

Chemistry - A Molecular Science

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Periodic Table of the Elements

3 Li 6.941	4 Be 9.0122													1 H 1.0079					
11 Na 22.990	12 Mg 24.305	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.478	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29		
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Uun (269)	111 Uuu (272)	112 Uub (277)								
58 Ce 140.11	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97						
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	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 (262)						

Chapter 1

The Early Experiments

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1.0 INTRODUCTION

Chemistry is the science of matter, its properties, and the changes it undergoes. Chemists seek to understand our material universe at a molecular level and to use this understanding to improve our interaction with it, often creating new products that enhance our lives. These products include pharmaceuticals, fuels, plastics, batteries, soaps, perfumes, foods, fertilizers and pesticides, to name just a few. Chemists often design these products by considering the properties of the desired substance and then proposing reactions of atoms or molecules that might yield the substances of choice. This design process involves particles and processes chemists can envision but cannot see. Chemists can observe the results of a reaction, such as a color change, the formation of a gas or a solid, or the formation of the substance with the desired properties. However, they cannot view directly the collisions of the atoms or molecules in a reaction or the changes these collisions produce. Yet, chemists are confident that these collisions and changes do occur. How did we get to the point where we can envision these invisible processes? How do we know the nature of these invisible atoms and molecules? We start our study of chemistry by beginning to answer these two questions.

THE OBJECTIVES OF CHAPTER 1 ARE TO:

- define the scientific method and illustrate its importance in scientific discovery;
- introduce Coulomb's law and the electromagnetic force;
- introduce the early scientists and the experiments that eventually led to the description of the nuclear atom and its components;
- describe the subatomic particles and their characteristics; and
- explain the use of the Periodic Table in predicting an element's physical and chemical properties.

1.1 SCIENTIFIC METHOD

Chemistry is a science, which means that all chemical knowledge is gained by the application of a set of principles and procedures known as the scientific method. To understand how chemistry progressed to where it is today and how it will progress in the future, you must first understand how this method is applied. The *scientific method* involves the following steps:

1. *observation* and collection of quantitative or qualitative data.*
2. *formulation of a hypothesis* to explain the observation;
3. *prediction* based on the hypothesis; and
4. *testing* the prediction.

If a test supports a hypothesis, another experiment is devised to further test the hypothesis. If a test does not support a hypothesis, then the hypothesis is changed or even discarded depending upon how badly it fails the test. After a hypothesis has been supported by many independent observers, it becomes a law or a theory. A **law** summarizes many observations, while a **theory** provides an explanation for them. Theories cannot be proven and are valid only as long as they are supported or