn^{2+}$
$3\,Fe^{3+} + Al \rightarrow 3Fe^{2+} + Al^{3+}$
$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
$2\,MnO_4^- + 16\,H^+ + 5\,Fe \rightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,Fe^{2+}$

<u>NonSpontaneous reactions</u>
$Ba^{2+} + 2\,F^- \rightarrow Ba + F_2$
$Ni^{2+} + Sn \rightarrow Ni + Sn^{2+}$
$3\,Fe^{2+} \rightarrow Fe + 2\,Fe^{3+}$
$Na^+ + Ag \rightarrow Na + Ag^+$
$Mg^{2+} + Cu \rightarrow Mg + Cu^{2+}$

27. $Sn^{2+} + 2\,e^- \rightarrow Sn \qquad E^\circ = -0.14$ V
$Sn^{4+} + 2\,e^- \rightarrow Sn^{2+} \qquad E^\circ = +0.15$ V
Therefore, $Sn + Sn^{4+} \rightarrow 2\,Sn^{2+}$ occurs spontaneously and any Sn^{4+} formed is returned to Sn^{2+}.

28. Yes. The overall reaction would be:
Red: $Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^\circ = 0.77$ V
Oxid: $Fe^\circ \rightarrow Fe^{2+} + 2e^- \qquad E^\circ = -\ 0.44$ V
Overall: $2\,Fe^{3+} + Fe^\circ \rightarrow 3\,Fe^{2+} \qquad E^\circ_{rx}\!: = 1.21$ V
E° for the reaction is positive and the reaction is spontaneous.

29. $BaSO_3 + 2\,H^+ \rightarrow Ba^{2+} + H_2SO_3$
Air oxidation on standing;

$$\begin{array}{l} 2(H_2SO_3 + H_2O \longrightarrow SO_4^{2-} + 4\,H^+ + 2\,e^-) \\ O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2H_2O \\ \hline 2\,H_2SO_3 + O_2 \longrightarrow 2\,SO_4^{2-} + 4\,H^+ \\ SO_4^{2-} + Ba^{2+} \longrightarrow \underline{BaSO_4} \end{array}$$

30. Add each free metal to the solutions of the compounds and observe which free metals are produced. For example:

$$Mg + Zn^{2+} \longrightarrow Zn + Mg^{2+}$$

but

$$Ag + Zn^{2+} \longrightarrow \text{no reaction}$$

31. Standard electrode potentials indicate that MnO_4^- will oxidize HCl but will not oxidize H_2SO_4.

32. Zinc is more easily oxidized than iron. See $E°$ values.

33. (a) All ion concentrations are 1.0 *M*, so $E°$ values may be used.

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = E^\circ_{\text{Fe}} - E^\circ_{\text{Cu}}$$
$$= 0.77\text{ V} - 0.34\text{ V} = 0.43\text{ V}$$

(b) At equilibrium there is no driving force for the reaction and ΔG reaches zero. Therefore, the measured potential at equilibrium will be 0 V.

(c) The Fe^{3+} would be converted to Fe^{2+} causing the iron solution to decrease in charge, while the Cu° metal would become Cu^{2+}, increasing the charge on the copper solution. Unless these charges were balanced by ion flow from or to the salt bridge, electrons would no longer flow away from the copper solution and to the iron solution and the reaction would cease.

(d) In the spontaneous reaction, copper metal is being oxidized to Cu^{2+}. Therefore, the mass of the copper electrode would decrease.

(e) Anode: Copper half-reaction
Cathode: Iron half-reaction

34. (a) yes

(b) E°_{rx} must be positive for a spontaneous reaction:
Red: $Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg(l)$ $E° = 0.79$ V
Oxid: $Sn^{2+} \rightarrow Sn^{4+} + 2\,e^-$ $E° = 0.15$ V
$E^\circ_{\text{rx}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}} = 0.79 - 0.15 = 0.64$ V which is positive.

(c) In both half-reactions Ag^+ is reduced to Ag°. In the first reaction, the $[Ag^+]$ is defined to be 1.0 *M* (standard conditions for $E°$ values). In the second reaction, the $[Ag^+]$ in solution arises from the dissociation of AgCl when the $[Cl^-]$ is 1.0 *M*. This dissociation is controlled by the K_{sp} for AgCl (1.8×10^{-10}) and is calculated to be 1.8×10^{-10} *M*. Substitution of this $[Ag^+]$ into the Nernst equation for the first reaction will give an *E* value of 0.22 V.

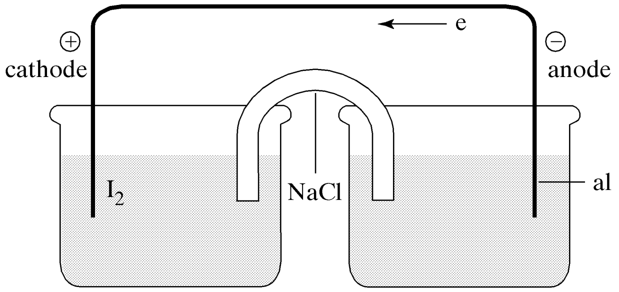
35. Red: $Hg_2^{2+} + 2e^- \rightarrow Hg^\circ$ $E° = +0.79\ v$
Oxid: $Hg^\circ \rightarrow Hg^{2+} + 2\,e^-$ $E° = +0.85$ V

$$E^\circ_{\text{rx}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}} = 0.79 - 0.85 = -\,0.06\text{ V}$$

$$\text{Log } K = \frac{n\,E^\circ_{\text{rx}}}{0/059} = \frac{2(0.06)}{0.059} = 2$$

$K = 1 \times 10^2$
$\Delta G° = -\,n\,\text{F}\,E° = -2\ (96.48\text{ kJ/V})\ (0.06\text{ V}) = -12$ kJ
$\Delta G^\circ_{\text{rx}} = \Delta G^\circ_{\text{prod}} - \Delta G^\circ_{\text{react}} = [\Delta G_f^\circ Hg^{2+} + \Delta G_f^\circ Hg^\circ] - \Delta G_f^\circ Hg_2^{2+} - 12\text{ kJ} = [\Delta G_f^\circ Hg^{2+} + 0\text{ kJ}] - 155\text{ kJ}$
$\Delta G_f^\circ Hg^{2+} = -12\text{ kJ} + 155\text{ kJ} = 143$ kJ/mol

36. Calculate $E°$ for $Ti^\circ \rightarrow Ti^{3+} + 3e^-$.
Red: $Ti^{2+} + 2e^- \rightarrow Ti^\circ$ $E° = -0.37$ V
Oxid: $Ti^\circ \rightarrow Ti^{2+} + 2\,e^-$ $E° = -1.63$ V
$E^\circ_{\text{rx}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}} = -\,0.37 - (-1.63) = +\,1.26$ V



37. I_2 has highest reduction potential; Al has highest oxidation potential.

$$I_2 + 2e^- \rightarrow 2I^-\quad Al \longrightarrow Al^{+3} + 3e^-$$

Overall reaction	EMF°
$3I_2 + 2Al \longrightarrow 6I^- + 2Al^{+3}$	$0.54 - (-1.66)$

ΔG°
$\Delta G° = -6(23.1)(2.20) = 2.20\text{ V} = -305$ kcal or 1.3×10^3 kJ

38. (a) $\log K = \dfrac{6(1.33 - 1.09)}{0.059} = 24.41$

$K = 2.6 \times 10^{24}$

(b) $\log K = \dfrac{2(1.36 - 0.22)}{0.059} = 38.64$

$K = 4.4 \times 10^{38}$

(c) $\log K = \dfrac{6[-0.74 - (-0.44)]}{0.059} = -30.51$

$K = 3.1 \times 10^{-31}$

39. (a) $K = 1.2 \times 10^{24}$
(b) $K = 1.4 \times 10^{9}$
(c) $K = 3.8 \times 10^{14}$
(d) $K = 5.8 \times 10^{25}$
(e) $K = 1.0 \times 10^{2\circ}$
(f) $K = 3.5 \times 10^{92}$

40. (a) $2VO_2^+ + Zn^\circ + 4\,H^+ \rightarrow 2\,VO^{2+} + Zn^{2+} + 2\,H_2O$

$$E^\circ_{\text{rx}} = E^\circ_{VO_2^+} - E^\circ_{\text{Zn}} = 1.00\text{ V} - (-\,0.76\text{ V}) = 1.76\text{ V}$$

(b) $E = E^\circ_{\text{Cu}} - \dfrac{0.059}{n}\log\dfrac{1}{[Cu^{2+}]}$

$$E = 0.34\text{ V} - \frac{0.059}{2}\log\frac{1}{[0.10]} = 0.31\text{ V}$$

(c) Red: $E = E_{\text{Ag}} - \dfrac{0.059}{n}\log\dfrac{1}{[Ag^+]} =$

$$0.80\text{ V} - \frac{0.059}{1}\log\frac{1}{[0.035]} = 0.71\text{ V}$$

Oxid: $E = E_{\text{Fe}} - \dfrac{0.059}{n}\log\dfrac{[Fe^{2+}]}{[Fe^{3+}]} =$

$$0.77\text{ V} - \frac{0.059}{1}\log\frac{[0.010]}{[0.0010]} = 0.83\text{ V}$$

$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = 0.71 - 0.83 = -\,0.12$ V

(d) Red: $E = E^\circ_{\text{AgCl}} - \frac{0.059}{n}\log\,[\text{Cl}^-] =$

$$0.22\text{ V} - \frac{0.059}{1}\log\,[0.20] = 0.81\text{ V}$$

Oxid: $E = E^\circ_{\text{TiO}^{2+}} - \frac{0.059}{n}\log\frac{[\text{Ti}^{3+}]}{[\text{TiO}^{2+}][\text{H}^+]^2} =$

$$0.10\text{ V} - \frac{0.059}{1}\log\frac{[0.010]}{[0.20][0.0020]^2} = -0.14\text{ V}$$

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = 0.81 - (-0.14) = 0.95\text{ V}$$

(e) Reaction that proceeds to completion:

	Co^{3+}	+	V^{2+}	$\longrightarrow$	Co^{2+}	+	V^{3+}
s:	0.015 mol		0.0050 mol		0		0
r:	−0.0050		−0.0050		+0.0050 mol		+0.0050 mol
f:	0.010 mol		0.00		+0.0050 mol		+0.0050 mol

Defined redox couple is the Co^{3+}/Co^{2+} system

$$[\text{Co}^{2+}] = \frac{0.0050\text{ mol}}{0.200\text{ L}} = 0.025\ M$$

$$[\text{Co}^{3+}] = \frac{0.010\text{ mol}}{0.200\text{ L}} = 0.050\ M$$

$$E_{\text{sol}} = E^\circ_{\text{Co}} - \frac{0.059}{n}\log\frac{[\text{Co}^{2+}]}{[\text{Co}^{3+}]} = 1.82\text{ V} -$$

$$\frac{0.059}{1}\log\frac{[0.025]}{[0.050]} = 1.84\text{ V}$$

41. (a) $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$

(b) $\text{Fe}^{31} + 1\,e^- \rightarrow \text{Fe}^{2+}$

(c) $E_{(+)} = 0.77\text{ V} - \frac{RT}{nF}\ln\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0.77\text{ V} - \frac{(\text{R})(273)}{(1)\text{ F}}$

$$\ln\left(\frac{0.10}{1.0}\right) = 0.82\text{ V}$$

$$E_{(-)} = 0.25\text{ V} - \frac{0.0592}{2}\log = \frac{1}{(0.1)} - 0.28\text{ V}$$

$$E_{\text{cell}} = 0.82\text{ V} - -0.28\text{ V} = 1.10\text{ V}$$

(d) 1.10 V

42. (a) $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

(b) $E_{\text{cell}} = E_{(+)} - E_{(-)} = 0.34 - {}^{-}2.37 = 2.71\text{ V}$

(c) As written the equilibrium implies that Mg^{2+} is reduced and Cu is oxidized. Therefore,

$E = -2.37 - 0.34 = -2.71$

$\Delta G = -\text{nFe} = (-)(2)(96{,}485\text{ J/V mole})(-2.71\text{ V}) =$ 523 kJ/mole

$K_{\text{eq}} = e^{-\Delta G/RT} = 2.15 \times 10^{-92}$

43. $2\,\text{Cr}^{3+} + 7\,\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\,\text{H}^+ + 6\,e^-$

$3\,(\text{Br}_2 + 2e^- \rightarrow 2\,\text{Br}^-)$

$2\,\text{Cr}^{3+} + 3\,\text{Br}_2 + 7\,\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 6\,\text{Br}^- + 14\,\text{H}^+$

$\Delta G = -\text{nFE} \quad E = E_{(+)} - E_{(-)} = 1.09 - 1.33 = -0.24\text{ V}$

$\Delta G = (-)(6)(\text{F})(-0.24\text{ V}) = 1.4 \times 10^2\text{ kJ/mol}$

$\Delta G > 0$ therefore not spontaneous

44. $0.00 = E_{(+)} - E_{(-)} = -1.90\text{ V} - E_{(-)}$

$E_{(-)} = -1.90 - 1.90 = \text{E}_{\text{Be}}{}^{2+} + 2e^- \rightarrow \text{Be} - \frac{0.0592}{2}\log$

$$\frac{1}{(0.020)}$$

$$E_{\text{Be}^{2+} + 2e^- \rightarrow \text{Be}} = -1.85\text{ V}$$

45. (a) $\text{Pb}^{2+} + 2\,e^- \rightarrow \text{Pb}$

(b) 1.53 V

(c) $K = 10^{155}$

46. $\text{Cr}_2\text{O}_7^{2-}(aq) + 2\,\text{Mo} + 14\,\text{H}^+ \rightarrow 2\,\text{Cr}^{3+}(aq) + 2\,\text{Mo}^{3+}(aq) + 7\,\text{H}_2\text{O}$

Reaction is spontaneous because $\Delta G^\circ < 0$.

47. $0 = E_{(+)} - E_{(-)} = E_{(+)} - -1.63$

Therefore $E_{(+)} = -1.63 - 1.63 = -1.53 - \frac{0.0592}{4}$

$$\log\frac{1}{[\text{Zr}^{4+}]}$$

$[\text{Zr}^{4+}] = 1.8 \times 10^{-7}\ M$

48. (a) $E_{\text{Pb}} = E^\circ{}_{\text{Pb}} - \frac{0.059}{n}\log\frac{1}{[\text{Pb}^{2+}]} - 0.13\text{ V} - \frac{0.059}{2}\log$

$$\frac{1}{[2.0 \times 10^{-4}]} = -0.24\text{ V}$$

E° S.H.E. = 0.0 V

For a galvanic cell, E_{cell} must be > 0, so the S.H.E. is reduced and Pb oxidized,

$E_{\text{cell}} = 0.00\text{ V} - (-\,0.24\text{ V}) = +\,0.24\text{ V}$

Lead is oxidized, so the half-reaction functions as the anode.

(b) $E_{\text{AgBr}} = E^\circ{}_{\text{AgBr}} - \frac{0.059}{n}\log\,[\text{Br}^-] = 0.07\text{ V} -$

$$\frac{0.059}{1}$$

$\log\,[1.0 \times 10^{-4}] = 0.31\text{ V}$

For a galvanic cell,

$E_{\text{cell}} = 0.31 - 0.00 = 0.31\text{ V}$

AgBr half-reaction is undergoing reduction and acts as the cathode.

(c) $E_{\text{Mn}} = E^\circ{}_{\text{Mn}} - \frac{0.059}{n}\log\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4{}^{2-}][\text{H}^+]^8} = 1.51\text{ V} -$

$$\frac{0.059}{5}\log\frac{[0.15]}{[0.10][0.01]^8} = 1.32\text{ V } 1.32\text{ V}$$

$E_{\text{cell}} = 1.32 - 0.00 = 1.32\text{ V}$

The $\text{MnO}_4{}^{2-}$ half-reaction is undergoing reduction and acts as the cathode.

49. In this reaction, Pb^{2+} from the dissociation of $PbCl_2$ is reduced to Pb°. The concentration of Pb^{2+} in the solution is controlled by the K_{sp} of $PbCl_2$ (1.0×10^{-4}) when the $[Cl^-] = 1.0$ M (by definition E° requires all aqueous concentrations to be 1.0 M).

$1 \times 10^{-4} = [\text{Pb}^{2+}]\,[\text{Cl}^-]^2 = (x)\,(1.0)^2$

$x = 1 \times 10^{-4}\text{ M} = [\text{Pb}^{2+}]$

$$E^\circ_{\mathrm{PbCl_2}} = E^\circ_{\mathrm{Pb}} - \frac{0.059}{n}\log\frac{1}{[\mathrm{Pb^{2+}}]}$$

$$E^\circ_{\mathrm{PbCl_2}} = -0.13 - \frac{0.059}{n}\log\frac{1}{[10\times10^{-4}]} = 0.25\ \mathrm{V}$$

50. Spontaneous Reactions

$Cl_2 + 2\,I^- \rightarrow 2\,Cl^- + I_2$ $K_{eq} = 6.3\times10^{27}$
$2\,H^+ + Zn \rightarrow H_2 + Zn^{2+}$ $K_{eq} = 5.8\times10^{25}$
$3\,Fe^{3+} + Al \rightarrow 3Fe^{2+} + Al^{3+}$ $K_{eq} = 3.6\times10^{123}$
$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ $K_{eq} = 1.9\times10^{37}$
$2\,MnO_4^- + 16\,H^+ + 5\,Fe \rightarrow 2\,Mn^{2+} + 8\,H_2O$
$+\,5\,Fe^{2+}$ $K_{eq} = 3.2\times10^{330}$

Nonspontaneous reactions

$Ba^{2+} + 2\,F^- \rightarrow Ba + F_2$ $K_{eq} = 1.2\times10^{-196}$
$Ni^{2+} + Sn \rightarrow Ni + Sn^{2+}$ $K_{eq} = 1.9\times10^{-4}$
$3\,Fe^{2+} \rightarrow Fe + 2\,Fe^{3+}$ $K_{eq} = 3.0\times10^{-62}$
$Na^+ + Ag \rightarrow Na + Ag^+$ $K_{eq} = 3.2\times10^{-60}$
$Mg^{2+} + Cu \rightarrow Mg + Cu^{2+}$ $K_{eq} = 3.0\times10^{-92}$

51. (a) $Cu(OH)_2 + ClO_3^- \rightarrow ClO_4^- + Cu^\circ$ (basic solution)
$Cu(OH)_2 + ClO_3^- \rightarrow Cu^\circ + ClO_4^- + H_2O$
Red: $Cu(OH)_2 + 2\,e^- \rightarrow Cu^\circ + 2\,OH^-$
Oxid: $ClO_3^- + 2\,OH^- \rightarrow ClO_4^- + H_2O + 2\,e^-$
$E_{rx} = E^\circ_{Cu} - E^\circ_{ClO_4^-} = -0.22\ \mathrm{V} - 0.36\ \mathrm{V} = -\,0.58\ \mathrm{V}$

$$\mathrm{Log}\,K = \frac{nE^\circ_{rx}}{0.059} = \frac{2(-0.58)}{0.059} = -20$$

$K = 1\times10^{-20}$

(b) $2\,NO_3^- + Cu^\circ + 4\,H^+ \rightarrow Cu^{2+} + 2\,NO_2 + 2\,H_2O$
Red: $NO_3^- + 2\,H^+ + e^- \rightarrow NO_2 + H_2O$
Oxid: $Cu^\circ \rightarrow Cu^{2+} + 2\,e^-$
$E_{rx} = E^\circ_{NO_3^-} - E^\circ_{Cu^0} = 0.78\ \mathrm{V} - 0.34\ \mathrm{V} = 0.44\ \mathrm{V}$

$$\mathrm{Log}\,K = \frac{nE^\circ_{rx}}{0.059} = \frac{2(0.44)}{0.059} = 15$$

$K = 1\times10^{15}$

(c) $2\,S_2O_3^{2-} + I_2 \rightarrow 2\,I^- + S_4O_6^{2-}$
Red: $I_2 + 2\,e^- \rightarrow 2\,I^-$
Oxid: $2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\,e^-$
$E_{rx} = E^\circ_{I_2} - E^\circ_{S_2O_3^{2-}} = 0.54\ \mathrm{V} - 0.09\ \mathrm{V} = 0.45\ \mathrm{V}$

$$\mathrm{Log}\,K = \frac{nE^\circ_{rx}}{0.059} = \frac{2(0.45)}{0.059} = 15$$

$K = 1\times10^{15}$

52. $Mg(OH)_2 + 2\,e^- \rightarrow Mg + 2\,OH^-$ $E^\circ = -2.67\ \mathrm{V}$
$Mg^{2+} + 2\,e^- \rightarrow Mg$ $E^\circ = -2.36\ \mathrm{V}$

$$Mg^{2+} + 2\,OH^- \rightarrow \underline{Mg(OH)_2} \quad K = \frac{1}{K_{sp}}$$

$$\log K = \frac{2[-2.36 - (-2.67)]}{0.059} = 10.51$$

$$K = \frac{1}{K_{sp}} = 3.2\times10^{10}$$

$K_{sp} = 3.1\times10^{-11}$

53. $Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2\,NH_3$ $E^\circ = 0.37\ \mathrm{V}$
$Ag^+ + e^- \rightarrow Ag$ $E^\circ = 0.80\ \mathrm{V}$
$Ag^+ + 2\,NH_3 \rightarrow Ag(NH_3)_2^+$ $K = K_f$

$$\log K_f = \frac{(0.08 - 0.37)}{0.059} = 7.29 \qquad K_f = 1.9\times10^7$$

54. $K_a = \dfrac{[H^+][A^-]}{[HA]}$ we know $[A^-] = 0.040$ M and $[HA] =$ 0.010 M, we need to find $[H^+]$ to calculate K_a

Cell reactions: $E_{cell} = E_{Ag} - E_{H_2} = 0.45\ \mathrm{V}$
Red: $Ag^+ + e^- \rightarrow Ag^\circ$ $E = E^\circ = 0.80$ V (Ag^+ is 1.00 M)
Oxid: $H_2 \rightarrow 2H^+ + 2e^-$ $E = E^\circ - \dfrac{0.059}{2}\log\dfrac{[H_2]}{[H^+]^2}$

E_{H_2} is dependent on $[H^+]$ and $E_{H_2} = 0.80\ \mathrm{V} - 0.45\ \mathrm{V} =$ 0.35 V

$$0.35\ \mathrm{V} = 0.00\ \mathrm{V} - \frac{0.059}{2}\log\frac{1}{[H^+]^2}$$

$$\log\frac{1}{[H^+]^2} = \frac{2(-0.35)}{0.059} = 12$$

$$\frac{1}{[H^+]^2} = 10^{12} \quad [H^+] = 1\times10^{26}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(1\times10^{-6})(0.040)}{(0.010)} = 4\times10^{-6}$$

55. (a) $Al^\circ + 3\,Ag^+ \rightarrow Al^{3+} + 3\,Ag^\circ$
$E_{cell} = E_{red} - E_{ox} = E_{Ag} - E_{Al}$
Because all ionic concentrations are 1.0 M, $E = E^\circ$
$E_{cell} = 0.80\ \mathrm{V} - (-\,1.66\ \mathrm{V}) = 2.46\ \mathrm{V}$

(b) $q = I \times t = 10.0\times10^{-3}\ \mathrm{C/sec} \times 3.60\times10^6\ \mathrm{sec} =$ 3.60×10^4 C

$$\frac{3.60\times10^4\ \mathrm{C}}{96.500\ \mathrm{C/mol}\ e^-} = 0.373\ \mathrm{mol}\ e^-$$

(c) Al° must lose 0.373 mol e^-. There are 3 e^- per atom of Al° transferred in the reaction, so the total Al° that reacts is:

$$\frac{0.373\ \mathrm{mol}\ e^-}{3\ \mathrm{mol}\ e^-/\mathrm{mol}\ Al^\circ} = 0.124\ \mathrm{mol}\ Al^\circ$$

For every 1 Al° that reacts, 1 Al^{3+} is formed, so there will be an additional 0.124 mol Al^{3+} in the solution and the new concentration of Al^{3+} will be 1.12 M

Based on the reaction stoichiometry, if 0.124 mol Al° react, then 3 (0.124), or 0.372 mol Ag^+ must have reacted.

The new concentration of Ag^+ will be:

$$\frac{1.00\ \mathrm{mol} - 0.372\ \mathrm{mol}}{1.00\ \mathrm{L}} = 0.682\ M$$

(d) $E_{Al} = E^\circ_{Al} - \dfrac{0.059}{3}\log\dfrac{1}{[Al^{3+}]} = -1.66\ \mathrm{V} - \dfrac{0.059}{3}\log$

$$\frac{1}{[1.12]} = -1.66\ \mathrm{V}$$

$$E_{Ag} = E^\circ_{Ag} - \frac{0.059}{1}\log\frac{1}{[Ag^+]} = 0.80\ \mathrm{V} - \frac{0.059}{1}\log$$

$$\frac{1}{[0.628]} = 0.79\ \mathrm{V}$$

$E_{cell} = 0.79\ \mathrm{V} - (-\,1.66\ \mathrm{V}) = 2.45\ \mathrm{V}$

(e) The battery only lost 0.01 V after 1000 hours of use, or a rate of − 0.01 V,1000 hr = $-\,1\times10^{-5}$ V/hr

The battery will be "dead" when its voltage is:
0.90(2.46 V) = 2.21 V

Thus, a total of 0.25 V would be lost which would take,

$$\frac{0.25\text{ V}}{1 \times 10^{-5}\text{ V/hr}} = 25000\text{ hr}$$

56. $E_{\text{cell}} = E_{\text{Ag}} - E_{\text{SHE}}$

$E_{\text{Ag}} = E_{\text{cell}} + E_{\text{SHE}} = 0.48\text{ V} + 0.00\text{ V} = 0.48\text{ V}$

$$E_{\text{Ag}} = E^{\circ}_{\text{Ag}} - \frac{0.059}{n}\log\frac{1}{[\text{Ag}^+]}$$

$$0.48\text{ V} = 0.80 - \frac{0.059}{1}\log\frac{1}{[\text{Ag}^+]}$$

$[\text{Ag}^+] = 3.8 \times 10^{-6}\text{ M}$

57. Overall reaction: $\text{AgI}(s) \rightarrow \text{Ag}^+(aq) + \text{I}^-(aq)\ K_{sp} = [\text{Ag}^+][\text{I}^-]$

Reduction: $\text{AgI} + e^- \rightarrow \text{Ag}^{\circ} + \text{I}^-$ $E^{\circ} = -0.15\text{ V}$

Oxidation: $\text{Ag}^{\circ} \rightarrow \text{Ag}^+ + e^-$ $E^{\circ} = 0.80\text{ V}$

Overall: $\text{AgI} \rightarrow \text{Ag}^+ + \text{I}^-$ $E^{\circ} = -0.95\text{ V}$

$$E^{\circ}_{\text{rx}} = \frac{0.059}{n}\log K$$

$$\log K = \frac{n\,E^{\circ}_{\text{rx}}}{0.059} = \frac{1(-0.95)}{0.059} = -16$$

$K_{sp} = 1 \times 10^{-16}$

$\Delta G^{\circ} = -\text{RT}\ln\text{K} = -(8.31\text{ J/K})(298\text{ K})\ln(1 \times 10^{-16}) = +91\text{ kJ}$

58. (a) Overall reaction: $\text{Ag}^+(aq) + 2\,\text{CN}^-(aq) \rightarrow$

$$\text{Ag(CN)}_2^-(aq) \quad K_f = \frac{[\text{Ag(CN)}_2]}{[\text{Ag}^+][\text{CN}^-]^2}$$

Reduction: $\text{Ag}^+ + e^- \rightarrow \text{Ag}^{\circ}$ $E^{\circ} = 0.80\text{ V}$

Oxidation: $\text{Ag}^{\circ} + 2\,\text{CN}^- \rightarrow \text{Ag(CN)}_2^-$ $E^{\circ} = -0.31\text{ V}$

Overall: $\text{Ag}^+ + 2\,\text{CN}^- \rightarrow \text{Ag(CN)}_2^-$ $E^{\circ} = 1.11\text{ V}$

$$E^{\circ}_{\text{rx}} = \frac{0.059}{n}\log K$$

$$\log K = \frac{n\,E^{\circ}_{\text{rx}}}{0.059} = \frac{1 \times 1.11}{0.059} = 19$$

$K_f = 1 \times 10^{19}$

(b) Ag^+ accepts an electron pair from the CN^- species, so Ag^+ is the Lewis acid and CN^- is the Lewis base.

59. $\underline{\text{PbSO}_4} \rightarrow \text{Pb}^{22+} + \text{SO}_4^{2-} \quad K = K_{sp}$

$$\log K = \frac{2[E_{\text{red}} - (-0.126)]}{0.059} = \log 1.6 \times 10^{-8}$$

$$-7.80 = \frac{2[E_{\text{red}} - (-0.126)]}{0.059}$$

$$E_{\text{red}} = \frac{-7.80 \times 0.059}{2} + (-0.126) = -0.230 - 0.126 = -0.36\text{ V}$$

60. (a) $\log K = \dfrac{2(1.10)}{0.059} - 37.29$

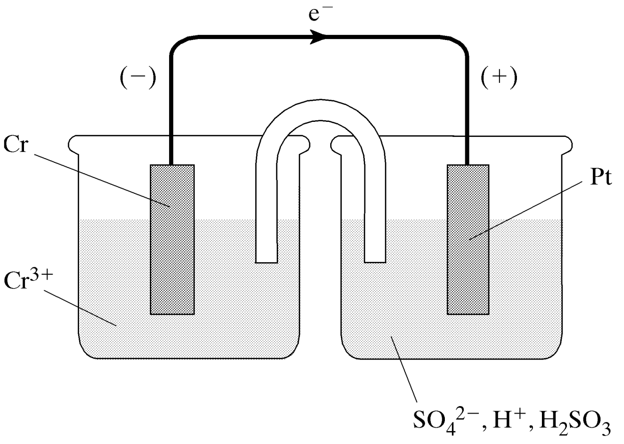
$K = 1.9 \times 10^{37}$

(b) $E_{\text{cell}} = E^{\circ}_{\text{red}} - E^{\circ}_{\text{ox}} = 1.10\text{ V}$

$E^{\circ}_{\text{red}} = 1.10 + E^{\circ}_{\text{ox}} = 1.10 + (-0.76) = 0.34\text{ V}$

(c) As pH is increased, the concentration of H^+ would decrease. Since H^+ is a reactant in the reaction equation, decreasing its concentration would reduce the extent of the forward reaction making the reaction less likely. A less likely reaction would have a lower cell potential, so increasing the pH would decrease the E value for the reaction.

61. (a)



(b) $3\,\text{SO}_4^{2-} + 2\,\text{Cr} + 12\,\text{H}^+ \rightarrow 2\,\text{Cr}^{3+} + 3\,\text{H}_2\text{SO}_3 + 3\,\text{H}_2\text{O}$

(c) $0.172 - (-0.744) = 0.916\text{ V}$

62. (a) $\Delta G^{\circ} = -nFE^{\circ}$

$\Delta G^{\circ} = -2 \times 96.48\text{ kJ/V}\,(1.36 - 1.06)\text{V} = -58\text{ kJ}$

(b) $\Delta G^{\circ} = -6 \times 96.48\,(2.01 - 1.70) = -1.8 \times 10^2\text{ kJ}$

(c) $\Delta G^{\circ} = -6 \times 96.48\,(1.00 - 1.45) = +260\text{ kJ}$

63. (a) cathode: $2\,\text{H}_2\text{O} + 2\,e^- \rightarrow \text{H}_2 + 2\,\text{OH}^-$

anode: $2\,\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,e^-$

overall: $6\,\text{H}_2\text{O} \rightarrow 2\,\text{H}_2 + \text{O}_2 + 4\,\text{H}^+ + 4\,\text{OH}^-$

(b) cathode: $\text{Sn}^{2+} + 2\,e^- \rightarrow \text{Sn}$

anode: $2\,\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,e^-$

overall: $2\,\text{Sn}^{2+} + 2\,\text{H}_2\text{O} \rightarrow 2\,\text{Sn} + \text{O}_2 + 4\,\text{H}^+$

(c) cathode: $\text{Ni}^{2+} + 2\,e^- \rightarrow \text{Ni}$

anode: $2\,\text{I}^- \rightarrow \text{I}_2 + 2\,e^-$

overall: $\text{Ni}^{2+} + 2\,\text{I}^- \rightarrow \text{Ni} + \text{I}_2$

(d) cathode: $2\,\text{H}_2\text{O} + 2\,\text{e}^- \rightarrow \text{H}_2 + 2\,\text{OH}^-$

anode: $4\,\text{OH}^- \rightarrow \text{O}_2 + 2\,\text{H}_2\text{O} + 4\,e^-$

overall: $2\,\text{H}_2\text{O} \rightarrow 2\,\text{H}_2 + \text{O}_2$

64. (a) cathode: $2\,\text{H}^+ + 2\,e^- \rightarrow \text{H}_2$

anode: $2\,\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,e^-$

overall: $2\,\text{H}_2\text{O} \rightarrow 2\,\text{H}_2 + \text{O}_2$

(b) cathode: $2\,\text{H}_2\text{O} + 2\,e^- \rightarrow \text{H}_2 + 2\,\text{OH}^-$

anode: $2\,\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,e^-$

overall: $6\,\text{H}_2\text{O} \rightarrow 2\,\text{H}_2 + \text{O}_2 + 4\,\text{H}^+ + 4\,\text{OH}^-$

or $2\,\text{H}_2\text{O} \rightarrow 2\,\text{H}_2 + \text{O}_2$

(c) cathode: $\text{Cd}^{2+} + 2\,e^- \rightarrow \text{Cd}$

anode: $2\,\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,e^-$

overall: $2\,\text{Cd}^{2+} + 2\,\text{H}_2\text{O} \rightarrow 2\,\text{Cd} + \text{O}_2 + 4\,\text{H}^+$

(d) cathode: $2\,\text{H}_2\text{O} + 2\,e^- \rightarrow \text{H}_2 + 2\,\text{OH}^-$

anode: $4\,\text{OH}^- \rightarrow \text{O}_2 + 2\,\text{H}_2\text{O} + 4\,e^-$

overall: $2\,\text{H}_2\text{O} \rightarrow 2\,\text{H}_2 + \text{O}_2$

(e) cathode: $\text{Cu}^{2+} + 2\,e^- \rightarrow \text{Cu}$

anode: $2\,\text{Br}^- \rightarrow \text{Br}_2 + 2\,e^-$

overall: $\text{Cu}^{2+} + 2\,\text{Br}^- \rightarrow \text{Cu} + \text{Br}_2$

(f) cathode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$
anode: $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$
overall: $6\,H_2O \rightarrow 2\,H_2 + O_2 + 4\,H^+ + 4\,OH^-$
or $2\,H_2O \rightarrow 2\,H_2 + O_2$

(g) cathode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$
anode: $2\,I^- \rightarrow I_2 + 2\,e^-$
overall: $2\,H_2O + 2\,I^- \rightarrow H_2 + 2\,OH^- + I_2$

(h) cathode: $Hg^{2+} + 2\,e^- \rightarrow Hg$
anode: $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$
overall: $2\,Hg^{2+} + 2\,H_2O \rightarrow 2\,Hg + O_2 + 4\,H^+$

65. $$\frac{6.0\text{ C/s} \times 3600\text{ s/hr} \times 2\text{ hr}}{96{,}500\text{ C/mol }e^-} \times \frac{1\text{ mol Cr}}{3\text{ mol }e^-} \times 52.0\text{ g/mol Cr} =$$
7.8 g Cr

66. $$\frac{1.0\text{ L O}^2}{22.4\text{ L/mol}} \times \frac{4\text{ mol }e^-}{1\text{ mol O}_2} \times \frac{96{,}500\text{ C/mol }e^-}{2.5\text{ C/sec} \times 3600\text{ s/hr}} = 1.9\text{ hr}$$

67. $$\frac{1\text{ mol H}_2 \times 2\text{ mol }e^-/\text{mol H}_2 \times 96{,}500\text{ C/mol }e^-}{30\text{ min} \times 60\text{ s/min}} =$$
1.1×10^{2} C/s = 1.1×10^{2} A

68. $$\frac{(1.203 \times 0.709)\text{ g}}{107.9\text{ g/mol}} = 0.007906\text{ mol Ag}$$
$$0.007905\text{ mol Ag} \times \frac{1\text{ mole }e^-}{1\text{ mol Ag}} \times \frac{96{,}500\text{ C}}{\text{mol }e^-} = 762.9\text{ C from}$$
silver
$$\frac{(1.203 \times 0.2909)\text{ g}}{65.38\text{ g/mol}} = 0.005353\text{ mol Zn}$$
$$0.005353\text{ mol Zn} \times \frac{2\text{ mol }e^-}{1\text{ mol Zn}} \times \frac{96{,}500\text{ C}}{\text{mol }e^-} = 1033\text{ C from}$$
zinc

Total: 767.2 C + 1033 C = 1796 C

69. $$\frac{0.100\text{ g}}{197\text{ g/mol Au}} \times \frac{3\text{ mol }e^-}{1\text{ mol Ag}} \times 96{,}500\text{ C/mol }e^- \times$$
$$\frac{1}{7.50\text{ C/s}} = 19.6\text{ s}19.6\text{ s}$$

70. $$\frac{10.0\text{ C/s} \times 20.0\text{ min} \times 60\text{ s/min}}{96{,}500\text{ C/mol }e^-} \times \frac{1\text{ mol Co}^{3+}}{1\text{ mol }e^-} \times 58.9$$
g/mol Co = 7.32 g

71. (a) $$\frac{28.77\text{ g}}{39.10\text{ g/mol}} = 0.7358\text{ mol }K\ \frac{23.65\text{ g}}{32.06\text{ g/mol}} =$$
0.7377 mol S
$$\frac{47.58\text{ g}}{15.9994\text{ g/mol}} = 2.974\text{ mol O}$$
0.736:0.738:2.97 = 1:1:4
Empirical formula = KSO_4
$$\frac{270\text{ g/form}}{135\text{ g/emp form}} = 2$$
$K_2S_2O_8$

(b) cathode: $2\,H^+ + 2\,e^- \rightarrow H_2$
anode: $2\,SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,e^-$

72. $$\frac{125\text{ C/s} \times 2\text{ min} \times 60\text{ s/min}}{96{,}500\text{ C/mol }e^-} \times \frac{1\text{ mol Pb}}{2\text{ mol }e^-} \times 207.2\text{ g/mol}$$
Pb = 16.1 g Pb

73. (a) $$\begin{array}{l} 3(\text{Sn} + 2\,\text{H}_2\text{O} \rightarrow \underline{\text{SnO}_2} + 4\,\text{H}^+ + 4\,e^-) \\ \underline{4(\text{NO}_3^- + 4\,\text{H}^+ + 3\,e^- \longrightarrow \text{NO} + 2\,\text{H}_2\text{O})} \\ 3\,\text{Sn} + 4\,\text{NO}_3^- + 4\,\text{H}^+ \longrightarrow 3\,\underline{\text{SnO}_2} + 4\,\text{NO} + 2\,\text{H}_2\text{O} \end{array}$$

(b) $$0.0127\text{ g SnO}_2 \times \frac{118.69\text{ g Sn}}{150.69\text{ g SnO}_2} \times \frac{1}{1.00\text{-g sample}} \times$$
100% = 1.00% Sn
$$\frac{100\text{ C/s} \times 0.591\text{ hr} \times 3600\text{ s/hr}}{\text{L}(96{,}500)\text{ C/mol }e^-} \times \frac{1\text{ mol Cu}}{2\text{ mol }e^-} \times$$
63.546 g/mol Cu = 0.701 g Cu
$$\frac{0.701\text{ g Cu}}{1.00\text{ g sample}} \times 100\% = 70.1\%\text{ Cu}$$
100 − (70.1 + 1.0) = 28.9% Zn

74. $2\,MnO_4^- + 16\,H^+ + 5\,C_2O_4^{2-} \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$
$$\frac{1.5703\text{ g Na}_2\text{C}_2\text{O}_4}{134.0\text{ g/mol Na}_2\text{C}_2\text{O}_4} \times \frac{2\text{ mol MnO}_4^-}{5\text{ mol Na}_2\text{C}_2\text{O}_4} \times \frac{1000\text{ mL/L}}{43.25\text{ mL}} =$$
0.1084 M
$$\frac{1.4823}{134.0} \times \frac{2}{5} \times \frac{1000}{41.24} = 0.1073\ M$$
$$\text{average} = \frac{0.1084 + 0.1073}{2} = 0.1079\ M$$

75. $$\frac{0.500\text{ g}}{204\text{ g/mol Tl}^{3+}} \times \frac{3\ e^-}{\text{mol Tl}^{3+}} = 7.35 \times 10^{-3}\text{ mol }e^-$$
$$7.35 \times 10^{-3}\text{ mol }e^- \times \frac{96{,}500\text{ C}}{\text{mole }e^-} = 710\text{ C}$$
$$q = \text{I} \times t \quad \text{or} \quad t = \frac{q}{\text{I}}$$
$$t = \frac{710\text{ C}}{1.20\text{ C/sec}} = 592\text{ sec}$$

76. Weight gain of the electrode is due to the Ag°,
$$\frac{0.5671\text{ g Ag}^\circ}{12.34\text{-g sample}} \times 100\% = 4.596\%$$

77. (a) All of the manganese will be plated and the total amount of manganese in the mineral ore sample is,
$$4.1277\text{ g} \times 0.1456 = 0.6010\text{ g}$$
The total weight of the electrode will be,
$$23.4612\text{ g} + 0.6010\text{ g} = 24.0622\text{ g}$$

(b) $$[\text{Mn}^{2+}] = \frac{0.6010\text{ g}/54.94\text{ g/mol}}{0.15\text{ L}} = 0.073\ M$$
$$E = -1.18\text{ V} - \frac{0.059}{2}\log\frac{1}{0.073} = -1.21\text{ V, so} >$$
1.21 V must be applied.

(c) $$\frac{0.6010\text{ g}}{54.94\text{ g/mol Mn}} \times \frac{2\ e^-}{\text{mol Mn}} \times \frac{96{,}500\text{ C}}{\text{mol }e^-} = 2.11 \times$$
10^3 C
$$\text{I} = \frac{1}{t} = \frac{2.11 \times 10^3\text{ C}}{2100\text{ sec}} = 1.00\text{ A}$$

78. 4.84 A × 375 min × 60 sec/min = 1.09×10^5 C
1.09×10^5 C/ 96,485 C/mol = 1.13 mol of electrons
1 mol of Ni requires 2 mol of electrons, therefore

1.13 mol electrons/2 mol electrons per mole Ni = 0.565 mol Ni grams Ni = 0.565 mol × 58.70 g/mol = 33.2 g

79. $Cu^{2+} + 2e^- \rightarrow Cu$

$$\frac{1.0\text{ g Cu}}{63.5\text{ g/mol}} - 1.57 \times 10^{-2}\text{ mol Cu}$$

Requires $1.57 \times 10^{-2} \times 2$ mol e^-

$$\text{Requires } 1.57 \times 10^{-2} \times 2 \times 96{,}500\,\frac{\text{C}}{\text{mol}} = 3.04 \times 10^3\text{ C}$$

1 Amp = 1 C/sec

$$\frac{3.04 \times 10^3\text{ C}}{3600\text{ sec} \times 2} = 0.42\text{ A}$$

80. $Al^{+3} + 3e^- \rightarrow Al$

3600 s/hr × 10 hr = 36000 s × 1 C/s = 36,000 C

$$\frac{36{,}000\text{ C}}{96{,}500\text{ C/mol}} = 0.373\text{ mol } e^-$$

$$\frac{0.370}{3} \times 27\text{ g/mol} = 3.4\text{ g Al}$$

81. moles Ni^{2+} = 0.100 L × 0.30 mol/L = 0.030 mol
moles of electrons = (0.030 mol Ni^{2+})(2 mol e^-/mol Ni^{2+}) = 0.060 mol e^-

$$\text{required current} = \frac{0.060\text{ mol} \times 96485\text{ C/mol}}{15\text{ min} \times 60\text{ sec/min}} = 6.4\text{ A}$$

82. (a) Cathode: $Al^{3+} + 3\,e^- \rightarrow Al$
Anode: $C + 2\,O^{2-} \rightarrow CO_2 + 4\,e^-$

(b) 24 cans/case × 5.00 g/can = 120 g Al
(120 g Al/26.9815 g/mol Al) × 3 mol e^-/mol Al = 13.35 mol e^-
13.35 mol e^- × 96,485 C/mol e^- = 1.288×10^6 C
1.288×10^6 C = (50.00 C/sec)t
$t = 2.576 \times 10^4$ sec or 429.3 min if the process is 100% efficient. Because it is only 90% efficient, the time must be increased, 429.3/0.90 = 477 min.

83. (a) $$\text{Co: } E = E^\circ\text{ Co} - \frac{0.059}{2}\log\frac{1}{[Co^{2+}]} = -0.28\text{ V} - \frac{0.059}{2}\log\frac{1}{[0.15]} = -0.30\text{ V}$$

$$\text{Cd: } E = E^\circ\text{ Cd} - \frac{0.059}{2}\log\frac{1}{[Cd^{2+}]} = -0.40\text{ V} - \frac{0.059}{2}\log\frac{1}{[0.075]} = -0.43\text{ V}$$

Cobalt has a more positive reduction potential so it will plate out first.

(b) 0.30 V applied potential

(c) $$\text{Co: } E = E^\circ_{Co} - \frac{0.059}{2}\log\frac{1}{[Co^{2+}]} = -0.28\text{ V} - \frac{0.059}{2}\log\frac{1}{[1 \times 10^{-5}]} = -0.43\text{ V}$$

A potential greater than 0.43 V would need to be applied.

84. (a) $$\text{Ni: } E = E^\circ - \frac{0.059}{2}\log\frac{1}{[Ni^{2+}]} = -0.25\text{ V} - \frac{0.059}{2}\log\frac{1}{[0.15]} = -0.27\text{ V}$$

$$\text{Al: } E = E^\circ - \frac{0.059}{3}\log\frac{1}{[Al^{3+}]} = -1.66\text{ V} - \frac{0.059}{3}\log\frac{1}{[0.15]} = -1.68\text{ V}$$

Aluminum has the more negative reduction potential so it will be reduced after the nickel, and this reduction will occur at a potential of 1.68 V.

(b) The Al^{3+} begins to plate at −1.68 V. Using the Nernst equation, the concentration of Ni^{2+} remaining at this potential can be calculated.

$$\text{Ni: } E = E^\circ - \frac{0.059}{2}\log\frac{1}{[Ni^{2+}]} - 1.68\text{ V} =$$

$$-0.25\text{ V} - \frac{0.059}{2}\log\frac{1}{[Ni^{2+}]}\log\frac{1}{[Ni^{2+}]} =$$

$$\frac{2}{0.59}\,(-0.25\text{ V} - (-1.68\text{ V})) = 48\,\frac{1}{[Ni^{2+}]} = 1 \times 10^{48}$$

$[Ni^{2+}] = 1 \times 10^{-48}\,M$

(c) $$0.15\,\frac{1}{\text{mol}} \times 1.0\text{ L} = 0.15\text{ mol } Ni^{2+} \times \frac{2\text{ mol } e^-}{\text{mol } Ni^{2+}} = 0.30\text{ mol } e^-$$

$$0.30\text{ mol } e^- \times \frac{96{,}500\text{ C}}{\text{mol } e^-} = 2900\text{ C}$$

$$I = \frac{q}{t} = \frac{2900\text{ C}}{600\text{ sec}} = 48\,\frac{\text{C}}{\text{sec}} = 48\text{ A}$$

85.
1. loss, oxidation number
2. reducing
3. charge
4. reduction, oxidation
5. ions
6. cathode, anode
7. cell potential, E_{cell}, or emf
8. hydrogen
9. +3
10. reduction
11. Pb, PbO_2
12. 0
13. O_2, H_2
14. Hg
15. coulomb

86. 1. (b), 2. (c), 3. (c), 4. (b), 5. (d), 6. (a), 7. (c), 8. (d), 9. (b), 10. (a)

APPENDIX 1

Constants and Conversion Factors

CONSTANTS

Avogadro's number, N_A	6.022×10^{23} mol^{-1}
Faraday constant, F	96,485 C mol^{-1}
Faraday constant, F	96.5 kJ mol^{-1}
Proton charge, e	1.602×10^{-19} C
Proton charge, e	4.80×10^{-10} esu
Electron mass, m_e	9.11×10^{-28} g
Proton mass	1.67×10^{-24} g
Planck constant, h	6.626×10^{-34} J s
Speed of light, c	2.998×10^{8} m/s
Gas constant, R	8.314 J/mol K, 0.0821 L atm/mol K
Boltzmann constant, k	1.381×10^{-23} J/K
Pi, π	3.14159

CONVERSION FACTORS

Natural logarithm base, e 2.718
1 cal = 4.184 J
1 eV = 1.602×10^{-19} J
1 kcal = 2.39×10^{-11} erg
1 esu^2/cm = 1 erg
ln y = 2.303 log y
1 cm^{-1} = 0.01196 kJ/mol
1 atm = 101,325 Pa = 760 torr
1 Å (angstrom) = 10^{-10} m = 100 pm
1 amu = 1.66×10^{-24} g
1 in = 2.54 cm
1 mi = 1.609 km
1 lb = 0.4536 kg
1 qt = 0.946 L

APPENDIX

2

Bond Energies and Bond Lengths

BOND D,	kJ/mol	r, pm
Hydrogen		
H—H	432	74
H—B	389	119
H—C	411	109
H—Si	318	148
H—Ge	288	153
H—Sn	251	170
H—N	386	101
H—P	322	144
H—As	247	152
H—O	459	96
H—S	363	134
H—Se	276	146
H—Te	238	170
H—F	565	92
H—Cl	428	127
H—Br	362	141
H—I	295	161
Group III		
B—B	293	
B—O	536	
B—F	613	
B—Cl	456	175
B—Br	377	
Group IV		
C—B	356	
C—C	346	154
C═C	602	134
C≡C	835	120
C—Si	318	185
C—Ge	238	195
C—Sn	192	216
C—Pb	130	230
C—N	305	147
C═N	615	129
C≡N	887	116
C—P	264	184
C—O	358	143
C═O	799	120
C≡O	1072	113

Continued on the nex page

BOND D,	kJ/mol	r, pm
Group IV ***Continued***		
C—S	272	182
C=S	573	160
C—F	485	135
C—Cl	327	177
C—Br	285	194
C—I	213	214
Si—Si	222	233
Si—N	355	
Si—O	452	163
Si—S	293	200
Si—F	565	160
Si—Cl	381	202
Si—Br	310	215
Si—I	234	243
Ge—Ge	188	241
Ge—N	257	
Ge—F	470	168
Ge—Cl	349	210
Ge—Br	276	230
Ge—I	212	
Sn—F	414	
Sn—Cl	323	233
Sn—Br	273	250
Sn—I	205	270
Pb—F	331	
Pb—Cl	243	242
Pb—Br	201	
Pb—I	142	279
Group V		
N—N	167	145
N=N	418	125
N≡N	942	110
N—O	201	140
N=O	607	121
N—F	283	136
N—Cl	313	175
P—P	201	221
P—O	335	163
P=O	544	150
P=S	335	186
P—F	490	154
P—Cl	326	203
P—Br	264	
P—I	184	
As—As	146	243
As—O	301	178
As—F	484	171
As—Cl	322	216
As—Br	458	233
As—I	200	254
Sb—Sb	121	
Sb—F	440	
Sb—Cl ($SbCl_5$)	248	
Sb—Cl ($SbCl_3$)	315	232

Continued on the next page

BOND D,	kJ/mol	r, pm
Group VI		
O—O	142	148
O=O	494	121
O—F	190	142
S=O	522	143
S—S (S_8)	226	205
S=S	425	149
S—F	284	156
S—Cl	255	207
Se—Se	172	
Se=Se	272	215
Group VII		
F—F	155	142
Cl—Cl	240	199
Br—Br	190	228
I—I	148	267
At—At	116	
I—O	201	
I—F	273	191
I—Cl	208	232
I—Br	175	
Group VIII		
Kr—F (KrF_2)	50	190
Xe—O	84	175
Xe—F	130	195

APPENDIX
3
Heats of Formation and Absolute Entropies

ELEMENT AND INORGANIC COMPOUNDS

Name	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K
$H_2(g)$	0	0	130.5
$H(g)$	218	203.3	114.6
$Li(s)$	0	0	28
$Li(g)$	155.2	122.2	138.5
$Li_2O(s)$	−595.8	−560.7	37.9
$Li_2O_2(s)$	−634.7	−564.8	56.5
$LiH(s)$	−90.4	−69.9	24.7
$LiCl(s)$	−408.8	−383.7	55.2
$LiF(s)$	−612.1	−584.1	36
$LiI(s)$	−271.1	−270.3	86.8
$Na(s)$	0	0	51
$Na(g)$	108.8	78.2	153.6
$NaH(s)$	−57.3	−33.5	40.0
$NaF(s)$	−569	−541	58.6
$NaCl(s)$	−410.9	−384.1	72.4
$NaBr(s)$	−359.8	−347.7	86.8
$NaI(s)$	−287.9	−286.1	98.5
$Na_2SO_4(s)$	−1384.5	−1266.9	149.4
$NaNO_3(s)$	−466.5	−365.7	116.3
$NaNO_2(s)$	−359.4	−284.6	103.8
$Na_2CO_3(s)$	−1130.9	−1047.7	136
$Na_2O(s)$	−415.9	−376.6	72.8
$Na_2O_2(s)$	−504.6	−430.1	95.0
$NaO_2(s)$	−260.7	−218.8	115.9
$NaC_2H_3O_2(s)$	−710.4	−607.3	123.0
$NaOH(s)$	−430.5	−377	52.3
$K(s)$	0	0	63.6
$K(g)$	90	61.1	160.2
$KF(s)$	−562.7	−533	66.5
$KCl(s)$	−436	−408.4	83
$KClO_3(s)$	−391.2	−290	143.1
$K_2O(s)$	−361.5	−318.8	94.1
$K_2O_2(s)$	−493.7	−418.4	102.1
$KO_2(s)$	−282.8	−248.5	116.7
$KOH(s)$	−425.9	−374.5	79
$KNO_3(s)$	−492.9	−393.3	133
$KClO_4(s)$	−433.5	−304.2	151
$Rb(s)$	0	0	69.5
$Rb(g)$	85.8	56.5	169.9
$RbF(s)$	−549.4		75.3

ELEMENTS AND INORGANIC COMPOUNDS *Continued*

Name	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K
$RbCl(s)$	−430.5	−407.8	95.9
$Rb_2O(s)$	−330.1	−292.9	
$Rb_2O_2(s)$	−425.5	−351.5	
$RbO_2(s)$	−263.6		
$Cs(s)$	0	0	82.8
$Cs(g)$	78.7	51	175.3
$CsF(s)$	−530.9	−525.5	92.8
$CsCl(s)$	−433	−414.5	101.2
$CsI(s)$	−336.8	−333.5	123.0
$Cs_2O(s)$	−317.6	−326.4	146.8
$Cs_2O_2(s)$	−402.5	−359.8	
$CsO_2(s)$	−259.4		
$Be(s)$	0	0	9.6
$Be(g)$	320.5	282.8	136
$BeCl_2(s)$	−511.7	−449.5	75.8
$Mg(s)$	0	0	32.6
$Mg(g)$	150.2	115.5	148.5
$MgF_2(s)$	−1102.5	−1049.3	57.3
$MgCl_2(s)$	−641.8	−592.5	89.5
$MgO(s)$	−601.7	−559.4	26.8
$MgSO_4(s)$	−1278.2	−1173.6	91.6
$Mg(NO_3)_2(s)$	−789.5	−588.3	164
$Ca(s)$	0	0	41.6
$Ca(g)$	192.5	167.4	154.8
$CaH_2(s)$	−188.7	−149.8	41.8
$CaO(s)$	−635.5	−604.2	39.7
$Ca(OH)_2(s)$	−986.6	−896.6	76.1
$CaF_2(s)$	−1214.6	−1161.9	69
$CaCl_2(s)$	−795	−750.2	113.8
$CaCO_3(s)$	−1207.1	−1128.8	92.9
$Sr(s)$	0	0	54.4
$Sr(g)$	164	110	164.4
$SrCl_2(s)$	−828.4	−781.2	−117.2
$Ba(s)$	0	0	66.9
$Ba(g)$	175.7	144.8	170.3
$BaCl_2(s)$	−860.2	−810.9	125.5
$BaCl_2 \cdot 2H_2O(s)$	−1461.9	−1295.8	202.9
$BaCO_3(s)$	−1218.8	−1138.9	112.1
$B(s)$	0	0	6.7
$B_2O_3(s)$	−1263.6	−1184.1	54
$BF_3(g)$	−1136.8	−1120.5	254
$BCl_3(g)$	−402.9	−387.9	290
$B_2H_6(g)$	31.4	82.8	233
$Al(s)$	0	0	28.5
$Al_2O_3(s)$	−1669.8	−1576.5	51
$Al_2(SO_4)_3(s)$	−3440.9	−3506.6	239.3
$C(s, \text{graphite})$	0	0	5.9
$C(s, \text{diamond})$	2.1	2.9	2.5
$C(g)$	718.4	672.8	158.2
$CF_4(g)$	−933	−888.3	261.5
$CCl_4(g)$	−100.4	−58.2	310
$CCl_4(l)$	−132.6	−62.8	216.3
$Cl_2CO(g)$	−220.9	−206.7	283.7
$CO(g)$	−110.5	−137.2	197.9
$CO_2(g)$	−393.3	−394.6	213.8
$OCS(g)$	−138.5	−165.7	231.4

Continued on the next page

ELEMENTS AND INORGANIC COMPOUNDS *Continued*

Name	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K
$CS_2(g)$	117.2	66.9	237.7
$HCN(g)$	130.5	120.1	201.7
$Si(s)$	0	0	19
$SiO_2(s)$	−859.4	−805.0	41.8
$SiH_4(g)$	34.3	57.0	203.8
$SiCl_4(g)$	−609.6	−569.9	331.4
$SiCl_4(l)$	−640.2	−572.8	239.3
$Ge(s)$	0	0	42.2
$GeCl_4(l)$	−543.9	−462.8	245.6
$Sn(s)$	0	0	51.5
$SnO(s)$	−286.2	−257.3	56.5
$SnO_2(s)$	−580.7	−520.5	52.3
$SnCl_2(s)$	−349.8		129.7
$SnCl_4(l)$	−545.2	−440.1	258.6
$N_2(g)$	0	0	191.6
$NH_3(g)$	−45.6	−16.3	192.5
$N_2H_4(g)$	95	159	238.5
$NO(g)$	90.4	86.6	210.5
$NO_2(g)$	33.9	51.9	239.7
$N_2O(g)$	81.6	103.8	220.1
$N_2O_4(g)$	9.6	98.3	304.2
$NH_4Cl(s)$	−315.5	−203.8	94.6
$NH_4NO_3(s)$	−365.3	−184.0	151.1
$NH_4NO_2(s)$	−264		
$HNO_3(l)$	−173.2	−79.9	155.6
$P(s$, white)	0	0	44.4
$P(s$, red)	−18.4	−13.8	29.3
$P(s$, black)	−43.1		
$P_4O_{10}(s)$	−3012.5	−2697.8	228.9
$PH_3(g)$	9.2	18.4	210
$PCl_3(g)$	−278.7	−258.6	311.7
$PCl_5(g)$	−371.1	−296.6	352.7
$As(s)$	0	0	35.1
$AsH_3(g)$	66.4	68.9	222.7
$Sb(s)$	0	0	45.6
$SbCl_3(s)$	−382	−323.8	184.1
$SbCl_5(l)$	−440.2	−350.2	301.2
$O_2(g)$	0	0	205
$O_3(g)$	142.3	163.6	237.7
$H_2O(g)$	−241.8	−228.4	188.7
$H_2O(l)$	−285.8	−237.2	69.9
$H_2O_2(l)$	−187.4	−120.4	109.6
$OCl_2(g)$	76.1	93.7	266.5
$S(s$, rhombic)	0	0	31.8
$H_2S(g)$	−20.1	−33.1	205.9
$SF_6(g)$	−1096.2	−991.6	290.8
$SO_2(g)$	−296.2	−300.4	248.5
$SO_3(g)$	−395.4	−370.3	256.1
$H_2SO_4(l)$	−811.3	−690.1	156.9
$Se(s)$	0	0	42.3
$H_2Se(g)$	85.8	71.1	221.3
$SeO_2(s)$	−236		
$Te(s)$	0	0	49.8
$H_2Te(g)$	154.4	138.5	243.2
$F_2(g)$	0	0	203.3
$HF(g)$	−268.6	−270.7	173.6
$Cl_2(g)$	0	0	223

ELEMENTS AND INORGANIC COMPOUNDS *Continued*

Name	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K
$HCl(g)$	−92.5	−95.4	186.6
$Br_2(l)$	0	0	152.3
$Br_2(g)$	30.5	3.3	245.2
$HBr(g)$	−36.4	−53.1	198.3
$BrF(g)$	−46	−61.5	229.3
$BrF_3(g)$	−313.8	−288.7	292.5
$I_2(s)$	0	0	116.7
$I_2(g)$	62.3	19.2	260.7
$HI(g)$	25.9	1.3	206.3
$IF_5(g)$	−816.3	−746	329.3
$ICl_3(s)$	−88.3	−22.6	172
$Co(s)$	0	0	30.1
$CoCl_2(s)$	−312.5	−269.9	109.2
$Cr(s)$	0	0	23.8
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
$CrCl_2(s)$	−395.4	−356.1	115.5
$CrCl_3(s)$	−556.5	−486.2	123
$Fe(s)$	0	0	27.2
$FeO(s)$	−266.5	−244.3	54
$Fe_2O_3(s)$	−822.2	−741	90
$Ni(s)$	0	0	30.1
$NiCl_2{\cdot}6H_2O(s)$	−2103.3	−1713.3	344.3
$Ti(s)$	0	0	30.5
$TiCl_4(l)$	−802.1	−737.2	252.3
$TiO_2(s)$	−944.7	−889.1	50.2
$Cu(s)$	0	0	33.5
$CuO(s)$	−157.3	−129.7	42.7
$CuCl_2{\cdot}2H_2O(s)$	−821.3	−656.1	167.4
$CuSO_4(s)$	−769.9	−661.9	113.4
$Zn(s)$	0	0	41.4
$ZnO(s)$	−348.1	−318.4	43.5
$ZnCl_2(s)$	−415.5	−369.4	111.7
$Cd(s)$	0	0	51.9
$CdS(s)$	−161.9	−156.5	64.9
$Hg(l)$	0	0	77.4
$HgCl_2(s)$	−230.1	−185.8	144.3
$Hg_2Cl_2(s)$	−264.8	−210.9	195.8
$HgO(s)$	−90.4	−58.6	72
$Ag(s)$	0	0	42.7
$AgF(s)$	−204.6	−229.6	84.0
$AgCl(s)$	−127.2	−109.6	96.2
$AgBr(s)$	−100.4	−96.9	107.1
$AgI(s)$	−61.8	−66.2	115.5
$AgNO_3(s)$	−123	−32.2	141

ORGANIC COMPOUNDS

COMPOUND	STATE	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K	CLASS
Methane	*g*	−74.9	50.6	186	alkane
Ethane	*g*	−84.5	−33.0	230	alkane
Propane	*g*	−104.0	−23.0	270	alkane
Butane	*g*	−127.2	−17.0	310	alkane
Pentane	*g*	−146.4	−8.4	349	alkane
Pentane	*l*	−173.2	−9.5	263	alkane
Hexane	*g*	−167.2	−0.3	388	alkane
Hexane	*l*	−198.8	−4.4	296	alkane
Heptane	*g*	−187.8	8.0	429	alkane
Heptane	*l*	−224.4	1.8	326	alkane
2-Methylpropane	*g*	−135.6	−21.0	295	alkane
2-Methylbutane	*g*	−154.4	−14.8	344	alkane
2-Methylbutane	*l*	−179.9	−15.2	260	alkane
2,2-Dimethylpropane	*g*	−166.0	−15.2	306	alkane
Cyclopropane	*g*	53.1	104.4	237	alkane
Cyclobutane	*g*	27.0	110.0	265	alkane
Cyclopentane	*g*	−77.4	38.6	293	alkane
Cyclopentane	*l*	−105.9	36.4	49	alkane
Cyclohexane	*g*	−123.0	31.8	298	alkane
Cyclohexane	*l*	−156.2	26.7	204	alkane
cis-1,2-Dimethylcyclohexane	*l*	−211.9	31.5	274	alkane
trans-1,2-Dimethylcyclohexane	*l*	−218.4	25.2	273	alkane
Propene	*g*	20.4	62.7	267	alkene
1,3-Butadiene	*g*	110.2	150.7	279	alkene
1-Butene	*g*	−0.1	71.3	306	alkene
Z-2-Butene	*g*	−7.0	65.9	301	alkene
E-2-Butene	*g*	−11.2	63.0	296	alkene
2-Methylpropene	*g*	−16.9	58.1	294	alkene
2-Methyl-1-butene	*g*	−36.3	65.6	340	alkene
2-Methyl-2-butene	*g*	−42.6	59.7	339	alkene
3-Methyl-1-butene	*g*	−29.0	74.8	333	alkene
Cyclohexene	*l*	−38.8	101.6	216	alkene
Cyclohexene	*g*	−5.4	106.9	311	alkene
1-Methylcyclopentene	*g*	−5.4	102.1	326	alkene
3-Methylcyclopentene	*g*	8.7	115.0	331	alkene
4−Methylcyclopentene	*g*	14.8	121.6	329	alkene
Ethene	*g*	52.3	68.1	219	alkene
Ethyne	*g*	226.7	209.0	201	alkyne
Propyne	*g*	185.4	194.6	248	alkyne
1-Butyne	*g*	165.2	202.1	291	alkyne
2-Butyne	*g*	146.3	185.4	283	alkyne
Benzene	*g*	82.8	129.7	268	aromatic
Benzene	*l*	49.0	124.3	172	aromatic
Styrene	*l*	103.8	202.5	238	aromatic
Toluene	*g*	50.0	122.0	320	aromatic
Toluene	*l*	12.0	113.8	221	aromatic
Ethylbenzene	*l*	−12.5	119.7	255	aromatic
m-Xylene	*l*	−25.4	107.7	252	aromatic
o-Xylene	*l*	−24.4	110.5	246	aromatic
p-Xylene	*l*	−24.4	110.0	248	aromatic
n-Propylbenzene	*l*	−38.4	124.7	288	aromatic
Isopropylbenzene (cumene)	*l*	−41.2	124.3	280	aromatic
Nitrobenzene	*l*	15.9	146.2	224	aromatic
1,2-Dibromobutane	*g*	−99.2	−13.1	409	alkyl halide
1,3-Dichloropropane	*g*	−161.5	−82.6	367	alkyl halide

ORGANIC COMPOUNDS *Continued*

COMPOUND	STATE	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K	CLASS
1-Bromobutane	*g*	−107.3	−12.9	370	alkyl halide
1-Bromopropane	*g*	−87.9	−22.5	331	alkyl halide
1-Chloro-2-methylpropane	*g*	−159.4	−49.7	354	alkyl halide
1-Chlorobutane	*g*	−147.3	−38.8	358	alkyl halide
1-Chloropropane	*g*	−130.1	−50.7	319	alkyl halide
2,3-Dibromobutane	*g*	−102.1	−11.9	395	alkyl halide
2-Bromo-2-methylpropane	*g*	−133.9	−28.2	332	alkyl halide
2-Bromobutane	*g*	−120.1	−25.8	370	alkyl halide
2-Bromopropane	*g*	−97.1	−27.2	316	alkyl halide
2-Chloro-2-methylpropane	*g*	−183.3	−64.1	322	alkyl halide
2-Chlorobutane	*g*	−161.5	−53.5	360	alkyl halide
2-Chloropropane	*g*	−146.4	−62.5	304	alkyl halide
Benzyl bromide	*g*	83.7	141.3	380	alkyl halide
Bromomethane	*g*	−37.7	−28.2	246	alkyl halide
Chloroform	*g*	−101.3	−68.5	296	alkyl halide
Chloroform	*l*	−132.2	−71.8	203	alkyl halide
Chloromethane	*g*	−86.3	−62.9	234	alkyl halide
Dichloromethane	*g*	−95.4	−68.9	270	alkyl halide
Dichloromethane	*l*	−124.3	−70.4	179	alkyl halide
Diiodomethane	*g*	122.0	101.4	310	alkyl halide
Fluoromethane	*g*	−233.9	−210.0	223	alkyl halide
Iodomethane	*g*	14.0	15.6	254	alkyl halide
Iodomethane	*l*	−13.8	15.1	163	alkyl halide
Tetrachloromethane	*g*	−95.8	−53.6	310	alkyl halide
Tetrafluoroethene	*g*	−649.0	−623.7	300	alkyl halide
Tetrafluoromethane	*g*	−933.0	−888.3	262	alkyl halide
Tribromomethane (bromoform)	*g*	25.1	15.8	331	alkyl halide
Trifluoromethane	*g*	−693.0	−658.9	259	alkyl halide
Methanol	*l*	−238.6	−166.2	127	alcohol
Methanol	*g*	−201.2	−162.5	240	alcohol
Ethanol	*l*	−277.0	−174.1	161	alcohol
Ethanol	*g*	−234.8	−168.3	283	alcohol
1-Propanol	*l*	−304.6	−170.7	193	alcohol
1-Propanol	*g*	−257.5	−163.0	325	alcohol
2-Propanol	*l*	−318.0	−180.4	181	alcohol
2-Propanol	*g*	−272.6	−173.6	310	alcohol
1-Butanol	*l*	−325.8	−161.1	226	alcohol
1-Butanol	*g*	−274.4	−150.7	363	alcohol
2-Butanol	*g*	−292.3	−167.3	359	alcohol
2-Methyl-2-propanol	*g*	−325.8	−191.0	326	alcohol
2-Methyl-2-propanol	*l*	−359.3	−184.8	193	alcohol
2-Methyl-2-propanol	*s*	−365.9	−184.8	171	alcohol
1-Pentanol	*l*	−357.9	−161.3	255	alcohol
1-Pentanol	*g*	−302.4	−149.7	403	alcohol
2-Methyl-2-butanol	*l*	−379.5	−175.2	229	alcohol
2-Methyl-2-butanol	*g*	−329.1	−165.8	367	alcohol
Cyclohexanol	*l*	−348.2	−133.3	200	alcohol
Cyclohexanol	*g*	−294.6	−117.9	328	alcohol
Benzyl alcohol	*l*	−161.0	−27.5	217	alcohol
Diethyl ether (ether)	*g*	−252.2	−122.3	343	ether
Diethyl ether (ether)	*l*	−279.5	−122.9	253	ether
Dimethyl ether	*g*	−184.1	−112.9	267	ether
Diphenyl ether	*l*	−14.6	144.2	291	ether
Ethyl vinyl ether	*g*	−140.2			ether
Ethylene oxide	*g*	−52.6	−13.1	242	ether

Continued on the next page

ORGANIC COMPOUNDS *Continued*

COMPOUND	STATE	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K	CLASS
Ethylene oxide	*l*	−77.4	−11.4	154	ether
Methyl ethyl ether	*g*	−216.4	−117.7	311	ether
Methyl isopropyl ether	*g*	−252.0	−120.9	338	ether
Methyl phenyl ether	*l*	−119.7			ether
Methyl propyl ether	*g*	−237.7	−109.9	349	ether
Propylene oxide	*g*	−92.8	−25.8	287	ether
Propylene oxide	*l*	−120.7	−26.7	196	ether
Tetrahydrofuran	*l*	−216.2			ether
Benzaldehyde	*l*	−89.1	9.4		aldehyde
Butanal	*g*	−205.0	−114.8	345	aldehyde
Butanal	*l*	−238.7	−119.2	247	aldehyde
Ethanal	*g*	−166.4	−133.3	264	aldehyde
Methanal	*g*	−115.9	−109.9	219	aldehyde
2-Methylbutanal	*l*	−250.2			aldehyde
Propanal	*g*	−192.0	−130.5	305	aldehyde
Benzoic acid	*s*	−385.1	−245.3	168	acid
Benzoic acid	*g*	−290.2	−210.4	369	acid
Butanoic acid	*l*	−533.9	−377.7	226	acid
Ethanoic acid (acetic acid)	*l*	−484.1	−389.4	160	acid
Hexanoic acid	*l*	−583.7			acid
Methanoic acid (formic acid)	*l*	−424.8	−361.5	129	acid
Pentanoic acid	*l*	−560.2	−373.4	260	acid
Propanoic acid	*l*	−510.9	−383.5		acid
2-Chlorobenzoic acid	*s*	−424.7			acid
2-Nitrobenzoic acid	s	−423.4	−196.4	208	acid
3-Chlorobenzoic acid	*s*	−400.0			acid
3-Nitrobenzoic acid	s	−413.8	−220.5	205	acid
4-Chlorobenzoic acid	*s*	−427.2			acid
4-Nitrobenzoic acid	s	−420.9	−220.0	210	acid
Adipic acid	*s*	−989.5			diacid
Fumaric acid	*s*	−811.1	−653.7	166	diacid
Maleic acid	*s*	−790.6	−631.2	159	diacid
Malonic acid	*s*	−891.1			diacid
Succinic acid	*s*	−940.9	−747.4	176	diacid
Ethyl ethanoate	*l*	−479.0	−332.7	259	ester
Ethyl methanoate	*l*	−399.3			ester
Ethyl propionate	*l*	−477.8	−331.2		ester
Methyl benzoate	*l*	−340.6			ester
Methyl ethanoate	*l*	−409.6			ester
Methyl methanoate	*g*	−349.8	−297.2	301	ester
2-Butanone	*g*	−238.4	−146.1	338	ketone
2-Butanone	*l*	−273.3	−151.4	239	ketone
2-Pentanone	*g*	−258.7	−137.1	376	ketone
2-Pentanone	*l*	−300.0	−147.5	272	ketone
2-Propanone (acetone)	*g*	−217.6	−153.1	295	ketone
2-Propanone (acetone)	*l*	−248.1	−155.4	200	ketone
3-Pentanone	*g*	−258.7	−135.3	370	ketone
Acetophenone	*l*	−142.5	−17.0	249	ketone
Cyclohexanone	*g*	−230.1	−90.8	322	ketone
Phenol	*g*	−96.4	−32.9	316	phenol
Phenol	*s*	−165.0	−50.4	144	phenol
2-Nitrophenol	*s*	−210.5			phenol
3-Nitrophenol	*s*	−194.1			phenol
4-Nitrophenol	*s*	−194.1			phenol
2-Methylphenol (o-cresol)	*g*	−128.6	−37.1	358	phenol

ORGANIC COMPOUNDS *Continued*

COMPOUND	STATE	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K	CLASS
3-Methylphenol (m-cresol)	*g*	−132.3	−40.5	357	phenol
4-Methylphenol (p-cresol)	*g*	−125.4	−30.9	348	phenol
Hydroquinone	*s*	−366.1	−207.0	140	phenol
Acetyl chloride	*g*	−243.9	−206.2	295	acid halide
Benzoyl chloride	*l*	−164.4			acid halide
Benzoyl bromide	*l*	−106.7			acid halide
Acetic anhydride	*g*	−575.7	−476.7	390	anhydride
Acetic anhydride	*l*	−624.0	−488.8	269	anhydride
Benzoic anhydride	*s*	−431.4			anhydride
Acetamide	*s*	−317.6			amide
Formamide	*l*	−186.2	−141.0	248	amide
Acetanilide	*s*	−210.5			amide
Benzamide	*s*	−202.8			amide
Benzanilide	*s*	−90.0			amide
Methylamine	*g*	−23.0	32.3	243	amine
Ethylamine	*g*	−46.0	37.3	285	amine
Dimethylamine	*g*	−18.8	68.0	273	amine
n-Propylamine	*g*	−72.4	39.8	324	amine
Trimethylamine	*g*	−23.8	98.9	289	amine
n-Butylamine	*g*	−92.0	49.2	363	amine
Diethylamine	*g*	−72.4	72.1	352	amine
2-Aminobutane	*g*	−104.2	40.6	351	amine
2-Amino-2-methylpropane	*g*	−119.9	28.9	338	amine
Triethylamine	*g*	−99.6	110.3	405	amine
N,N-Dimethylaniline	*g*	84.1	231.2	366	amine
N,N-Dimethylaniline	*l*	34.3	214.2	256	amine
N-Ethylaniline	*g*	56.1	207.4	352	amine
N-Ethylaniline	*l*	3.8	188.7	239	amine
Aniline	*g*	86.9	166.7	319	amine
Aniline	*l*	31.1	149.1	191	amine
2-Nitroaniline	*s*	−12.6	178.2	176	amine
3-Nitroaniline	*s*	−17.2	174.0	176	amine
4-Nitroaniline	*s*	−41.5	151.0	176	amine
Acetonitrile	*g*	87.9	105.6	243	nitrile
Acetonitrile	*l*	53.1	98.9	150	nitrile
Benzonitrile	*g*	218.8	260.9	321	nitrile
Propionitrile	*g*	50.6	96.1	287	nitrile
Propionitrile	*l*	14.6	89.2	189	nitrile
Methyl radical	*g*	144	194	194	radical
Ethyl radical	*g*	111	243	248	radical
1-Propyl radical	*g*	87.9	287		radical
2-Propyl radical	*g*	73.6	279		radical
2-Methyl-2-propyl radical	*g*	35	302		radical
2-Methyl-1-propyl radical	*g*	57.3	315		radical
Allyl radical	*g*	170	260		radical
Benzyl radical	*g*	188	315		radical
Phenyl radical	*g*	328	290		radical
Cyclohexyl radical	*g*	54	318		radical
Cyclohexen-3-yl radical	*g*	126	314		radical
1,3-Cyclohexadien-5-yl	*g*	209	289		radical
Vinyl radical	*g*	289	236		radical
Trifluoromethyl radical	*g*	−465	267		radical
Trichloromethyl radical	*g*	77.4	296		radical

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ORGANIC COMPOUNDS *Continued*

COMPOUND	STATE	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K	CLASS
Perfluoroethyl radical	*g*	−891	341		radical
Ethynyl radical	*g*	510	208		radical
Methylene (carbene)	*g*	360	194		radical
Dichlorocarbene	*g*	197	267		radical
Difluorocarbene	*g*	−187	241		radical
Methyoxyl radical	*g*	15	230		radical
Ethoxyl radical	*g*	−17	273		radical
2-Methyl-2-propoxyl radical	*g*	−90.4	317		radical
Acyl radical	*g*	−23	270		radical

Standard Formation Data for Aqueous Ions

A. CATIONS

ION	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	S°, J/mol K
H^+	0	0	0
Li^+	−278	−294	14
Na^+	−240	−262	59
K^+	−251	−282	103
Rb^+	−246	−282	124
Cs^+	−248	−282	133
Cu^+	72	50	41
Ag^+	106	77	73
Tl^+	5	−32	126
NH_4^+	−132	−79	113
Be^{2+}	−383	−380	−130
Mg^{2+}	−467	−455	−138
Ca^{2+}	−543	−554	−53
Sr^{2+}	−546	−559	−33
Ba^{2+}	−538	−561	10
Cr^{2+}	−144	−164	
Mn^{2+}	−221	−228	−74
Fe^{2+}	−89	−79	−138
Co^{2+}	−58	−54	−113
Ni^{2+}	−54	−46	−129
Cu^{2+}	65	66	−100
Zn^{2+}	−154	−147	−112
Cd^{2+}	−76	−78	−73
Hg^{2+}	171	164	−32
Sn^{2+}	−9	−27	−17
Pb^{2+}	−2	−24	10
Al^{3+}	−531	−485	−322
Ga^{3+}	−212	−159	−331
In^{3+}	−105	−98	−264
Tl^{3+}	197	215	−192
Cr^{3+}	−251	−205	
Fe^{3+}	−49	−5	−316
Co^{3+}	92	134	−305
$Ag(NH_3)_2^+$	−112	−18	242
F^-	−333	−279	−14
Cl^-	−167	−131	57
Br^-	−121	−104	83
I^-	−57	−52	107
ClO^-	−107	−37	42

Standard Formation Data for Aqueous Ions ***Continued***

A. CATIONS

ION	$\Delta H_f°$, kJ/mol	$\Delta G_f°$, kJ/mol	$S°$, J/mol K
ClO_2^-	−67	17	101
ClO_3^-	−99	−3	162
ClO_4^-	−129	−9	192
BrO_3^-	−84	2	163
IO_3^-	−221	−128	118
OH^-	−230	−157	−11
SH^-	−18	12	63
S_2^{2-}	33	86	−15
HSO_4^-	−887	−756	132
SO_3^{2-}	−635	−487	−29
SO_4^{2-}	−909	−745	20
SeO_3^{2-}	−509	−370	13
SeO_4^{2-}	−599	−441	54
NO_2^-	−105	−37	140
NO_3^-	−207	−111	146
N_3^-	275	348	108
PO_4^{3-}	−1290	−1032	−222
CO_3^{2-}	−677	−528	−57
HCO_3^-	−692	−587	91
CN^-	151	172	94
BF_4^-	−1575	−1487	180
MnO_4^-	−541	−447	191
CrO_4^{2-}	−881	−728	50
$Cr_2O_7^{2-}$	−1490	−1301	262

APPENDIX
4
K_{sp}

BROMIDES

$PbBr_2$	4.6×10^{-6}
Hg_2Br_2	1.3×10^{-22}
$AgBr$	7.7×10^{-13}

CARBONATES

$BaCO_3$	8.1×10^{-9}
$CdCO_3$	2.5×10^{-14}
$CaCO_3$	8.7×10^{-9}
$CuCO_3$	1.3×10^{-10}
$FeCO_3$	5×10^{-11}
$PbCO_3$	1.6×10^{-13}
$MgCO_3$	8×10^{-11}
$NiCO_3$	1.3×10^{-7}
Ag_2CO_3	1.3×10^{-11}
$SrCO_3$	1.3×10^{-9}
$ZnCO_3$	1.0×10^{-7}

CHLORIDES

$AgCl$	1.8×10^{-10}
$PbCl_2$	1.0×10^{-4}
Hg_2Cl_2	2.0×10^{-18}

CYANIDES

$Hg_2(CN)_2$	5×10^{-40}
$AgCN$	1.6×10^{-14}

CHROMATES

$PbCrO_4$	1.7×10^{-14}
Ag_2CrO_4	1.9×10^{-12}
$BaCrO_4$	2.3×10^{-10}
$CuCrO_4$	3.6×10^{-6}
$CaCrO_4$	7.1×10^{-4}
Hg_2CrO_4	2.0×10^{-9}

FLUORIDES

BaF_2	1.6×10^{-6}
CaF_2	4×10^{-11}
LiF	5×10^{-3}
PbF_2	4×10^{-8}
MgF_2	6×10^{-9}
SrF_2	3×10^{-9}

HYDROXIDES

$Al(OH)_3$	5×10^{-33}
$Cd(OH)_2$	2×10^{-14}
$Ca(OH)_2$	6×10^{-6}
$Cr(OH)_3$	7×10^{-31}
$Co(OH)_3$	1×10^{-43}
$Co(OH)_2$	3×10^{-16}
$Cu(OH)_2$	2×10^{-19}
$Fe(OH)_3$	6×10^{-38}
$Fe(OH)_2$	2×10^{-15}
$Pb(OH)_2$	4×10^{-15}
$Mg(OH)_2$	1.8×10^{-11}
$Mn(OH)_2$	2×10^{-13}
$Ni(OH)_2$	2×10^{-16}
$Zn(OH)_2$	5×10^{-17}

IODIDES

Hg_2I_2	5×10^{-29}
AgI	8×10^{-17}
PbI_2	1.4×10^{-8}

OXALATES

BaC_2O_4	1.6×10^{-7}
CaC_2O_4	1.9×10^{-9}
MgC_2O_4	9.6×10^{-5}
SrC_2O_4	6.0×10^{-8}
$Ag_2C_2O_4$	8.9×10^{-12}
PbC_2O_4	3×10^{-11}

PHOSPHATES

Ag_3PO_4	1.4×10^{-16}
$Ca_3(PO_4)_2$	1×10^{-25}
$Mg_3(PO_4)_2$	4×10^{-25}

SULFATES

$BaSO_4$	1.0×10^{-10}
$CaSO_4$	2×10^{-5}
$PbSO_4$	1.6×10^{-8}
Hg_2SO_4	7×10^{-7}
Ag_2SO_4	6×10^{-5}
$SrSO_4$	3×10^{-7}

SULFIDES			
CdS	1×10^{-28}	MnS	1×10^{-11}
CoS	1×10^{-22}	HgS	1×10^{-54}
CuS	1×10^{-36}	NiS	1×10^{-22}
FeS	1×10^{-18}	Ag_2S	1×10^{-50}
PbS	1×10^{-28}	SnS	1×10^{-25}
		ZnS	1×10^{-23}

APPENDIX 5

K_a, K_b

ACID CONSTANTS

COMPOUND	K_a	COMPOUND	K_a
HF	3.5×10^{-4}	*o*-FC_6H_4COOH	5.4×10^{-4}
$HOCl$	3.0×10^{-8}	*m*-FC_6H_4COOH	1.4×10^{-4}
$HClO_2$	1.0×10^{-2}	*p*-FC_6H_4COOH	7.2×10^{-5}
H_2S	1×10^{-7}, 1×10^{-13}	*o*-ClC_6H_4COOH	1.2×10^{-3}
H_2SO_3	1.3×10^{-2}, 5.6×10^{-8}	*m*-ClC_6H_4COOH	1.5×10^{-4}
H_2Se	2.0×10^{-4}, 1.0×10^{-11}	*p*-ClC_6H_4COOH	1.0×10^{-4}
H_2Te	2.5×10^{-3}, 5.0×10^{-11}	*o*-$NO_2C_6H_4COOH$	7.0×10^{-3}
HNO_2	4.6×10^{-4}	*m*-$NO_2C_6H_4COOH$	3.4×10^{-4}
HCN	4.9×10^{-10}	*p*-$NO_2C_6H_4COOH$	3.9×10^{-4}
H_2CO_3	4.2×10^{-7}, 4.8×10^{-11}	*p*-$CH_3C_6H_4COOH$	4.2×10^{-5}
$H_2C_2O_4$	5.9×10^{-2}, 6.4×10^{-5}	*p*-$CH_3OC_6H_4COOH$	3.4×10^{-5}
H_3PO_4	7.5×10^{-3}, 6.2×10^{-8},	*p*-$H_2NC_6H_4COOH$	1.2×10^{-5}
	2.2×10^{-13}	C_2H_5SH	2.5×10^{-11}
$HOOCCH_2COOH$	1.5×10^{-3}, 2.0×10^{-6}	$BrCH_2COOH$	1.4×10^{-3}
$HCOOH$	1.8×10^{-4}	ICH_2COOH	7.6×10^{-4}
CH_3COOH	1.8×10^{-5}	CH_3CH_2COOH	1.3×10^{-5}
FCH_2COOH	2.2×10^{-3}	C_6H_5COOH	6.5×10^{-5}
$F_2CHCOOH$	6.0×10^{-2}	*o*-$C_6H_4(COOH)_2$	1.3×10^{-3}, 3.9×10^{-6}
F_3CCOOH	6.0×10^{-1}	C_6H_5OH	1.3×10^{-10}
$ClCH_2COOH$	1.4×10^{-3}	*o*-$NO_2C_6H_4OH$	6.8×10^{-8}
$Cl_2CHCOOH$	3.3×10^{-2}	*m*-$NO_2C_6H_4OH$	5.3×10^{-9}
Cl_3CCOOH	2.0×10^{-1}	*p*-$NO_2C_6H_4OH$	7.0×10^{-8}

BASE CONSTANTS

COMPOUND	K_b	COMPOUND	K_b
NH_3	1.8×10^{-5}	$C_6H_5NH_2$	3.8×10^{-10}
H_2NNH_2	1.0×10^{-6}	$C_6H_5N(CH_3)_2$	1.0×10^{-9}
H_2NOH	1.1×10^{-8}	*o*-$FC_6H_4NH_2$	1.6×10^{-11}
$(CH_3)_3N$	6.5×10^{-5}	*m*-$FC_6H_4NH_2$	2.5×10^{-11}
$(C_2H_5)_3N$	4.0×10^{-4}	*p*-$FC_6H_4NH_2$	4.5×10^{-10}
$(C_2H_5)_2NH$	1.3×10^{-3}	*o*-$NO_2C_6H_4NH_2$	2.0×10^{-14}
$C_2H_5NH_2$	5.6×10^{-4}	*m*-$NO_2C_6H_4NH_2$	2.5×10^{-12}
$C_6H_5CH_2NH_2$	2.0×10^{-5}	*p*-$CH_3C_6H_4NH_2$	1.0×10^{-9}
$(C_2H_5)_3P$	5.0×10^{-8}	*p*-$CH_3OC_6H_4NH_2$	2.2×10^{-9}
$(C_2H_5)_3As$	5.0×10^{-12}	pyridine	1.4×10^{-9}

APPENDIX 6

Standard Electrode Potentials

ACIDIC MEDIA

HALF-REACTION		$E°$, V	HALF-REACTION		$E°$, V
$F_2(g) + 2\ H^+ + 2e^-$	$= 2\ HF(aq)$	3.06	$SO_4^{2-} + 4\ H^+ + 2e^-$	$= H_2SO_3 + H_2O$	0.17
$F_2 + 2e^-$	$= 2\ F^-$	2.87	$Sn^{4+} + 2e^-$	$= Sn^{2+}$	0.15
$S_2O_8^{2-} + 2e^-$	$= 2SO_4^{2-}$	2.01	$S(\text{rhombic}) + 2\ H^+ + 2e^-$	$= H_2S(aq)$	0.14
$Co^{3+} + e^-$	$= Co^{2+}$	1.82	$CuCl + e^-$	$= Cu + Cl^-$	0.14
$H_2O_2 + 2\ H^+ + 2e^-$	$= 2\ H_2O$	1.78	$TiO^{2+} + 2\ H^+ + e^-$	$= Ti^{3+} + H_2O$	0.10
$MnO_4^- + 4\ H^+ + 3e^-$	$= MnO_2(s) + 2\ H_2O$	1.70	$S_4O_6^{2-} + 2e^-$	$= 2S_2O_3^{2-}$	0.09
$H_5IO_6 + H^+ + 2e^-$	$= IO_3^- + 3\ H_2O$	1.64	$AgBr(s) + e^-$	$= Ag + Br^-$	0.07
$Ce^{4+} + e^-$	$= Ce^{3+}$	1.61	$2H^+ + 2e^-$	$= H_2(g)$	0.00
$BrO_3^- + 6\ H^+ + 5e^-$	$= 1/2\ Br_2(l) + 3H_2O$	1.52	$Pb^{2+} + 2e^-$	$= Pb$	−0.13
$MnO_4^- + 8\ H^+ + 5e^-$	$= Mn^{2+} + 4\ H_2O$	1.51	$Sn^{2+} + 2e^-$	$= Sn(\text{white})$	−0.14
$PbO_2 + 4\ H^+ + 2e^-$	$= Pb^{2+} + 2\ H_2O$	1.46	$AgI(s) + e^-$	$= Ag + I^-$	−0.15
$Cl_2 + 2e^-$	$= 2Cl^-$	1.36	$Mo^{3+} + 3e^-$	$= Mo$	−0.20
$Cr_2O_7^{2-} + 14\ H^+ + 6e^-$	$= 2Cr^{3+} + 7\ H_2O$	1.33	$Ni^{2+} + 2e^-$	$= Ni$	−0.25
$MnO_2(s) + 4\ H^+ + 2e^-$	$= Mn^{2+} + 2\ H_2O$	1.23	$V^{3+} + e^-$	$= V^{2+}$	−0.26
$O_2(g) + 4\ H^+ + 4e^-$	$= 2\ H_2O(l)$	1.23	$Co^{2+} + 2e^-$	$= Co$	−0.28
$IO_3^- + 6\ H^+ + 5e^-$	$= 1/2\ I_2 + 3\ H_2O$	1.20	$[Ag(CN)_2]^- + e^-$	$= Ag + 2\ CN^-$	−0.31
$Br_2(aq) + 2e^-$	$= 2\ Br^-$	1.09	$Cd^{2+} + 2e^-$	$= Cd$	−0.40
$VO_2^+ + 2\ H^+ + e^-$	$= VO^{2+} + H_2O$	1.00	$Cr^{3+} + e^-$	$= Cr^{2+}$	−0.41
$HNO_2 + H^+ + e^-$	$= NO(g) + H_2O$	1.00	$Fe^{2+} + 2e^-$	$= Fe$	−0.44
$NO_3^- + 3\ H^+ + 2e^-$	$= HNO_2 + H_2O$	0.94	$2CO_2 + 2\ H^+ + 2e^-$	$= H_2C_2O_4$	−0.49
$2\ Hg^{2+} + 2e^-$	$= Hg_2^{2+}$	0.92	$U^{4+} + e^-$	$= U^{3+}$	−0.61
$Ag^+ + e^-$	$= Ag$	0.80	$Cr^{3+} + 3e^-$	$= Cr$	−0.74
$Hg_2^{2+} + 2e^-$	$= 2Hg(l)$	0.79	$Zn^{2+} + 2e^-$	$= Zn$	−0.76
$NO_3^- + 2\ H^+ + e^-$	$= NO_2 + H_2O$	0.78	$Mn^{2+} + 2e^-$	$= Mn$	−1.18
$Fe^{3+} + e^-$	$= Fe^{2+}$	0.77	$Zr^{4+} + 4e^-$	$= Zr$	−1.53
$O_2(g) + 2\ H^+ + 2e^-$	$= H_2O_2(aq)$	0.68	$Ti^{2+} + 2e^-$	$= Ti$	−1.63
$Hg_2SO_4(s) + 2e^-$	$= 2\ Hg + SO_4^{2-}$	0.62	$Al^{3+} + 3e^-$	$= Al$	−1.66
$H_3AsO_4(aq) + 2\ H^+ + 2e^-$	$= HAsO_2 + 2\ H_2O$	0.56	$Th^{4+} + 4e^-$	$= Th$	−1.90
$I_3^- + 2e^-$	$= 3I^-$	0.54	$Mg^{2+} + 2e^-$	$= Mg$	−2.37
$I_2 + 2e^-$	$= 2I^-$	0.54	$Ce^{3+} + 3e^-$	$= Ce$	−2.48
$Cu^+ + e^-$	$= Cu$	0.52	$La^{3+} + 3e^-$	$= La$	−2.52
$O_2 + 2H_2O + 4e^-$	$= 4OH^-$	0.40	$Na^+ + e^-$	$= Na$	−2.71
$VO^{2+} + 2\ H^+ + e^-$	$= V^{3+} + H_2O$	0.36	$Ca^{2+} + 2e^-$	$= Ca$	−2.87
$[Fe(CN)_6]^{3-} + e^-$	$= [Fe(CN)_6]^{4-}$	0.36	$Sr^{2+} + 2e^-$	$= Sr$	−2.89
$Cu^{2+} + 2e^-$	$= Cu$	0.34	$Ba^{2+} + 2e^-$	$= Ba$	−2.91
$UO_2^{2+} + 4\ H^+ + 2e^-$	$= U^{4+} + 2H_2O$	0.33	$Cs^+ + e^-$	$= Cs$	−2.92
$BiO^+ + 2\ H^+ + 3e^-$	$= Bi + H_2O$	0.32	$K^+ + e^-$	$= K$	−2.92
$Hg_2Cl_2(s) + 2e^-$	$= 2\ Hg + 2Cl^-$	0.27	$Li^+ + e^-$	$= Li$	−3.04
$AgCl(s) + e^-$	$= Ag + Cl^-$	0.22	$ClO^- + H_2O + 2e^-$	$= Cl_2 + 2\ OH_2$	0.89
$SbO^+ + 2\ H^+ + 3e^-$	$= Sb + H_2O$	0.21	$HO_2^- + H_2O + 2e^-$	$= 3\ OH^-$	0.88

BASIC MEDIA					
HALF-REACTION		E°, V	HALF-REACTION		E°, V
$BrO^- + H_2O + 2e^-$	$= Br^- + 2\,OH^-$	0.76	$2Cu(OH)_2 + 2e^-$	$= Cu_2O + 2OH^- + H_2O$	−0.09
$ClO_2^- + 2\,H_2O + 4e^-$	$= Cl^- + 4\,OH^-$	0.76	$CrO_4^{2-} + 4\,H_2O + 3e^-$	$= Cr(OH)_3 + 5\,OH^-$	−0.12
$ClO_3^- + 3\,H_2O + 6e^-$	$= Cl^- + 6\,OH^-$	0.62	$Cu(OH)_2 + 2e^-$	$= Cu + 2\,OH^-$	−0.22
$BrO_3^- + 3\,H_2O + 6e^-$	$= Br^- + 6\,OH^-$	0.61	$Bi_2O_3 + 3\,H_2O + 6e^-$	$= 2Bi + 6\,OH^-$	−0.46
$MnO_4^{2-} + 2\,H_2O + 2e^-$	$= MnO_2 + 4OH^-$	0.60	$NO^- + H_2O + e^-$	$= NO + 2\,OH^-$	−0.46
$MnO_4^- + 2\,H_2O + 3e^-$	$= MnO_2 + 4OH^-$	0.59	$S + H_2O + 2e^-$	$= HS^- + OH^-$	−0.48
$IO^- + H_2O + 2e^-$	$= I^- + 2\,OH^-$	0.49	$HPbO_2^- + H_2O + 2e^-$	$= Pb + 3\,OH^-$	−0.54
$O_2 + 2\,H_2O + 4e^-$	$= 4\,OH^-$	0.40	$Fe(OH)_3 + e^-$	$= Fe(OH)_2 + OH^-$	−0.56
$ClO_4^- + H_2O + 2e^-$	$= ClO_3^- + 2\,OH^-$	0.36	$PbO + H_2O + 2e^-$	$= Pb + 2\,OH^-$	−0.58
$Ag_2O + H_2O + 2e^-$	$= 2\,Ag + 2\,OH^-$	0.34	$Ni(OH)_2 + 2e^-$	$= Ni + 2\,OH^-$	−0.72
$IO_3^- + 3\,H_2O + 6e^-$	$= I^- + 6\,OH^-$	0.26	$Co(OH)_2 + 2e^-$	$= Co + 2\,OH^-$	−0.73
$NO_3^- + H_2O + 2e^-$	$= NO_2^- + 2\,OH^-$	0.01	$Cd(OH)_2 + 2e^-$	$= Cd + 2\,OH^-$	−0.82
$O_2 + H_2O + 2e^-$	$= HO_2^- + OH^-$	−0.08	$2H_2O + 2e^-$	$= H_2 + 2\,OH^-$	−0.83

APPENDIX

7

Molal Boiling Point and Freezing Point Data

SOLVENT	K_f, °C kg/mol	Mpt, °C	K_b, °C kg/mol	Bpt, °C
Acetamide	4.04	80		221
Acetic acid	3.90	17	3.07	118
Acetone		−95	1.71	56
Aniline		−6	3.22	184
Antimony(III) chloride	17.95	73		220
Benzene	5.12	5.5	2.53	80
Bromobenzene		−31	6.26	156
Bromoform	14.4	8		150
2-Butanone		−87	2.28	80
DL-Camphor	39.7	179.7	5.611	204
Carbon disulfide		−112	2.35	46
Carbon tetrachloride	29.8	−23	5.03	77
Chlorobenzene		−46	4.15	132
Chloroform	4.68	−64	3.62	61
o-Cresol	5.60	31		191
p-Cresol	6.96	35		202
Cyclohexane	20.0	6	2.75	81
Cyclohexanol	39.3	25		161
Dibenzyl ether	6.27	4		298
1,2-Dibromoethane	12.5	9	6.608	131
Diethyl ether		−117	1.824	35
Dimethoxymethane		−105	2.125	42
N,N-Dimethylacetamide		−20	3.22	166
2,2-Dimethyl-1-propanol	11.0	53		113
Dimethyl sulfoxide	4.07	19		189
1,4-Dioxane	4.63	12	3.270	101
Diphenyl ether	7.88	27		258
Ethanol		−114	1.160	78
Ethyl acetate		−84	2.583	77
Formamide	3.85	3		211
Formic acid	2.77	8		101
Heptane		−91	3.43	98
N-Methylacetamide	6.65	31		206
Methyl acetate		−98	2.061	56
2-Methyl-2-propanol	8.37	26		82
Naphthalene	6.94	80	5.80	218
Nitrobenzene	6.852	6	5.24	211
Phenol	7.40	41	3.60	182
Piperidine		−10	2.84	106
1-Propanol		−126	1.59	97
Propionic acid		−21	3.51	140
Pyridine		−42	2.710	115
Sulfolane	64.1	27		285
1,1,2,2-Tetrabromoethane	21.7	0		244
Toluene		−95	3.29	111
Water	1.86	0	0.515	100
p-Xylene	4.3	13		138

Periodic Table

Main Group =	I	II											III	IV	V	VI	VII	VIII
	1 **H** 1,00794																1 **H** 1.00794	2 **He** 4.002602
	3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.998403	10 **Ne** 20.179
	11 **Na** 22.98977	12 **Mg** 24.305	**—Transition Elements—**										13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.95591	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.710	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
	55 **Cs** 132.9045	56 **Ba** 137.33	57 **La** 138.9055	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
	87 **Fr** (223)	88 **Ra** 226.0254	89 **Ac** 227.0278	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (269)	109 **Mt** (268)									

Lanthanides

58 **Ce** 140.12	59 **Pr** 140.9077	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.50	67 **Ho** 164.9304	68 **Er** 167.26	69 **Tm** 168.9342	70 **Yb** 173.04	71 **Lu** 174.967

Actinides

90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** 237.0482	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

APPENDIX
9

Metallic, Covalent and Ionic Radii (r, pm)[a]

ATOM/ION	r, pm
Ag	144
Ag^{+}	115
Al	143(140)
Al^{3+}	53
Ar	(95)
As	(122)
As^{3+}	58
Au	144
Au^{+}	137
B	(90)
Ba	224
Ba^{2+}	135
Be	112(125)
Be^{2+}	45
Bi	182
Bi^{3+}	103
Br	114
Br^{-}	196
C	(77)
Ca	197
Ca^{2+}	100
Cd	152
Cd^{2+}	95
Ce	182
Ce^{3+}	102
Cl	(99)
Cl^{-}	184
Co	125
Co^{2+}	70
Co^{3+}	60
Cr	129
Cr^{3+}	62
Cs	272
Cs^{+}	167
Cu	128
Cu^{+}	77
Cu^{2+}	73
F	(71)
F^{-}	133
Fe	126
Fe^{2+}	70
Fe^{3+}	60
Ga	153
Ga^{3+}	62
Ge	139(122)
H	(37)
He	(32)
Hf	159
Hg	155
Hg^{2+}	102
I	(133)
I^{-}	220
In	167
In^{3+}	80
Ir	136
Ir^{3+}	82
K	235
K^{+}	138
Kr	(110)
La	188
La^{3+}	103
Li	157
Li^{+}	76
Lu	172
Lu^{3+}	86
Mg	160
Mg^{2+}	72
Mn	137
Mn^{2+}	70
N	(75)
Na	191
Na^{+}	102
Ne	(69)
Ni	125
Ni^{2+}	70
O	(73)
O^{2-}	140
Os	135
P	(110)
Pb	175
Pb^{2+}	119
Pd	137
Pd^{2+}	86
Po	153
Pt	139
Pt^{2+}	80
Pt^{4+}	77
Rb	250
Rb^{+}	152
Rh	134
Rn	(145)
Ru	134
S	(102)
S^{2-}	184
Sb	161(143)
Sb^{3+}	76
Sc	164
Sc^{3+}	75
Se	(117)
Se^{2-}	198
Si	(118)
Sn	158(140)
Sn^{2+}	118
Sr	215
Sr^{2+}	118
Te	(135)
Te^{2-}	221
Th	180
Ti	147
Ti^{3+}	67
Tl	171
Tl^{+}	150
Tl^{3+}	88
U	156
V	135
V^{2+}	79
W	141
Xe	(130)
Y	182
Y^{3+}	90
Zn	137
Zn^{2+}	74
Zr	1

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[a] Metallic radii for 12-coordination are given for all metals. Covalent radii are in parentheses. Ionic radii are for six-coordination.

Measurement

When we measure something, what is it that we are actually doing? What is the purpose of the act of measurement? In general, measurements are designed to obtain and communicate information about a system under investigation. A measurement will generate a datum, or set of data (the word datum is singular, data plural), and that set of data is often used as a basis for making some type of decision. An experiment is a well-thought-out method designed to obtain the data necessary to answer a question or make a decision. We read a thermometer (an experiment or measurement) in the morning to obtain the temperature (a datum) which allows us to decide whether or not to wear our heavy jackets (a decision). If we do not have a thermometer, we can listen to the local weather to find out the current temperature. In this case, someone else has taken the measurement and is communicating the results to us, and we will make a decision based on our understanding of these results. The more effective the communication, the more sound our decision will be.

Results of scientific measurements may be used in a number of ways. The experiments may test new hypothesis and the data obtained may play a role in the development or rejection of a theory; analysis of blood may provide data that are critical in decisions related to the diagnosis and treatment of a life threatening disease; comparison of DNA data of a suspect to that obtained from body fluid found at a crime scene may be crucial to proving the suspect's guilt or innocence; and multi-million dollar business or legal judgments may depend on a few pieces of experimental data obtained from a sample. In each of these cases, it is essential for the person doing the experiment to be able to communicate clearly and concisely the outcome of the experiment. Often, data are used by persons not trained in science, and in these cases the ability to clearly communicate the scientific validity of the data is even more important. This laboratory prerequisite booklet is designed to provide an introduction to the concepts of measurement, errors, and the communication of results.

MEASUREMENTS

The information obtained by a measurement may be grouped into two categories, qualitative and quantitative. **Qualitative measurements** are general in nature, subjective, and open to interpretation and bias. They generally do not include numerical values or units. Examples like "the sky is blue" and "the water is hot" allow the recipient of the information to subjectively define "blue" or "how hot", and these definitions may not be at all close to the definition intended by the person having done the experiment, resulting in a failure to communicate. These types of measurements may serve a purpose and are generally easier to perform, but the information communicated is less detailed and of less value than data from a quantitative measurement.

A **quantitative result** consists of both a number and a unit of measurement. The number provides a relative value for the measurement, while the unit of measurement precisely defines the quantity, or dimension, which provides the basis on which the relative value is defined. For example, a qualitative measurement of temperature may be "it is cold", whereas a quantitative measurement would be "it is 1.2 °C", where the 1.2 provides a relative value and the °C provides the units which precisely define the relative basis for the number. Notice how the meaning of "it is cold" can be significantly different if we simply change the units on 1.2 from °C to kelvin, since 1.2 K is near absolute zero and much, much colder than 1.2 °C. Clearly, if you were told the temperature is 1.2 with no units provided, you would not be able to make any decisions based on this value until the question "1.2 what?" is answered. The answer to this question lies in the units of measurement, and they are essential to any quantitative measurement and should always be included in calculations and reports.

The magnitude of the measured quantity has been traditionally expressed by the metric system. In this decimal system, all units are powers of ten of some basic unit. The unit names are derived from the prefixes shown in **Table 1**. Thus, one kilometer (km) is equal to 10^3 meters (m) and one milligram (mg) is equal to 10^{-3} gram (g).

Table 1: Metric System Prefixes

FACTOR	PREFIX	SYMBOL
10^{12}	tetra	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{1}	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	m
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

UNITS

There are two distinct types of units, fundamental and derived. Fundamental units are defined and cannot be obtained from other units. In an effort to establish a uniform system of measurements which could be used by scientists throughout the world, the General Conference of Weights and Measurements in 1960 recommended that a single unit be used for each measured quantity. This *Système Internationale d'Unités* (**International System of Units)** abbreviated **SI**, is simply an adaptation of the metric system, which consists of seven fundamental base units (**Table 2**). Larger or smaller quantities are expressed by the use of the prefixes in **Table 1** with the appropriate base unit. Thus, for example, a quantity of electric current equal to one one-millionth (10^{-6}) of one ampere is called a microampere and is abbreviated mA; one million seconds is a mega second (Ms); and so on.

Table 2: SI Base Units

QUANTITY	NAME OF UNIT	SYMBOL
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Luminous intensity	candela	cd
Amount of Substance	mole	mol

SI units for all other physical quantities are derived from these seven base units. Derived units originate from mathematical operations or combinations of the fundamental units. The unit for area originates from multiplying two lengths (meters x meters) to give meters^2. The units for density, kg/m^3, result from the definition of density, which is mass (kg) per unit volume (m^3). Again, larger or smaller quantities of these derived units are expressed by the use of appropriate prefixes. **Table 3** lists several other derived units of importance in the study of chemistry.

Table 3: Some SI Derived Units

QUANTITY	NAME OF UNIT	SYMBOL	DEFINITION
Area	square meter		m^2
Volume	cubic meter		m^3
Density	kilogram per cubic meter		$\frac{kg}{m^3}$
Force	newton	N	$\frac{kg\text{-}m}{s^2}$
Pressure	pascal	Pa	$\frac{N}{m^2}$
Energy	joule	J	$\frac{kg\text{-}m^2}{s^2}$
Electric charge	coulomb	C	A-s
Electric potential difference	volt	V	J(A-s)

In spite of the obvious advantages of a universal system of measurements, the complete adoption of SI units in the United States has not yet been realized. In dealing with physical quantities of matter, most practicing chemists find many of the SI derived units less convenient than other units with which they are more familiar and to which their equipment is better suited. Some of these commonly used units are discussed below, and their relationships to SI units are summarized in **Table 4**.

Length: Very small lengths (for example, diameters of atoms) are sometimes expressed in **Angstrom** units. The Angstrom unit is equal to 10^{-10} m, and therefore 10 A= 1 nm and 1 A = 100 pm.

Volume: Chemists frequently express volumes in terms of the **liter** (L) or its smaller derivative, the milliliter (mL). Because 1 L is defined as 1/1,000 m^3, 1 mL is equal to 1 cm^3.

Density: One of the important properties of a substance is its **density**, or the mass of a given volume of the substance. The recommended SI unit for expressing density is kilograms per cubic meter (kg/m^3). Densities are also often expressed in terms of grams per cubic centimeter, (g/cm^3) or grams per milliliter (g/mL), which is equivalent to grams per liter (g/L).

Pressure: A quantity that chemists often measure when working with gases is **pressure**. Pressure is defined as the force exerted on a given surface area. The SI unit of pressure is the **pascal** (Pa), which is equal to one newton per square meter (N/m^2).

Temperature: Temperature is measured in arbitrary units based on some convenient reference point. The temperature scale most widely used is the **Celsius** scale, on which the normal freezing point and normal boiling point of water are assigned values of 0 and 100, respectively. The difference between these temperatures is divided into 100 equal divisions, and each division is referred to as a degree Celsius (°C).

On the **Fahrenheit scale**, the normal freezing and boiling points of water are 32° and 212°, respectively. Because 100 Celsius degrees are equivalent in temperature difference to 180 Fahrenheit degrees (a ratio of 5:9), temperatures may be converted from one system to the other by the relationship,

$$°C = \frac{5}{9}(°F - 32) \quad \text{or} \quad °F = \frac{9}{5}(°C) + 32$$

The temperature scale most frequently used by scientists is the **Kelvin scale** (also called the **absolute scale)**. The zero point of the Kelvin scale is the temperature equal to -273.15 ° on the Celsius scale. Each Kelvin (K) is of the same magnitude as a degree Celsius, so the freezing and boiling points of water on the Kelvin scale are 273 K and 373 K, respectively. Conversions between Celsius temperatures and Kelvin temperatures can be made from the relationship

$$K = °C + 273$$

Thermal Energy: One of the basic units for expressing quantities of heat is the **calorie**, defined as the amount of heat required to raise the temperature of exactly 1 g of water from 14.5 to 15.5 °C. Although energy is still often expressed in calories (cal) or kilocalories (kcal), these units are being replaced by the recommended SI units, **joule** (J) and kilojoule (kJ). One calorie is equal to 4.184 J.

Table 4: Some SI Conversion Factors

SI Unit	Other Unit	Conversion Factor
meter	angstrom (A)	1 A = 10^{-10} m (= 100 pm)
cubic meter	liter	1 L = 10^{-3} m^3 (=1,000 cm^3)
pascal	atmosphere	1 atm = 1.10325 x 10^5 Pa
	torr	1 torr = 133.322 Pa
joule	calorie	1 cal = 4.184 J

Conversions of Units

Often, in chemical measurements and the corresponding calculations, it is necessary to convert one unit into another that is more useful. For example, in order to communicate with our European colleagues, we may wish to convert from the English volume of a 12-ounce beverage can to the SI units of liters or milliliters. In order to make such a conversion, we need a conversion factor which relates a value of one unit in terms of the other. On occasion, a direct conversion factor is not available and we may have to go through a series of steps to arrive at our answer. In order to determine how many mL the 12-oz can holds, we use a variety of conversion factors. Appendix 1 contains a number of conversion factors, and we find a conversion for quarts to liters, 1.0 quarts = 0.9464 liters. We can use this conversion factor and our known relationships of 1.0 quart = 32 ounces and 1000 mL = 1.0 liter to answer the question as shown below:

$$12.0 \text{ ounces} \times \frac{1.00 \text{ quart}}{32.0 \text{ ounces}} = 0.375 \text{ quarts}$$

$$0.375 \text{ quarts} \times \frac{0.9464 \text{ liters}}{1.00 \text{ quart}} = 0.355 \text{ liters}$$

$$0.355 \text{ liters} \times \frac{1000 \text{ mL}}{1.00 \text{ liter}} = 355 \text{ mL}$$

These three steps can be combined into one series of expressions to generate the overall result,

$$12.0 \text{ ounces} \times \frac{1.00 \text{ quart}}{32.0 \text{ ounces}} \times \frac{0.9464 \text{ liters}}{1.00 \text{ quart}} \times \frac{1000 \text{ mL}}{1.00 \text{ liter}} = 355 \text{ mL}$$

Note how the units (or dimensions) will cancel as the mathematical operations are performed, leaving the answer with the appropriate units. When the calculation is set up as one expression to emphasize cancellation of units, it is referred to as dimensional analysis. Other examples of dimensional analysis are given below (remember several conversion factors are provided in **Appendix 1**):

Example 1: If water is flowing from a pipe at the rate of 455 mL/minute, how many liters of water are flowing from the pipe per hour?

Solution:

$$\frac{455 \text{ mL}}{1 \text{ min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{1.0 \text{ liters}}{1000 \text{ mL}} = 27.3 \text{ liters/hr}$$

Example 2: If 500 marbles are packed in a bag and each marble weighs 4.50 grams, how many pounds does one bag of marbles weigh?

Solution:

$$\frac{4.50 \text{ g}}{\text{marble}} \times \frac{1.00 \text{ lb}}{453.6 \text{ g}} \times \frac{500 \text{ marbles}}{\text{bag}} = 4.96 \text{ lb/bag}$$

Example 3: The amount of energy released when a pound of coal is burned is 3.80×10^3 kcal. What quantity of energy is this expressed in joules?

Solution:

$$3.80 \times 10^3 \text{ kcal} \times \frac{10^3 \text{ cal}}{1\text{kcal}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 1.59 \times 10^7 \text{ J}$$

In order to gain a better understanding of conversions and develop your problem solving skills, you should always think through each step and understand why the conversion is taking place rather than simply trying to cancel units.

EXPONENTIAL NUMBERS

In studying chemistry, you will frequently be required to work with both very large numbers and very small numbers. For example, the common unit of electricity, the coulomb, is equal to 6,250,000,000,000,000,000 electrons; the mass of a single atom of lead is 0.0000000000000000000003440 grams. Numbers such as these are more conveniently expressed in **exponential** form, also known as scientific notation.

An exponent is a superscript number that indicates how many times the base number appears as a factor. Thus, the expression 3^4 means 3 x 3x 3 x 3 = 81. Similarly, 10^7 expresses the number that results from multiplying seven 10's together, or 10,000,000.

In the decimal system, any number can be expressed as the product of some number (the coefficient) and an exponential power of 10. If the number to be expressed is a whole-number multiple of 10, then the coefficient is 1. For example:

$$10 = 1 \times 10^1$$
$$100 = 1 \times 10^2$$
$$100{,}000 = 1 \times 10^5$$

If the number to be expressed is not an integral power of 10, then the coefficient is some number other than 1. For example:

$$2479 = 2.479 \times 1000 = 2.479 \times 10^3$$
$$102{,}451 = 1.02451 \times 100{,}000 = 1.02451 \times 10^5$$

Note that the number 2479 could also be written 24.79×10^2 or 247.9×10^1. However, the convention in scientific notation is to place the decimal point after the first digit in the coefficient.

A negative exponent of 10 indicates the number of times that the reciprocal of 10 appears as a factor. Thus:

$$0.0010 = \frac{1}{1000} = \frac{1}{10} \times \frac{1}{10} \times \frac{1}{10} = 1 \times 10^{-3}$$

$$0.023 = \frac{23}{1000} = \frac{2.3}{100} = 2.3 \times \frac{1}{10} \times \frac{1}{10} = 2.3 \times 10^{-2}$$

Writing Exponential Numbers

Any number can be quickly converted to its exponential form by following a simple procedure. First, we move the decimal point in the given number so that it falls after the first digit in the number. This manipulation gives us the coefficient. Then we multiply this coefficient by 10 with an exponent equal to the number of places we moved the decimal point form its original position. If we moved the decimal point to the left, the exponent is positive; if we moved it to the right, the exponent is negative. The following examples are illustrations of this procedure:

132.45 = 1.3245×10^2
two places to the left

1278 = 1.287×10^3
three places to the left

0.0045 = 4.5×10^{-3}
three places to the right

0.000978 = 9.78×10^{-4}
four places to the right

By applying the procedure to the number of electrons per coulomb and the weight of a single lead atom, you can see that the exponential forms of these numbers become 6.25×10^{18} electrons and 3.44×10^{-22} grams, respectively.

To convert a number from its exponential form to its unabbreviated form, we simply reverse the process of moving the decimal point. Thus, if the exponent of 10 is a positive number, we move the decimal point in the coefficient that number of places to the right.

$$3.87 \times 10^{5} = \underset{\text{five places to the right}}{387000}$$

If the exponent of 10 is negative, we move the decimal point in the coefficient to the left.

$$6.23 \times 10^{-4} = \underset{\text{four places to the left}}{0.000623}$$

Calculations with Exponential Numbers

Although calculators are commonly used for calculations involving exponents, there are times when the ability to perform a quick exponential calculation without a calculator may be useful, and a brief review of the rules for calculations involving exponential numbers may prove beneficial. These rules are particularly useful for making quick estimates of the result of various calculations.

Multiplication: Multiply the coefficients together and add the exponents. For example:

$$(3.21 \times 10^{3}) \times (2.40 \times 10^{4}) = 3.21 \times 2.40 \times 10^{3+4} = 7.70 \times 10^{7}$$

$$(6.24 \times 10^{18}) \times (3.25 \times 10^{-23}) = 20.3 \times 10^{18-23} = 20.3 \times 10^{-5} = 2.03 \times 10^{-4}$$

We could estimate the range of the result of any of these calculations by rounding down to the nearest whole number for a lower limit and rounding up for the upper limit and performing the simple math that results. This process is illustrated below for the preceding calculations.

$$(3.21 \times 10^{3}) \times (2.40 \times 10^{4}) = > (3 \times 2) \times 10^{3+4} \text{ and} < (4 \times 3) \times 10^{3+4}$$
$$= 6 \times 10^{7} < \text{product} < 1.2 \times 10^{8}$$

$$(6.24 \times 10^{18}) \times (3.25 \times 10^{-23}) = > (6 \times 3) \times 10^{18-23} \text{ and} < (7 \times 4) \times 10^{18-23}$$
$$= 1.8 \times 10^{-3} < x < 2.8 \times 10^{-3}$$

Of course, the closer the rounded value is to the true value, the narrower the estimated range will be. This estimation procedure can also be used in other mathematical operations such as those described below.

Division: Divide the coefficients in the usual manner; then subtract the exponent of the divisor from the exponent of the dividend. For example:

$$\frac{4.52 \times 10^{5}}{2.10 \times 10^{3}} = \frac{4.52}{2.10} \times 10^{5-3} = 2.15 \times 10^{2}$$

$$\frac{2.70 \times 10^{-2}}{9.00 \times 10^{-6}} = \frac{2.70}{9.00} \times 10^{-2+6} = 0.300 \times 10^{4} = 3.00 \times 10^{3}$$

Raising to a Power: First, raise the coefficient to a power, as you would any regular number. Then raise the exponential term to the power by multiplying the exponent by the number of the power to which it is to be raised. For example:

$$(2.0 \text{ x } 10^{3})^{3} = (2.0)^{3} \text{ x } 10^{3\text{x}3} = 8.0 \text{ x } 10^{9}$$

$$(6.0 \text{ x } 10^{-8})^{2} = (6.0)^{2} \text{ x } 10^{-8 \text{ x } 2} = 36 \text{ x } 10^{-16} = 3.6 \text{ x } 10^{-15}$$

Extracting a Root: First, extract the root of the coefficient. Then extract the root of the exponential term by dividing the exponent by the root to be extracted (2 for a square root; 3 for a cube root; and so on). For example:

$$\sqrt{9.0 \text{ x } 10^{-6}} = \sqrt{9.0} \text{ x } 10^{(-6/2)} = 3.0 \text{ x } 10^{-3}$$

$$\sqrt[3]{27.0 \text{ x } 10^{-9}} = \sqrt[3]{27.0} \text{ x } 10^{(-9/3)} = 3.00 \text{ x } 10^{-3}$$

Addition and Subtraction: To add or subtract exponential numbers that have the same exponents, simply add the coefficients; the exponential term remains the same. For example:

$$(2.35 \text{ x } 10^{3}) + (3.46 \text{ x } 10^{3}) = 5.81 \text{ x } 10^{3}$$

$$(7.42 \text{ x } 10^{-11}) - (1.21 \text{ x } 10^{-11}) = 6.21 \text{ x } 10^{-11}$$

If the numbers to be added or subtracted do not have the same exponents, then they must be rewritten in a form in which all exponents are the same, and then added or subtracted. For example:

$$(3.26 \text{ x } 10^{-3}) + (2.5 \text{ x } 10^{-4}) = (3.26 \text{ x } 10^{-3}) + (0.250 \text{ x } 10^{-3}) = 3.51 \text{ x } 10^{-3}$$

$$(2.55 \text{ x } 10^{7}) - (3.00 \text{ x } 10^{5}) = (2.55 \text{ x } 10^{7}) - (0.0300 \text{ x } 10^{7}) = 2.52 \text{ x } 10^{7}$$

LOGARITHMS

The logarithm of a number is the power to which some base must be raised to yield that number. The two most frequently used systems of logarithms are (1) natural or Naperian logarithms (abbreviated ln), in which the base is designated by e = 2.718, and (2) common logarithms (abbreviated log), in which the base is 10. Historically the common logarithms were easier to use and, for this reason, have been used more frequently. With the current use of calculators, both logarithms are often employed in chemistry and they can be related by a factor of 2.303,

$$\ln x = 2.303 \log x$$

Examples that illustrate the meaning of logarithms follow:

$\log 100 = \log 10^{2} = 2$
$\log 0.001 = \log 10^{-3} = -3$
$\log 7 = \log 10^{0.845} = 0.845$
$\ln 6 = \ln (2.718)^{1.79} = \ln e^{1.79} = 1.79$

$$\ln 100 = 2.303 \log 100 = 2.303\ (2) = 4.606$$

Values for the inverse log and ln functions can be determined by raising each side of the equation to the appropriate base power (10 for log and e for ln) as illustrated below.

$\log x = 0.5$

$10^{\log x} = 10^{0.5}$ and because $10^{\log x} = x$,

$x = 10^{0.5} = 3.16$

$\ln x = 13.2$

$e^{\ln x} = e^{13.2}$ and because $e^{\ln x} = x$,

$x = e^{13.2} = (2.718)^{13.2} = 5.40 \times 10^{5}$

Calculations using logarithms are based on the following relationships:

$\log xy = \log x + \log y$

$\log \frac{x}{y} = \log x - \log y$

$\log x^{n} = n \log x$

$\log \sqrt[n]{x} = \frac{\log x}{n}$

Although the use of calculators has become routine in chemistry, on occasion a problem will arise which exceeds the capacity of most current calculators to solve. For example, the equilibrium constant (K) of a particular reaction can be determined from the equation,

$$\log K = \frac{3\ (3.27)}{0.0591} = 166$$

Attempting to take the inverse log of 166 on many calculators would result in an "error" response, yet finding the equilibrium constant is easily accomplished. Instead of relying on our calculator, we can use our knowledge of logarithms to easily solve the problem as follows,

if $\log K = 166$, then $K = 10^{166}$

Because many calculators are limited to numbers less than 10^{100}, this calculation exceeded the calculator's capacity and an error resulted. This example illustrates the importance of not substituting a reliance on calculators for an understanding of basic mathematical concepts.

ERRORS IN MEASUREMENT

Although data in the form of a number with the appropriate unit convey the most information, these data are still subject to errors and uncertainties which must be identified, corrected if possible, and communicated. Errors associated with scientific measurements are normally classified into two types, indeterminate and determinate errors.

Indeterminate errors are always present, cannot be eliminated or their sources determined (hence the name), and become important when pushing the measurement technique to its limit. They are random, with an equal probability of being positive or negative, meaning above or below an average. These errors arise from the many uncontrollable variables present in a measurement and are a reflection of the natural limitations on our ability to physically take a measurement. Most often, the individual size of these errors is small and their sources are hard to isolate and identify, but the accumulation of many small indeterminate errors will affect the **precision** of measurements.

Precision communicates the reproducibility of the measurement, or how closely the data from several identical experiments are to one another. A common example of an indeterminate error which affects precision is the subjective visual interpolation of measured data, such as in reading a ruler or a buret, where the last number in the measurement is an estimate. If we measure the length of a stick more than one time, we may find our results to vary slightly due to a slight difference in the way we see the last figure on the ruler. These differences will be greater or less than some "average" value and these +/- deviations represent the indeterminate error. The more finely divided the divisions on the ruler are, the greater the limit of the measurement technique will be, and the indeterminate error associated with reading the ruler will be smaller. This relationship is illustrated in **Figure 1** which shows ruler C to be the most precise and ruler A to be the least precise and most subject to indeterminate errors. Electrical noise in an instrument is another common example of indeterminate error. Noise appears as random fluctuations of electrical signal and is more apparent when the instrument sensitivity is at its maximum (the limit of the technique). If we average enough individual measurements, we can expect the random +/- fluctuations to cancel one another and reduce the total indeterminate error associated with the experiment.

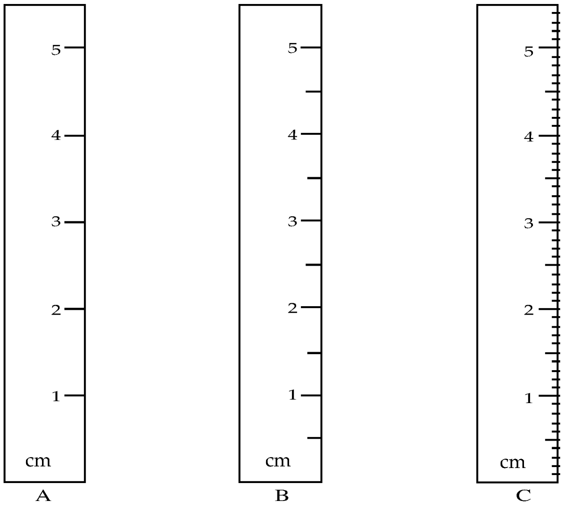

Figure 1: Three Rulers with Different Graduations and Therefore Different Levels of Precision, with A the Least Precise and C the Most Precise.

Determinate or **systematic** errors occur in the same direction (always positive or always negative in a systematic fashion), can be determined (hence the name), and impact **accuracy**. Accuracy is a measure of how close the experimental results are to a known "true" value, defined as a standard. In theory, these errors can be identified and compensated for in the results through a calibration procedure. Determinate errors are generally classified into three categories depending upon their source; instrument errors, method errors, or personal errors.

Instrument errors are inherent to the measuring device. For example, the markings on volumetric glassware are valid only for a certain temperature. If the glassware is used at a higher temperature, there is a slight expansion of the glassware and the volume increases slightly, introducing an error. In theory, we could calculate the expansion of the glassware at the new temperature and determine its effect on the volume, allowing us to correct for the error. Therefore, this error would be a determinate instrument error. Other common examples of instrument errors include using an electronic device that is not properly set to zero before use, pH meters that are not calibrated with an appropriate buffer solution, thermometers that do not read correctly, and electronic balances that always weigh either too high or too low. All of these errors could be eliminated by proper calibration.

Method errors are more difficult to identify and correct as they arise from nonideal chemical or physical behavior of the system under investigation. For example, the number of moles of a gas could be determined by measuring the temperature, pressure, and volume of the gas and employing the ideal gas law. However, if the gas under investigation deviates from ideal behavior, an error would be introduced. In theory, with some difficulty we could determine the extent of nonideal behavior and correct for this error. Other common examples of method errors include solubility loss when precipitating a solid for subsequent weighing, errors due to indicators in a titration because an indicator changes color only after the addition of an excess of reagent, and errors in procedures that assume reactions to go to completion when they do not. As in the case of instrument errors, all method errors could be identified and eliminated.

The third type of determinate error is one we are all familiar with --**personal errors**. These determinate errors result from mistakes or errors in judgment made by the person doing the experiment. Errors of this type are exemplified by writing down the wrong data value, errors in calculations, sloppy laboratory work, and personal bias in reading data to give the most precise or accurate value, especially if you think you know what the answer should be. Personal errors are easy to correct by being careful, thoughtful, and disciplined when carrying out the laboratory procedure.

Identification, correction, and communication of indeterminate and determinate errors take different forms and these forms are discussed in the following sections.

PRECISION

The precision present in a set of data may be communicated in a number of ways, from the simple application of significant figure conventions to more complex considerations of statistical analysis. Several of these methods are reviewed in the following sections.

Significant Figures

The number of significant figures in a measurement conveys an indication of the relative reproducibility of the measurement. For example, assume we are to repetitively measure the length of the piece of wood shown in **Figure 2** using the two rulers shown.

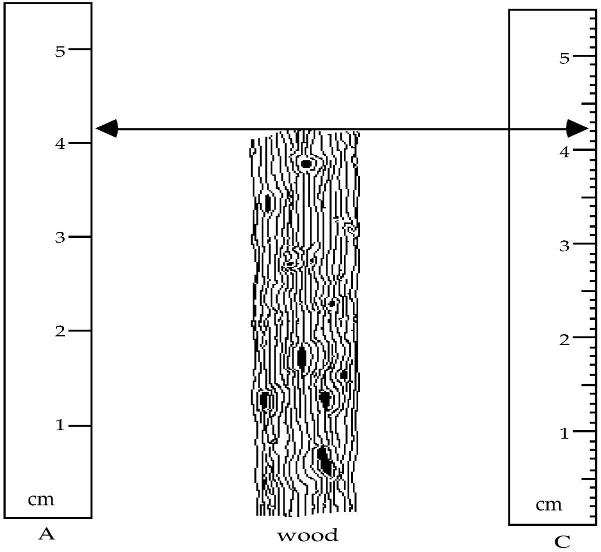

Figure 2: The Measurement of a Piece of Wood

When we use ruler A, the graduated divisions on the ruler allow us to clearly measure the length of the wood to be least 4 cm. We are not sure of the next digit in the measured value, but we can approximate that digit to be less than halfway to the 5, perhaps somewhere around 0.2. Although our approximation may not be exactly correct and will introduce some random error to the measurement (we could have guessed too high or too low), including the value provides more information than if we chose to ignore it (4.2 cm vs. 4 cm). The next time we perform the same measurement with ruler A, we again clearly see the wood is at least 4 cm in length, only this time we approximate the next digit to be 0.3, for a total length of 4.3 cm. As we perform more and more of these measurements, we always find the length to be 4.2 ± 0.1 cm. We could then write the average length as 4.2 cm. The final digit in the measurement is implied to be uncertain by ±1, and this is the last significant figure in the measurement. If we tried to add another significant figure and write out the length as 4.23 cm, we would realize that the final number 3 has no meaning because we never measured the wood stick to that degree of reliability, and in fact, we are not even completely sure about the preceding digit. Therefore, this number is not valid and should not be included in the value for the measurement.

If we use ruler C, we can see the length of the stick is clearly at least 4.2 cm but the next digit is not clearly delineated on this measuring device. Therefore, we approximate the next number and write down 4.21 cm for the measured value. The next time we take the measurement, we approximate the value as 4.23 cm. After several attempts at measuring the stick with this ruler, the average length is reported to be 4.21, with the 1 the last significant figure. With the more finely divided graduations on this ruler, the measured value can be reported to more significant figures.

In this example, we can clearly see that the number of significant figures is related to the precision, or reproducibility, of the measurement. The precision is dependent upon the measuring device, with ruler C providing more precision, and dependent to an extent on the person taking the measurement. If we wanted to measure the length of the stick to 1/100 of a centimeter, we would need to invest in an expensive micrometer whose graduations are very carefully determined to 1/1000 of a centimeter. If we wanted to reduce the uncertainty associated with visually interpreting the micrometer, we could purchase an instrument that provides a digital (numerical) readout, although it is important to remember that the digital readout still retains uncertainty associated with the last digit in the measured value.

In obtaining data, care should be taken to insure that all measurements and the calculations involving measurements include the proper number of significant figures. Too many significant figures communicate a higher degree of precision and reliability than is justified, leading to decisions made from data that is not valid. On the other hand, too few significant figures will needlessly throw away information that may have been obtained at a high cost. In general, the more significant figures associated with a measurement, the higher the cost of the instrumentation and the greater the effort required to obtain the data. The general rules for handling significant figures are provided in the next several sections.

To determine the number of significant figures present in a number, we simply count all the nonzero digits, all the zeros that are between nonzero digits, and zeros to the right of the decimal place. Zeros which precede the first nonzero digit simply hold the decimal place and are not significant, as is obvious when the number is written in scientific notation. Several examples are shown below.

1.07×10^5	three significant figures
10.45	four significant figures
0.045 or 4.5×10^{-2}	two significant figures (zeros to the left are not significant)
12.000	five significant figures
120	two or three - it is not clear if the zero is significant in this case.
120.	three - addition of the decimal point clearly indicates the zero to be significant.

Clarity could also be accomplished by writing the number in scientific notation:

1.20×10^2	three significant figures
1.2×10^2	two significant figures

Occasionally, integers and precisely defined numbers are used in calculations. These numbers are assigned an infinite number of significant figures and so will not influence the determination of the number of significant figures in a resulting calculation. For example, there are exactly 12 inches in 1 foot as defined, so the 12 inches would have an infinite number of significant figures. The integer 2 could be considered to be 2.00000000000. . . . ., which also contains an infinite number of significant figures.

Rounding Off

When one or more digits must be dropped from a calculated result to give that result the proper number of significant figures, the following rules apply:

1. When the first digit to be dropped is less than 5, the last digit retained remains unchanged.
2. When the first digit to be dropped is greater than 5, the last digit retained is increased by 1.
3. When the first digit to be dropped is 5, the last digit retained remains unchanged if it is even and is increased by 1 if it is odd. (This arbitrary rule is based on the assumption that on the average as many digits will be increased as will remain unchanged. Thus, any errors introduced in rounding off will tend to compensate for one another.)

These rules are illustrated by the following examples, in which the numbers are rounded off to three significant figures:

1.6723 rounds off to 1.67
1.677 rounds off to 1.68
1.6652 rounds off to 1.67
1.6752 rounds off to 1.68

Multiplication and Division

As a general rule, the answer to a calculation involving multiplication or division should contain the same number of significant figures as the factor with the smallest number of significant figures in the calculation. For example, in the problem

$$\frac{2.137 \times 5.62}{2.3425} = 5.13$$

the least precisely known factor is 5.62, which has three significant figures. The answer to the problem therefore contains three significant figures.

To further illustrate the application of this rule, the answers to the following calculations are expressed to the correct number of significant figures:

$$4.3 \times 10^{-13} \times 6.022 \times 10^{23} = 2.6 \times 10^{11}$$

$$\frac{26.98}{133.34} = 0.2023$$

$$\frac{5.0 \times 0.18}{4.00} \times 6.022 \times 10^{23} = 1.4 \times 10^{23}$$

$$\frac{4.785}{271.5} \times \frac{1000.0}{60.0} = 0.294$$

There are some exceptions to this general rule. For example, consider the calculation

$$\frac{32.4 \times 9.5}{252.7} = ?$$

The solution to this problem to four figures is 1.218. The least precise factor in the calculation is 9.5, which contains only two significant figures. Thus, according to our rule the solution should have two significant figures; that is, we should round off this particular answer to 1.2. But our least precise factor of 9.5 has a precision of 1 part in 95, whereas our answer of 1.2 implies a precision of only 1 part in 12. If we retain an additional digit in our answer, it becomes 1.22 and indicates a precision of 1 part in 122. We are justified in doing this because a precision of 1 part per 95 is closer to 1 part per 122 than to 1 part per 12. The correct answer to the calculation, then, is 1.22. This example illustrates the important point that the rules for significant figures are not hard and fast, but often involve a personal judgment as well.

Addition and Subtraction

In addition and subtraction, the rule for determining the proper number of significant figures in the answer is different form the rule that is applied in multiplication and division. When numbers are added or subtracted, the units of those numbers must all be the same; that is, we cannot add pound and inches or subtract grams from milliliters. The least precise number is not necessarily the number with the fewest significant figures; instead, it is the number with the fewest digits to the right of the decimal point.

The basis for this statement is clarified in the following illustration. Assume that we have determined the weights of a number of objects in grams, and we wish to total these to find the combined weight of the objects. The individual weights and the precision of each are:

$$\begin{array}{rl}
1.02\ \text{g} \pm & 0.01\ \text{g} \\
107.3\ \text{g} \pm & 0.1\ \text{g} \\
14.273\ \text{g} \pm & 0.001\ \text{g} \\
\underline{0.12\ \text{g}} \pm & 0.01\ \text{g} \\
122.713\ \text{g} = & 122.7\ \text{g} \pm 0.1\ \text{g}
\end{array}$$

Obviously, the least precise weight in the column is 107.3 g (although it is not the number with the fewest significant figures). Thus, the sum of these weights must indicate the same precision that is indicated in the 107.3; that is, ± 0.1 g.

The rule for addition and subtraction , then, is that the solution must have the same number of digits to the right of the decimal point as the number in the problem with the fewest digits to the right of the decimal point. Further illustrations of this rule are shown below:

$$107.62 + 3.1 = 110.7$$

$$1.69 - 0.4327 = 1.26$$

$$10.007 + 0.012 = 10.019$$

Addition/Subtraction with Multiplication/Division

The proper significant figures for the results of a mathematical procedure involving both addition/subtraction and multiplication/division may be found by carrying out all additions/subtractions with proper significant figures, followed by the multiplication/division operations. These types of calculations are illustrated below:

$$\frac{(12.34 + 1.2) \text{ x } 2.19}{9.0134} = \frac{13.5 \text{ x } 2.19}{9.0134} = \frac{29.6}{9.0134} = 3.28$$

$$\frac{14.894 \text{ x } 1.3 \text{ x } 10^7}{(2.189 - 0.91)} = \frac{14.894 \text{ x } 1.3 \text{ x } 10^7}{(1.28)} = \frac{1.9 \text{ x } 10^8}{(1.28)} = 1.5 \text{ x } 10^8$$

Because calculators generally show as many digits as their display field will hold, there is a tendency to provide too many significant figures. **Figure 3** shows a calculator display that results when determining the number of moles of copper present in a 0.2439-gram sample, which is calculated by dividing the mass of copper by the atomic weight of copper (63.546 g/mol).

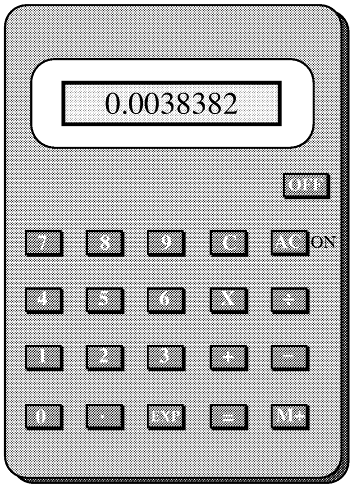

Figure 3: Calculator Showing Too Many Significant Figures in its Display Given the Number of Significant Figures in the Original Data

The proper number of significant figures in this calculation is 4, and the value you should report would be 0.003838 or 3.838×10^{-3} moles copper. Remember, just because your calculator provides you with many digits, it doesn't mean they all have meaning and should be reported.

MEAN AND MEDIAN

After expressing each of our results with the proper number of significant figures, we still need a method for expressing a final result from a series of identical measurements, each of which has some indeterminate error. We would like to communicate the "central" value of our series of measurements because this value represents the best single description of the total data set. There are two common methods for obtaining a single value from a series of measurements; taking the mean and taking the median.

The **mean** value of a set of measurements is simply the average of all of the measured values. The mean provides a good estimate of the central value for data sets that are large or for small sets whose values are all relatively close. However, if the data set is small and contains a value that is very different from the others, the mean value becomes distorted in the direction of the outlying value and the measurement that is very different has an impact on the mean that is unduly large. For example, if we have the following four measured values, 4.0, 3.0, 1.0, and 10, the mean would be 4.5. Now, consider how well the mean of 4.5 represents this data set. Of the four measurements, three are below the mean. Only the measured value of 10 exceeds the mean value. Clearly, the value 10 has had the greatest influence on the data set and has shifted the mean to an artificially high value that is not a very good representation of the overall result of the four measurements. Under these circumstances, an alternative method of expressing the final result, the median, would be useful.

The **median** of a set of data is defined as the middle measurement value in an odd number of measurements, or the average of the middle two measured values in an even number of measurements. Exactly half of the measured values will be greater than the median and half will be less than the median. In our previous example with measured values of 4.0, 3.0, 1.0, and 10, the median would be the average of 3.0 and 4.0, or 3.5. Now, two of our measured values are less than the median and two are greater. With this set of measurements, the median provides a better single representation of the data than the mean. Use of the median value tends to minimize the influence of a single measurement that is much different than the others and is normally used when reporting the results from small data sets.

The difference between each measurement and the mean or median of a data set can be expressed in terms of absolute or relative deviation. These values provide a method for communicating the extent of indeterminate error associated with the procedure used for the measurements. The lower the deviation the greater the precision and the lower the indeterminate errors. The absolute deviation is the difference between an individual measurement, x_i, and the mean or median value $\bar{x}$ and would have the same units as the measured quantity.

$$\text{Absolute deviation} = x_i - \bar{x}$$

Relative deviation is defined as a ratio of the absolute value of the absolute deviation over the average value and is often expressed in terms of a percentage or in terms of parts per thousand (ppt).

$$\text{Relative deviation (percent)} = \frac{|x_i - \bar{x}|}{\bar{x}} \times 100\ \%$$

$$\text{Relative deviation (parts per thousand)} = \frac{|x_i - \bar{x}|}{\bar{x}} \times 1000\ \text{ppt}$$

The relative deviation is a more effective means of communicating the indeterminate error associated with different measurement procedures because the quantity of deviation is not dependent on the size or units of the measurement. For example, assume that the absolute deviation of a measured volume was 10.0 mL in two experiments. In the first, the total average volume was 100 mL while in the second it was 1000 mL. Although the absolute deviations in the two experiments are the same, the relative deviation for the second experiment is ten times less (1% vs. 10%) than the first experiment and it is clear the second experimental procedure has less indeterminate error associated with it than the first. Clearly, use of the relative deviation more effectively communicates the errors in the two experiments.

Because data sets frequently contain many values, average deviations and average relative deviations are often determined. These values are simply the average of the absolute or relative deviations for each of the individual measurements.

Another, more sophisticated, method used to express precision is by the **standard deviation**. The standard deviation for a large set of measurements is termed the population standard deviation, s, and is defined as

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - m)^2}{N}}$$

where m is the "true average" value (the average value if we were able to take an infinite number of measurements), x_i is the value for each individual measurement, and N is the number of measurements. The term "standard deviation" arises from empirical studies of the frequency of occurrence of deviations (indeterminate errors) of a certain size as the same measurement is repeated over and over.

For example, assume that we measure the lead concentration in a municipal water supply 22 times and obtain the data listed in **Table 5**, which has a mean value of 18.2 parts per billion (ppb). Due to random errors, each individual measurement deviates by some amount from the mean and these deviations are also provided in **Table 5**.

Table 5: **Data for the Determination of Lead in Water**

Value	Deviation from Mean	Value	Deviation from Mean
18.1 ppb	- 0.1 ppb	18.4 ppb	+ 0.2 ppb
17.9	- 0.3	18.0	- 0.2
18.5	+ 0.3	18.2	0.0
18.2`	0.0	17.9	- 0.3
18.3	+ 0.1	18.2	0.0
18.3	+ 0.1	17.8	- 0.4
18.6	+ 0.4	18.1	- 0.1
18.2	0.0	18.4	+ 0.2
18.1	- 0.1	18.0	- 0.2
18.6	+ 0.4	18.2	0.0
18.1	- 0.1	18.3	+ 0.1

We can plot a bar graph of the frequency of occurrence of each deviation versus its magnitude (**Figure 4**). **Figure 4** shows an experimental Gaussian or normal error curve beginning to take shape. However, due to the limited number of experimental measurements this error distribution is not smooth and has not yet reached its theoretical shape. If, instead of taking only 22 measurements we took an infinite number, the frequency versus magnitude curve would become smooth and symmetrical as shown in **Figure 5**. (Remember that when discussing graphs, the dependent variable, plotted on the y-axis, is normally listed first and the independent variable, plotted on the x-axis, is given second. Thus, a plot of A vs B implies A is on the y-axis and B is on the x-axis). The standard deviation for this set of measurements is calculated to be 0.2 ppb.

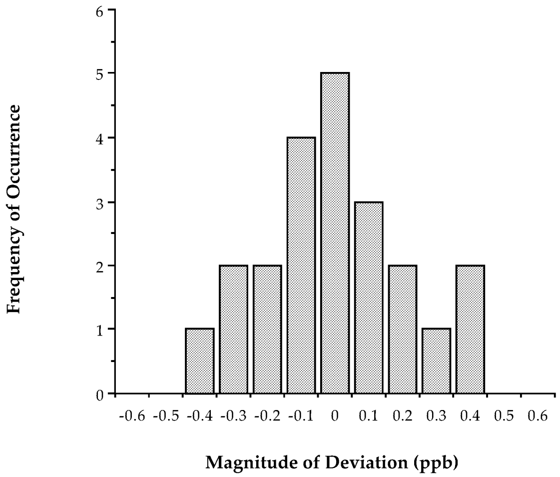

Figure 4: Frequency of Occurrence for Various Size Errors Based on the Data in **Table 5**

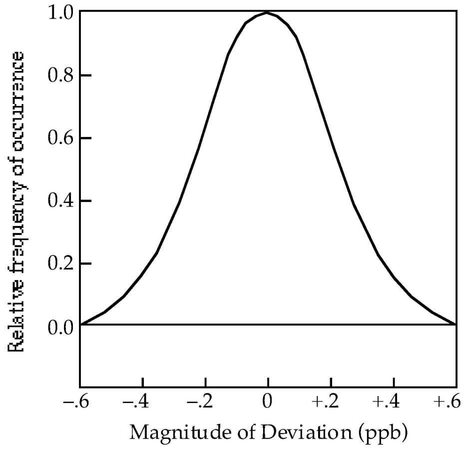

Figure 5: Theoretical Error Curve Based on an Infinite Number of Measurements for the Experiment Whose Results are Given in **Table 5**

Gaussian curves have a number of properties of interest. First, they are symmetrical, centered about a deviation of 0, which means that the indeterminate errors are most likely to cancel one another to provide zero deviation. Second, the width of the curve is directly proportional to the standard deviation, providing the mathematical basis for the term's definition. Experiments with greater indeterminate error provide results that show a greater deviation from the mean, and hence a broader error curve and a larger s value. Clearly, then, the magnitude of s is a measure of the precision of the measurement.

If we slightly modify the manner in which we plot the data another interesting and useful property of normal error curves may be visualized. We can convert the magnitude of deviation values plotted on the x-axis in Figure 5 into relative number of standard deviations. For example, a deviation of -0.2 ppb becomes -1s (the standard deviation of the data is 0.2 ppb so -1 x 0.2 ppb = -0.2 ppb) and a deviation of +0.6 is equivalent to +3s. If we then plot the frequency of occurrence values as a function of the number of standard deviations from the mean, a universal error curve results which is no longer dependent on the specific experiment performed or the specific measured value's units, but rather is valid for any set of data with the same standard deviation. The same curve would result if we measured parts per million, grams, ounces, or whatever, as long as the standard deviation of each data set was 0.2 whatevers. It turns out that 68% of all measured value will be contained within the region of the curve bounded by ± 1s, while 95% of all values are within ≈ ± 2s. This distribution probability plays an important role in the development of confidence intervals which will be covered shortly. Such a curve for this data set is shown in **Figure 6**.

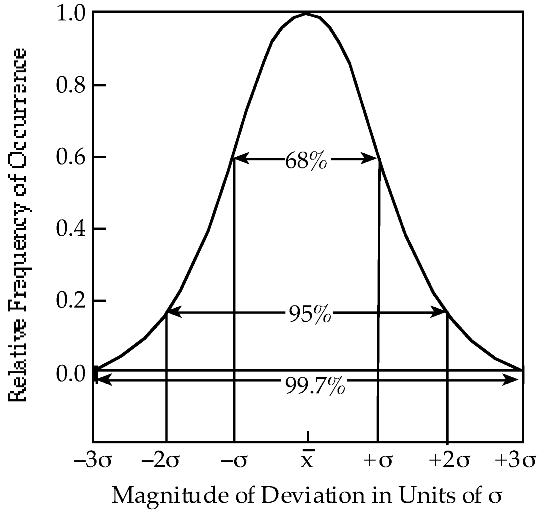

Figure 6: Error Curve Plotted With x-axis in Units of **s**

If the number of measurements in the data set is small (i.e., <20), the standard deviation term is slightly redefined as the sample standard deviation, s, which is given by,

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N - 1}}$$

where $\bar{x}$ is the measured average of the measurement set. This definition provides a slightly broader error curve to compensate for the fact that with fewer measurements the expected error is somewhat larger than that expected with many measurements. As N increases, the difference between N and N-1 becomes less pronounced and s approaches s. Both terms provide a measure of precision, with the larger the standard deviation the less precise the measurement. More thorough treatments of the development of the standard deviation term are available in textbooks on statistics and advanced analytical chemistry texts.

Looking at either definition of standard deviation, we can see that the larger the errors ($|x_i - m|$), the larger the standard deviation. We can also see that as more measurements are taken, N will increase and the size of the standard deviation must decrease. This relationship makes sense because as we take more measurements we are increasing the likelihood that the random errors will cancel one another and reduce the overall indeterminate error. As N approaches ∞, the standard deviation will approach 0 and no indeterminate error will be present. Therefore, *we can always reduce the impact of indeterminate errors on a measurement set by increasing the number of measurements*. However, the standard deviation is dependent on the $\sqrt{N}$, so there comes a point of diminishing returns when increasing the number of measurements. For example, going from 1 to 4 measurements should reduce the standard deviation by a factor of 2, a fairly substantial improvement for only 3 more measurements. Going from 1 to 9 measurements increases precision by a factor of 3, and going from 1 to 100 improves precision by a factor of 10. It took 96 more measurements to improve the precision from a factor of 2 to a factor of 10. If we wanted to improve precision by another factor of 2, to a factor of 20, we would need 400 measurements, and if we wanted to improve precision by a total factor of 50 relative to 1 measurement, we would need 2500 measurements. Clearly, for each subsequent improvement in precision, we need to take increasing numbers of measurements. Thus, there comes a point at which the increased precision available by taking more measurements is not worth the time, effort, and cost of the additional measurements required.

Each set of measurement data will always have some indeterminate error associated with it. The extent of the error will be determined both by the fundamental indeterminate error associated with the measurement procedure, described by s, and by the number of measurements taken. The "true" mean value with no indeterminate error present will lie within some range of our measured mean, with the range determined by (1) the standard deviation, (2) the number of measurements, and (3) the statistical likelihood of finding the true value in this range. These relationships are quantified in terms of a **confidence interval**, i.e., an interval around the measured average value in which we expect to find the true mean with a certain confidence (probability). The confidence interval is described by the following equation,

$$m = \bar{x} \pm \frac{zs}{\sqrt{N}}$$

where m is the true mean with no indeterminate error, $\bar{x}$ is our measured mean, s is the standard deviation, N is the number of measurements, and z is a constant dependent upon the probability level we choose to look at. The values for z originate from the probability of deviations being found within a certain region of the normal error curve as illustrated previously in Figure 6. For example, z=1 for a probability level of 68% because 68% of the time the true mean will be within ± 1s of the measured mean based on 1 measurement. If we wanted to be 95% sure our true mean was within our confidence interval, z would be 1.96, and 95% of the time our true mean would lie within ± 1.96s of our measured mean. **Table 6** provides the value of z for various confidence levels. Confidence intervals can be used to state with some degree of certainty the likelihood of finding the true mean within some range of an experimental mean, given a certain degree of precision associated with the method. This is important because all measurements are subject to indeterminate error and the experimental mean may or may not be close to the true mean value and, therefore, decisions made based on this experimental mean may or may not be valid.

Table 6: Values of Z for Various Confidence Intervals

Confidence Interval	Value for Z
50%	0.67
68	1.00
80	1.29
90	1.64
95	1.96
96	2.00
99	2.58
99.7	3.00
99.9	3.29

The important points to recognize in our discussion are that **the measured average is not necessarily the "true" average, therefore the results of measurements are often expressed in terms of a range which takes into account the indeterminate error. By minimizing the sources of indeterminate error or by taking more measurements this range can be narrowed.** The narrower the range, the more precisely we can communicate the results of our measurements, and the more useful the data become. Keep in mind that data can be no more precise than the instruments used to obtain them. If our thermometer only reads to ± 1 °C, reporting a temperature of 23.4591 °C is nonsense, and it should be reported as 23 °C. In addition, if we have not calibrated the thermometer, it may not be reading accurately and we cannot assure that the temperature is actually 23 °C.

ACCURACY

Even if our measurements are very precise and we get the same result every time we perform the measurement, they may not be very accurate. As you may recall from our earlier discussion, accuracy is defined as the difference between the experimental result and some known "true" value and is impacted by the presence of determinate errors. The **accuracy** of a measurement is normally expressed in terms of either an absolute or relative error, much like absolute and relative deviations express indeterminate error. An absolute error is defined as the difference between the "true" value (m) and the measured quantity (x) and has the same units as the measured quantity.

$$\text{Absolute error} = x - m$$

Relative error is defined as a ratio of the absolute error over the true value and is often expressed in terms of a percentage or in terms of parts per thousand (ppt).

$$\text{Relative error (percent)} = \frac{x - m}{m} \times 100\ \%$$

$$\text{Relative error (parts per thousand)} = \frac{x - m}{m} \times 1000\ \text{ppt}$$

The "true" value for a measurement is determined by using an appropriate standard whose measured quantity is well-known. For example, a thermometer can be tested for determinate errors by immersion in a beaker of boiling water at 1.0 atm. Because the boiling point of pure water at 1.0 atm is an accepted quantity of 100.0 °C, the boiling water can serve as our standard with a "true" temperature. If, after equilibration in the boiling water, the thermometer reads 97.8 °C, we know there is a determinate error of 2.2 °C (or $\frac{2.2\ ^\circ\mathrm{C}}{100.0\ ^\circ\mathrm{C}}$ x 100% = 2.2%) associated with the measurement when using this thermometer. This is an example of an instrumental determinate error. We could correct this determinate error by adding 2.2 °C to all temperature values obtained with this thermometer. Of course, in correcting the readings of our thermometer using error data obtained at 100.0 °C we are assuming that the error in the thermometer remains constant over our range of application. This may not be a very good assumption. To test the assumption, we can prepare a mixture of pure water and ice. We know that at 1.0 atm a mixture of ice and water will have a temperature of 0.0 °C so we have a second standard to test our thermometer against. If our assumption was correct and the error is constant regardless of temperature, the thermometer should read -2.2 °C. However, if the temperature now reads 0.9 °C, the error associated with the thermometer is not constant but is temperature-dependent. In order to correct this error, the magnitude of the error for each measured temperature would be necessary. We can obtain this information by taking the temperature of a series of standards with known temperatures (possibly prepared by using a thermometer known to be very accurate) and developing a mathematical relationship between the measured temperature and the known temperature. The mathematical relationship between a measured quantity and a known value is often determined by graphical plotting of a "calibration curve" and the entire procedure is one method of calibration.

Calibration may be considered an "adjustment" procedure used to force the experimental results to match known values. After calibration, a relationship between a measured physical quantity and the desired information (temperature, concentration, etc.) can be derived. For example, assume we have an instrument in which the measured quantity is a voltage, which is somehow related to temperature. This instrument is then used to measure the temperature of a water sample and an instrument response of 240 mV is observed. Without knowing the relationship between temperature and voltage, we have no idea of the temperature of the water sample. We can obtain this relationship by using the instrument to measure a series of samples whose temperatures are known, generating a table of voltages *vs.* temperature like the following:

Sample #	Temperature	Voltage
1	10.0 °C	110 mV
2	21.8 °C	228 mV
3	33.4 °C	371 mV
4	49.2 °C	521 mV
5	89.7 °C	978 mV

If we plot mV as a function of temperature, a linear graph will result as shown in **Figure 7**.

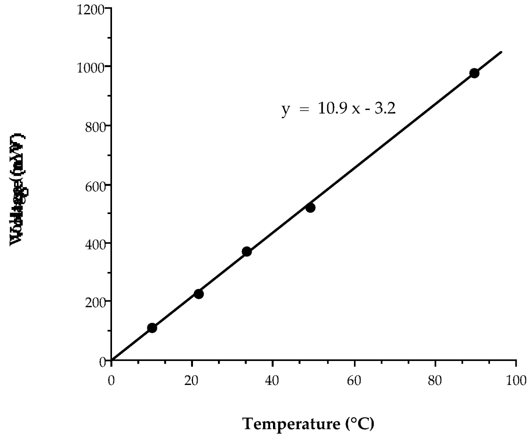

Figure 7: Calibration plot of Voltage vs. Temperature

This is our calibration curve and the linear equation for the best-fit line through the data points provides the mathematical relationship between temperature (x-axis, dependent variable) and instrument response in mV (y-axis, independent variable). Using this equation, we can find the temperature corresponding to the measured voltage of the unknown sample, 240 mV.

$$y = 10.9\,x - 3.2$$

$$240\text{ mV} = 10.9\,\frac{\text{mV}}{^{\circ}\text{C}}\quad x\,^{\circ}\text{C} - 3.2\text{ mV}$$

$$10.9\,\frac{\text{mV}}{^{\circ}\text{C}}\quad x\,^{\circ}\text{C} = 240\text{ mV} + 3.2\text{ mV}$$

$$x\,^{\circ}\text{C} = \frac{243.2\text{ mV}}{10.9\text{ mV}/^{\circ}\text{C}} = 22.3\,^{\circ}\text{C}$$

Alternatively, if the calibration curve were graphed on high-resolution graph paper, we could simply find the temperature value corresponding to 240 mV from the graph. Our instrument is now calibrated and many of the errors that impact accuracy in the unknown will cancel because they are also present in the standard.

There could be some determinate errors that impact the unknown differently than the standards. The instrument response may not be the same in both cases and our calibration may not be valid. These types of errors generally arise from a physical or chemical interference or an agent present in the unknown sample that causes it to behave differently than the standards. In such a case, the calibration curve is no longer valid for the unknown and the technique is said to suffer from matrix effects (the bulk unknown being the matrix which has an impact on the analytical method). Under such circumstances, considerable determinate error may be introduced and accuracy may suffer. For example, lead in a blood matrix (the unknown) may not behave in the same manner as lead in an aqueous solution (standards) when analyzed by a particular method. Under these circumstances, a different method of calibration called standard addition is often employed.

The **standard addition** method involves adding a known amount (the standard) of the species of interest to an unknown sample. The analytical signal is measured both before and after the addition of the standard, with an increase in signal observed upon addition of the standard. Provided a linear relationship exists between the measured signal and the desired quantity, this increase in signal is proportional to the amount of added standard, and this proportionality can then be used to calculate the concentration of unknown present in the original solution. For example, assume we have an analytical method that provides a signal (mV) specific for iron. We analyze an unknown with this method and obtain 7.1 mV of signal, but since we do not know the relationship of signal to concentration, we can't determine the unknown's iron concentration. Next, we add exactly 0.50% iron to the unknown and repeat the measurement and our signal increases to 14.2 mV. We have doubled the signal, so the addition of 0.50% iron must have doubled the amount of iron in the unknown, and therefore, the unknown must contain 0.50% iron. This method overcomes matrix effects since the same bulk solution is used for both the unknown and the known standards, so any interferences present will affect both the unknown and the standard to the same extent.

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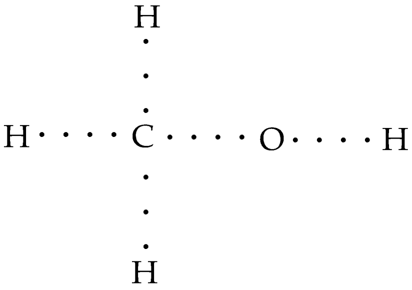
NOMENCLATURE OF ORGANIC COMPOUNDS

INTRODUCTION

Carbon forms a vast variety of covalent compounds, many of which occur naturally in biological systems. Besides their importance to plant and animal life, these compounds offer examples of a wide variety of structures that challenge chemists to synthesize them. The vast majority of carbon compounds are composed of only a small number of elements: carbon, hydrogen, oxygen, nitrogen, and the halogens.

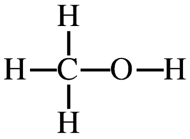
Structural Formulas

In order to write their structural formulas, it is important to remember that generally, in uncharged molecules, carbon forms four bonds, nitrogen forms three bonds, oxygen forms two bonds, and hydrogen and the halogens form one bond. With these rules for a compound of molecular formula CH_4O, there is only one possible structural formula



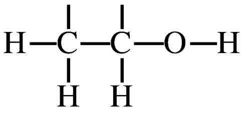
CH_3OH

Henceforth, rather than using a cumbersome system of dots to portray internuclear lines, electron dot formulas will be used in order to represent structures of compounds. Thus, the structural formula of CH_4O is written as



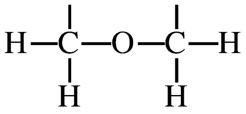
CH_3OH

Some molecular formulas can be represented by more than one structural formula. For example, there are two possible structures that exist for C_2H_6O:



CH_3CH_2OH

and

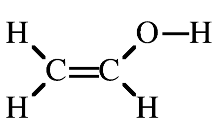


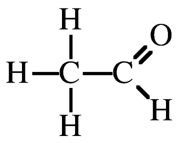
CH_3OCH_3

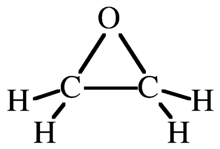
These two compounds, which have the same molecular formula but different structures, are isomers from the Greek *isos* and *meros* meaning “same parts.”

Example 1:
Write all possible structural formulas for compounds with the formula C_2H_4O.

Solution: The following three structural formulas can be written for C_2H_4O (note that each has four bonds to carbon, two to oxygen, and one to each hydrogen):

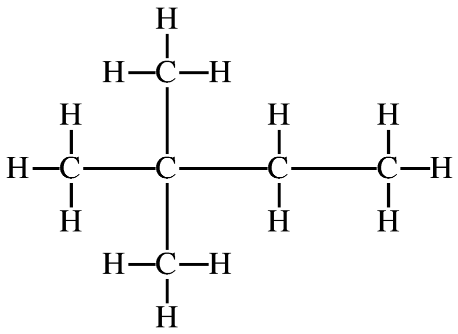




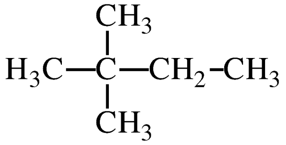


Because this molecular formula has two less hydrogens than C_2H_6O, either a double bond must be incorporated into the structure, as in the first two formulas, or a ring structure must be used.

Structural formulas for many large carbon compounds become quite unwieldy. For example, even a simple molecule, such as 2,2-dimethylbutane, has a rather awkward formula:

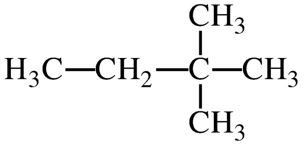


For convenience, formulas like this one may be condensed by simply writing the hydrogens next to the carbon to which they are attached:



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

or



$$H_3C-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

Note that these two structures represent the same compound; the second one is simply the first one rotated 180° in the plane of the paper.

HYDROCARBONS & RELATED COMPOUNDS

The simplest type of carbon compounds, the hydrocarbons, contain carbon atoms linked to one another and also to hydrogen. There are three main kinds of hydrocarbons: (1) **alkanes**, in which all the carbon-carbon linkages are single bonds, (2) **alkenes**, in which one or more of the carbon-carbon linkages are double bonds, and (3) **alkynes**, in which one or more of the carbon-carbon linkages are triple bonds. Alkenes and alkynes are sometimes referred to as **unsaturated compounds** because the linked carbon atoms are not bonded to as many hydrogen atoms as possible; i.e., the carbons are not saturated with hydrogen.

Alkanes

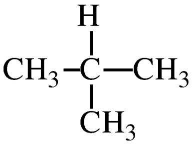
The formulas and names of some **straight-chain alkanes** (alkanes whose carbon atoms can be written on a straight line) are given in Table 1. All the names end in *-ane*, and from pentane to decane the names are derived from the Greek word for the number of carbon atoms in one molecule of the compound.

Many molecules often contain an alkane unit less one hydrogen atom as part of their structure. These groups are named by replacing the *–ane* ending in the alkane's name by *-yl*. For example, CH_3CH_3 is ethane, and CH_3CH_2 is an ethyl group. The names of these **alkyl groups** or **radicals** are given in Table 1.

TABLE 1 NOMENCLATURE FOR STRAIGHT-CHAIN ALKANES

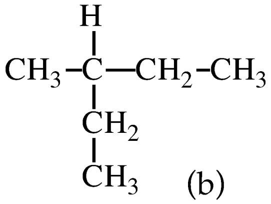
COMPOUND	NAME	NAME OF RADICAL
CH_4	methane	methyl
CH_3CH_3	ethane	ethyl
$CH_3CH_2CH_3$	propane	propyl
$CH_3CH_2CH_2CH_3$	butane	butyl
$CH_3(CH_2)_3CH_3$	pentane	pentyl
$CH_3(CH_2)_4CH_3$	hexane	hexyl
$CH_3(CH_2)_5CH_3$	heptane	heptyl
$CH_3(CH_2)_6CH_3$	octane	octyl
$CH_3(CH_2)_7CH_3$	nonane	nonyl
$CH_3(CH_2)_8CH_3$	decane	decyl

Alkanes may possess branched structures as illustrated by the following compounds:



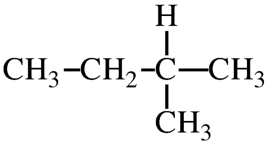
$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-CH_3$

(a)



$CH_3-\overset{\displaystyle H}{\underset{\substack{\displaystyle CH_2\\ |\\ \displaystyle CH_3}}{C}}-CH_2-CH_3$

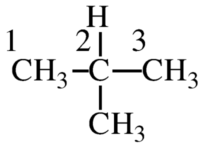
(b)



$CH_3-CH_2-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-CH_3$

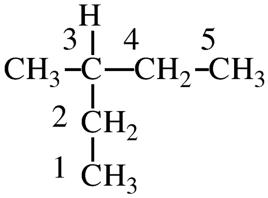
(c)

In the system of nomenclature developed by the International Union of Pure and Applied Chemistry (IUPAC), branched hydrocarbons are named by first selecting the longest chain of carbon atoms that *could* be written in a straight line and then numbering the carbon atoms of the longest chain starting from the end closest to the branch. For compound (a), the chain is numbered as follows:

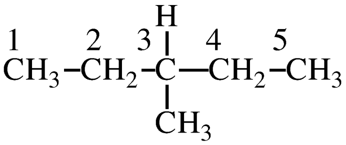


$\overset{1}{CH_3}-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{2}{C}}}-\overset{3}{CH_3}$

For compound (b) the longest chain is shown below, both as written above and as it could be written in a straight line.

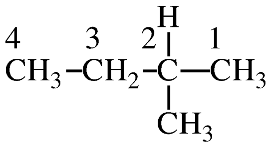


$CH_3-\overset{\displaystyle H}{\underset{\substack{\displaystyle 2\ CH_2\\ |\\ \displaystyle 1\ CH_3}}{\overset{3}{C}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$



$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{3}{C}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$

In both (a) and (b) the branch occurs midway in the longest chain, and so it is immaterial from which end the numbering begins. In compound (c), the branch occurs closer to one end of the chain; thus, numbering the carbons begins from the end position closest to the branch so that the methyl group is attached to carbon 2 rather than carbon 3.



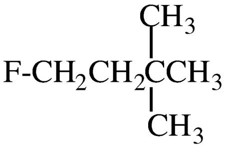
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{2}{C}}}-\overset{1}{CH_3}$

The base name of the branched hydrocarbon depends on the number of carbons in the longest chain; for (a) the base name is propane, and for (b) the base name is pentane. Finally, a name is applied to the group at the branch (also called the **substituent** because it substitutes for a hydrogen of the corresponding straight-chain alkane). Its position on the longest chain is designated by the number of the carbon atom to which it is attached.

The IUPAC name for compound (a) is 2-methylpropane; the IUPAC name for compound (b) is 3-methylpentane; and the IUPAC name for compound (c) is 2-methylbutane.

Alkanes that have one or more hydrogens replaced by halogens, such as CH_3Cl are known as halogenated alkanes. These compounds are named according to the rules above, using the following names for the halogen substituents: F, fluoro; Cl, chloro; Br, bromo; I, iodo. The compound CH_3Cl is chloromethane (also called methyl chloride); the compound $CHCl_3$ is trichloromethane (commonly called chloroform); and $CH_3CHBrCH_3$ is 2-bromopropane.

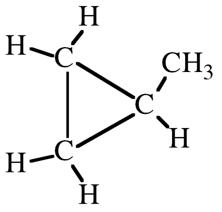
Example 2:
Name the following compound:



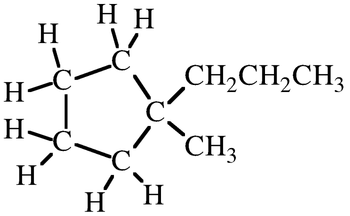
$$\text{F-CH}_2\text{CH}_2\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_3$$

Solution: The longest chain contains four carbons and the base name is therefore butane. There are three substituents--one fluoro group and two methyl groups. Each of these must be given a number corresponding to the carbon to which they are attached. There are two ways to number the carbon base. If we number from the right hand carbon, the name would be 4-fluoro-2,2-dimethylbutane. If we number from the left hand side, the name would be 1-fluoro-3,3-dimethylbutane. According to the IUPAC rules, the base should be numbered beginning at the end nearer the first branch or substituent point. Thus, the second name is the correct name. Notice that in the name the groups are listed in alphabetical order without regard to the prefixes (di, tri, etc.) in front of the group name.

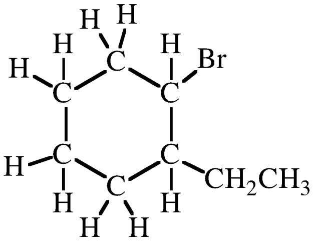
Alkanes also may be cyclic compounds. These cyclic hydrocarbons are known as cycloalkanes, and their names are based upon the number of carbons in the ring. Thus, a ring with three carbons is cyclopropane, one with four carbons is cyclobutane, one with five carbons is cyclopentane and so on. Like normal alkanes these compounds may have substituents. Consider the following examples:



methylcyclopropane



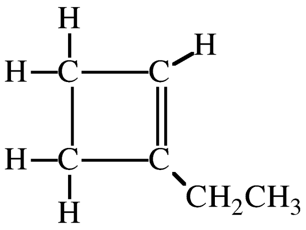
1-methyl-1-propylcyclopentane



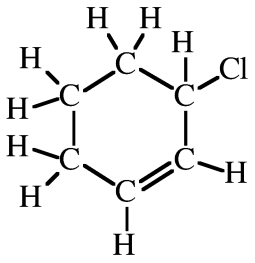
1-bromo-2-ethylcyclohexane

Alkenes

The simplest **alkene**, $H_2C{=}CH_2$, has the common name ethylene. The IUPAC name of ethylene is ethene, which is derived from the name of the analogous alkane, ethane, by replacing the *-ane* with *-ene*. For more complicated alkenes the position of the double bond in the longest carbon chain must be indicated by a number. For example, $CH_3CH{=}CHCH_3$ is 2-butene because the first carbon involved with the double bond is the second carbon in the chain; $CH_3CH_2CH_2CH{=}CH_2$ is 1-pentene, rather than 4-pentene, because the position of the double bond is given the lowest number possible. Cycloalkenes have a carbon-carbon double bond within the ring, and these two carbon atoms are assigned as number one and number two in naming compounds.

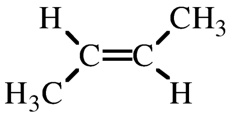


1-ethylcyclobutene

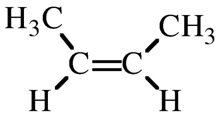


3-chlorocyclohexene

The rigid nature of the double bond results in isomers for some alkenes. For example, 2-butene may have the following two structures:

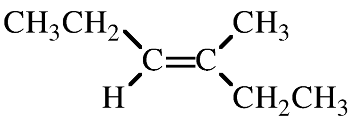


trans-2-butene

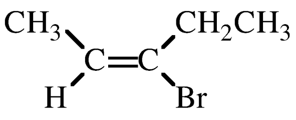


cis-2-butene

In the first structure the longest chain of carbon atoms includes two carbons that are across from each other and thus the compound is the *trans* isomer. In the second structure the corresponding carbons are on the same side, and the compound is the *cis* isomer. The following compounds provide two additional examples:



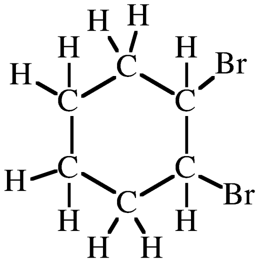
trans-3-methyl-3-hexene



cis-3-bromo-2-pentene

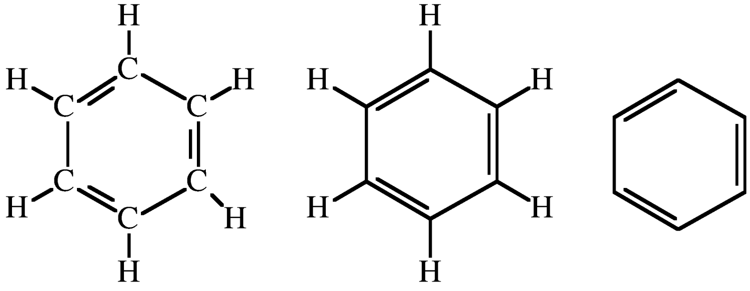
The double bond in alkenes makes them more reactive than alkanes toward some reagents. Although cyclohexane does not react with diatomic bromine (Br_2), cyclohexene will react readily with it. Similarly, cyclohexene reacts with potassium permanganate ($KMnO_4$) to produce manganese dioxide as a brown precipitate, but cyclohexane does not react.

Example 3:
Name the following compound, which is formed when bromine reacts with cyclohexene.



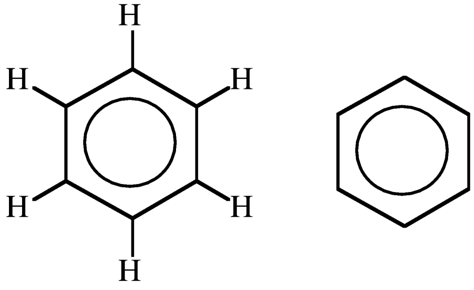
Solution: Cyclic compounds contain carbon atoms in a ring. They are named just like acyclic compounds, except that the word **cyclo-** is added as a prefix. In the compound above the longest chain of carbons contains six carbons; thus, the compound is a cyclohexane. There are two substituents: the two bromo groups. The hexane must be numbered to assign one substituent to carbon #1. The compound is 1,2-dibromocyclohexane.

A very special type of hydrocarbon that appears to be a cyclic alkene (an alkene with a carbon ring in its structure) is the compound benzene. This compound does not undergo reactions typical of alkenes, however, and for that reason and others the structural formula that shows three discrete double bonds is often an inadequate description of the bonding in this compound.



Three representations of benzene

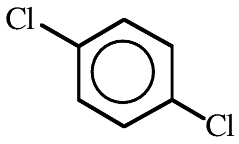
Note that the presence of the carbons is understood in the middle structure and the presence of carbon and hydrogen atoms is understood in the third structure.
An alternative structural description of the bonding in the compound uses a ring to indicate that the double bonds interact with each other to produce additional stability in benzene relative to a cyclic compound with three discrete double bonds.



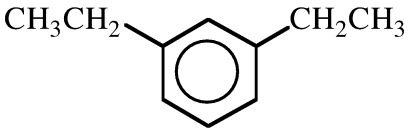
Two alternative representations of benzene

Compounds containing a benzene ring are termed **aromatic**, and the benzene ring is called the **aryl** portion of the compound. As a substituent benzene is called a **phenyl** group.

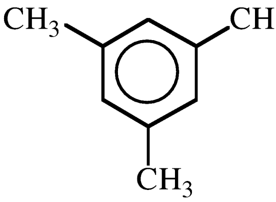
Substituted benzenes (benzenes in which substituents such as F, Cl or an alkyl group replace one or more of the hydrogen atoms) can be named by the usual IUPAC rules. For example:



1,4-dichlorobenzene

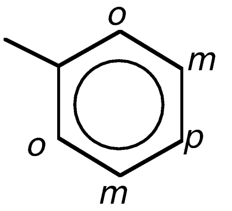


1,3-diethylbenzene



1,3,5-trimethylbenzene

These compounds can also be named by the **common system**, in which adjacent substituents are designated by the prefix *ortho* (*o*-), substituents two atoms removed are designated by *meta*- (*m*-), and substituents directly opposite are designated by *para*- (*p*-), as illustrated below.



Thus, the first compound above could be named *para*-dichlorobenzene, which is the name commonly used for a moth repellent. The second compound could be named *meta*-diethylbenzene.

Alkynes

The IUPAC rules for naming *alkynes*, those hydrocarbons that contain carbon-carbon triple bonds, are identical to the alkene rules except that the *-ane* ending of the parent alkane is replaced by *-yne* to indicate the presence of the triple bond. Propyne is CH_3CʃCH; the simplest alkyne, ethyne (HCʃCH), also has the common name acetylene. Two alkynes with the molecular formula C_4H_6 exist:

$H{-}C{\equiv}C{-}CH_2CH_3$ 1-butyne

$CH_3{-}C{\equiv}C{-}CH_3$ 2-butyne

Because the triple bond is at the end of the chain 1-butyne is called a terminal alkyne. The compound 2-butyne is an internal alkyne.

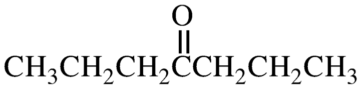
Example 4:
Name the following alkyne.

$$H{-}C{\equiv}C{-}CCl_3$$

Solution: The triple bond must be given the lowest possible number. Therefore, the carbon chain is numbered from left to right, and the compound is 3,3,3-trichloro-1-propyne. Notice that the 1 refers to the carbon where the triple bond begins. In addition, for this compound, the name 3,3,3-trichloropropyne is also acceptable because it leads to an unambiguous structure. Because the carbon bonded to three halogen substituents can form only one other bond, it is obvious that the triple bond occurs between the other two carbon members of the chain. Both names are therefore correct.

FUNCTIONAL GROUPS

Certain substituents or groups, called **functional groups**, give organic molecules characteristic chemical behaviors that are very different from those of hydrocarbons. For example, when a carbonyl group, (C=O), is present within a structure, many reagents that would not react with the parent hydrocarbon will react vigorously with the carbonyl group.

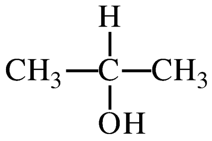


$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3$$

Note the carbonyl group in the center of this molecule, which is otherwise a simple hydrocarbon.

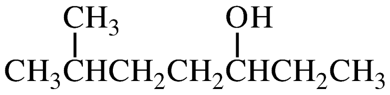
Alcohols

Alcohols contain hydroxyl functional groups (OH) bonded to tetrahedral carbons atoms; i.e., sp^3 hybridized carbon atoms. The general formula for alcohols is ROH, in which R generally represents a hydrocarbon group. In the IUPAC system, alcohols are named by first determining the longest chain of carbon atoms *that contains the OH group*. This chain is numbered in such a way as to give the OH group the lowest number. The name is produced from the name of the parent hydrocarbon by replacing the *-e* ending by *-ol*. For example, CH_3OH is called methanol. The position of the OH group on the chain is indicated by a number in front of the name. Thus, the saturated three-carbon alcohol that has the hydroxyl group on the second carbon atom is 2-propanol.



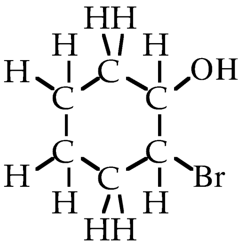
$CH_3-\overset{H}{\underset{OH}{C}}-CH_3$ 2-propanol

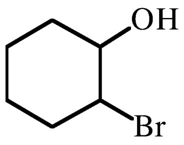
If the position of the alcohol functional group could be indicated by two different location numbers, then the name that assigns the lower number to the hydroxyl position is used. For example, in the structure shown below the proper name for the compound would be 6-methyl-3-heptanol and not 2-methyl-5-heptanol.



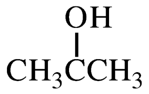
$CH_3\overset{CH_3}{C}HCH_2CH_2\overset{OH}{C}HCH_2CH_3$

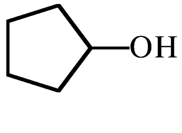
Cyclic alcohols are named using the same rules. Therefore, the compound represented by both structures below would be named 2-bromocyclohexanol. Note that in the second structural formula the carbon atoms and the hydrogen atoms are understood to be present just as the carbon and hydrogen atoms were represented in benzene in a previous section.





Many compounds containing functional groups are also named by the common system. In this system the carbon skeleton is named as a group. The common groups are summarized in Table 2. In the case of alcohols the group name is followed by the word alcohol.

CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	 $CH_3\overset{OH}{C}CH_3$
methanol methyl alcohol	ethanol ethyl alcohol	1-propanol n-propanol propyl alcohol	2-propanol isopropyl alcohol



cyclopentanol
cyclopentyl alcohol

TABLE 2 SOME COMMON ALKYL GROUPS

NUMBER OF CARBONS IN GROUP

1 CARBON

$-CH_3$

methyl

2 CARBONS

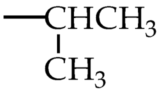
$-CH_2CH_3$

ethyl

3 CARBONS

$-CH_2CH_2CH_3$

propyl

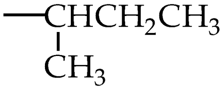

$-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

isopropyl

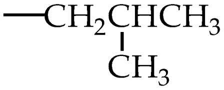
4 CARBONS

$-CH_2CH_2CH_2CH_3$

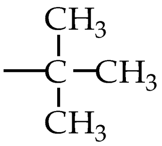
butyl


$-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

sec-butyl


$-CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

isobutyl

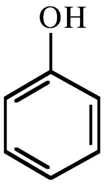

$-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

tert-butyl

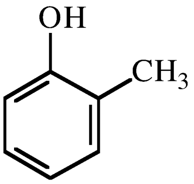
Phenols

Phenols are compounds that have hydroxyl groups attached to aromatic rings. These compounds are more acidic than alcohols because the hydroxyl group is attached to an aromatic ring. Phenols occur widely in nature and are used in many industrial preparations of important compounds. The parent compound of the group may be used as a disinfectant. Various substituted phenols may be used as flavoring agents, and some naturally occurring phenols are the compounds in poison ivy that produce allergic reactions.

The nomenclature of substituted phenols is based upon the assignment of position one to the carbon that bears the hydroxyl group. The structures below are examples. The assignment of position one is implied in the names. (Remember that in line structures the carbon and hydrogen atoms of the ring are understood to be present.)

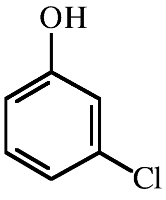


phenol



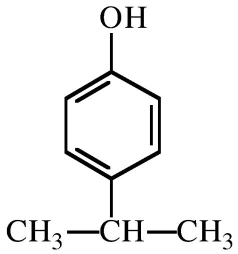
2-methylphenol

o-methylphenol



3-chlorophenol

m-chlorophenol



4-isopropylphenol

p-isopropylphenol

Ethers

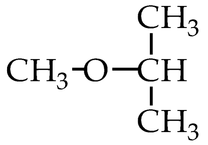
Ethers are compounds that have two organic groups attached to a central oxygen atom. The general structure is:

$$R-O-R'$$

In symmetric ethers R and R' are the same, and in asymmetric ethers R and R' are different groups. The IUPAC rules allow two methods for naming ethers. If the compound is a simple ether, then it is named by giving the identities of the two organic groups followed by the word ether. The common solvent frequently called "ether" is actually diethyl ether.

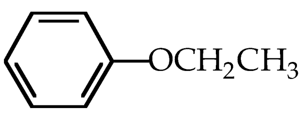
$CH_3CH_2-O-CH_2CH_3$

diethyl ether



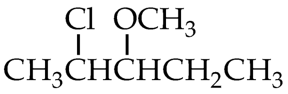
$$CH_3-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}$$

methyl isopropyl ether



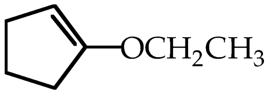
ethyl phenyl ether

If more than one ether functionality is present or if other functional groups are present, then the ether is named as an alkoxy substiutent by replacing the *–yl* ending of a group with *–oxy*.

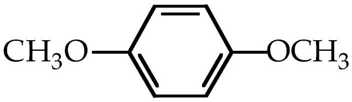


$$CH_3\overset{\overset{\displaystyle Cl}{|}}{C}H\overset{\overset{\displaystyle OCH_3}{|}}{C}HCH_2CH_3$$

2-chloro-3-methoxypentane



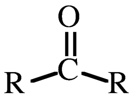
1-ethoxycyclopentene



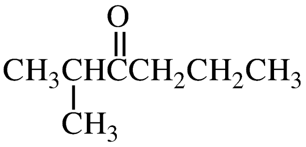
1,4-dimethoxybenzene

Ketones and Aldehydes

Ketones, which are another important class of organic compounds, have the generic formula:



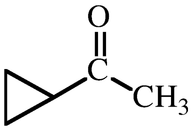
The atoms between the two R groups, C=O, is the carbonyl (car-bo-**neel**) functional group, and it is present in many of the most important functional groups. In the IUPAC system ketones are named by locating the longest chain of carbon atoms that contains the carbonyl group. The *-e* of the base carbon alkane is replaced by *-one* to designate a ketone. For example, the compound



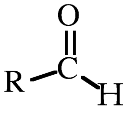
$$\mathrm{CH_3\underset{CH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3}$$

contains six carbons in the longest chain and one substituent, a methyl group. Just as with locating the hydroxyl group in alcohol, the chain must be numbered so that the carbonyl carbon receives the lowest possible number. Therefore, we number from the left-hand side of the given structure, and compound is named 2-methyl-3-hexanone.

In the common system the two groups attached to the carbonyl are named and are then followed by the word ketone. The previous compound is isopropyl n-propyl ketone. In this system, 2-butanone would be named methyl ethyl ketone (also known as the common solvent MEK). Similarly, the compound shown below is cyclopropyl methyl ketone.

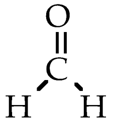


Aldehydes also have a carbonyl group with a general structure:



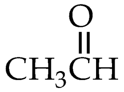
They are generally more reactive than ketones because the carbonyl group is slightly more polar in an aldehyde than it is in a similar ketone and because the hydrogen atom is smaller that an R group so reagents may more readily attack the carbonyl carbon atom.

As was the case in naming ketones, the carbonyl group is given priority in a numbering scheme. In the IUPAC system aldehydes are named by locating the longest chain of carbon atoms that contains the carbonyl group. The *-e* of the base carbon alkane is replaced by *–al* to designate an aldehyde. Thus, a straight chain aldehyde with five carbons would be pentanal. Four low molecular weight aldehydes with their IUPAC names and common names are:



methanal

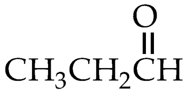
formaldehyde



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}H}$$

ethanal

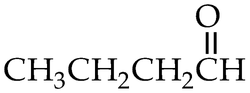
acetaldehyde



$$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}H}$$

propanal

propionaldehyde

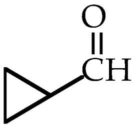


$$\mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H}$$

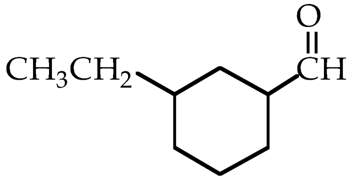
butanal

butyraldehyde

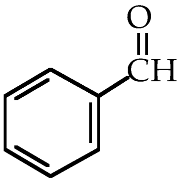
Cyclic compounds that are aldehydes are name by stating the name of the ring system followed by the term carbaldehyde. Simple aromatic aldehydes are benzaldehydes.



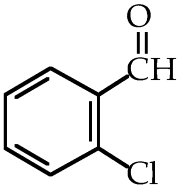
cyclopropanecarbaldehyde



3-ethylcyclohexanecarbaldehyde



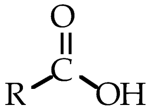
benzaldehyde



2-chlorobenzaldehyde
o-chlorobenzaldehyde

Carboxylic Acids

Carboxylic acids have the generic formula:



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

In these compounds the carbonyl is attached to a hydroxyl group. Because of the electronegativity of both oxygens, these compounds release the OH hydrogen as a proton to molecules that have a lone pair of electrons. Compounds that function in this way are called acids. In the IUPAC system the name of the compound is based on the longest carbon chain that includes the carbonyl carbon. The *-e* of the parent alkane is then replaced by *-oic acid*. For example, the compound

$$CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2\overset{\displaystyle O}{\overset{\|}{C}}OH$$

is 3-hydroxybutanoic acid. The IUPAC and common names for the simple carboxylic acids are give in Table 3.

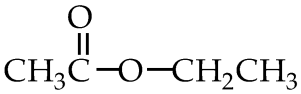
TABLE 3 IUPAC AND COMMON NAMES FOR CARBOXYLIC ACIDS

methanoic acid	formic acid	HCO_2H
ethanoic acid	acetic acid	CH_3CO_2H
propanoic acid	propionic acid	$CH_3CH_2CO_2H$
butanoic acid	butyric acid	$CH_3CH_2CH_2CO_2H$
pentanoic acid	valeric acid	$CH_3CH_2CH_2CH_2CO_2H$

If the carboxylic acid functionality is a substituent on benzene then the compound is named as benzoic acid.

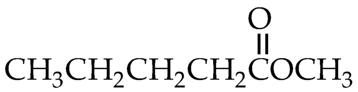
Esters

Esters are derivatives of carboxylic acids in which the H of the acid has been replaced by either an alkyl group or an aryl group. They are often characterized by their sweet or fruity odor. Esters are named by first giving the name of the group that replaced the H followed by the acid's name is which the *–oic acid* ending is replaced by *–ate*. For example, the compound below may be named as either ethyl acetate or ethyl ethanoate.



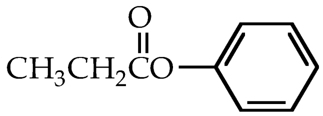
$$CH_3\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$$

Other examples include:

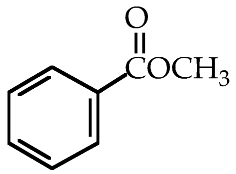


$$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3$$

methyl pentanoate
methyl valerate



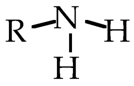
phenyl propanoate
phenyl propionate



methyl benzoate

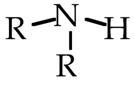
Amines

Organic derivatives of ammonia (NH_3) are know as amines. These compounds are structurally derived from ammonia just as ethers and alcohols are may be structurally derived from water. Amines are commonly found in plants and animals in three general forms with increasing numbers of organic groups attached to the central nitrogen atom.



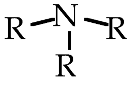
$R-\underset{H}{\underset{|}{N}}-H$

primary amine
1° amine



$R-\underset{R}{\underset{|}{N}}-H$

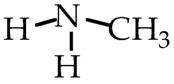
secondary amine
2° amine



$R-\underset{R}{\underset{|}{N}}-R$

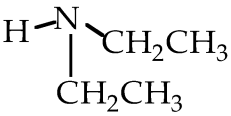
tertiary amine
3° amine

Amines may be named by adding the suffix *amine* to the alkyl or aryl group(s) name(s), or they may be named by replacing the *–e* ending of the parent compound's name with *–amine*. For example, the amine with one methyl group attached to the nitrogen could be called methylamine or methanamine. If more than one group is attached to the nitrogen, then they must be clearly identified in the name. For example, if two ethyl groups are bonded to the nitrogen atom, then the name would be diethylamine, and if three phenyl groups are bonded to the same nitrogen, then the appropriate name would be triphenylamine.



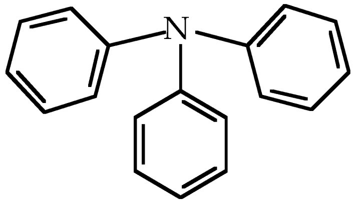
$H-\underset{H}{\underset{|}{N}}-CH_3$

methylamine
methanamine

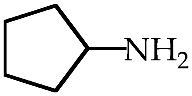


$H-\underset{CH_2CH_3}{\underset{|}{N}}-CH_2CH_3$

diethylamine



triphenylamine



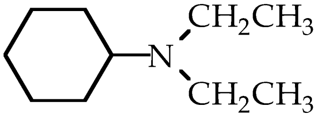
cyclopentylamine
cyclopentanamine

$H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$

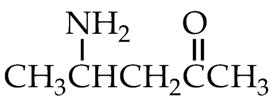
1,6-hexanediamine

Secondary and tertiary amines that are asymmetrical are named as *N*-substituted primary amines in which the largest group is chosen to determine the parent name of the compound. The prefix *N*- indicates that a substituent is bonded directly to the nitrogen atom. For example, compounds shown below are *N*-methylpropylamine and *N*,*N*-diethylcyclohexylamine, respectively.

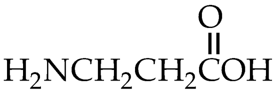
$CH_3\underset{H}{\underset{|}{N}}CH_2CH_2CH_3$



Amines that have other functional groups are usually named with the –NH_2 group considered to be an *amino* substituent. For example, the compounds below would be 4-amino-2-pentanone and 3-aminopropanoic acid, respectively.

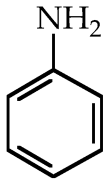


$$\mathrm{CH_3\overset{NH_2}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}CH_3}$$

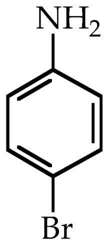


$$\mathrm{H_2NCH_2CH_2\overset{O}{\overset{\|}{C}}OH}$$

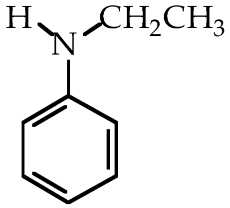
Benzene with an amino group is usually called aniline, although it could be aminobenzene or benzamine. Aniline may have substituents on the aromatic ring or on the nitrogen or both.



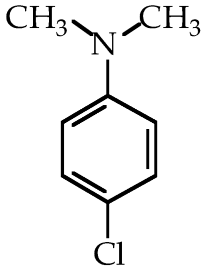
aniline



4-bromoaniline



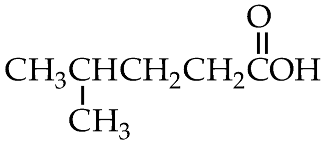
N-ethylaniline



4-chloro-*N,N*-dimethylaniline

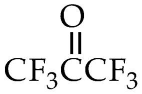
Example 5:

Name the following compounds using both the IUPAC and Common systems:



$$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2\overset{O}{\overset{\|}{C}}OH}$$

a)



$$\mathrm{CF_3\overset{O}{\overset{\|}{C}}CF_3}$$

b)

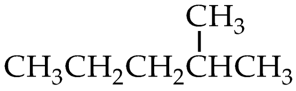
Solution: 4-methylpentanoic acid

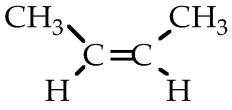
1,1,1,3,3,3-hexafluoropropanone or hexafluoropropanone

PROBLEMS

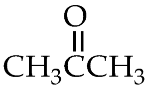
1. Name the following compounds:

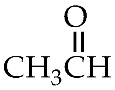
(a) $CH_3CH_2CH_3$

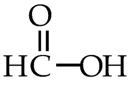
(b) 
$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

(c) 

(d) $CH_3C\equiv CH$

(e) 
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

(f) 
$CH_3\overset{\overset{O}{\|}}{C}H$

(g) 
$H\overset{\overset{O}{\|}}{C}-OH$

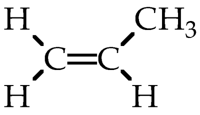
(h) $CH_3OCH_2CH_3$

(i) $CH_3CH_2NH_2$

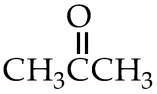
answers: a. propane; b. 2-methylpentane; c. cis-2-butene; d. propyne; e. propanone; f. ethanal or acetaldehyde; g. methanoic acid or formic acid; h. ethyl methyl ether; i. ethylamine or ethanamine

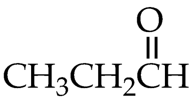
2. Write structural formulas for each of the following compounds:

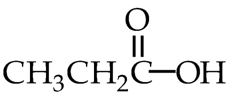
(a) propene (b) propyne (c) propanone
(d) propanal (e) propanoic acid (f) 2-propanol

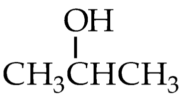
(a) 

(b) $H-C\equiv C-CH_3$

(c) 
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

(d) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}H$

(e) 
$CH_3CH_2\overset{\overset{O}{\|}}{C}-OH$

(f) 
$CH_3\overset{\overset{OH}{|}}{C}HCH_3$

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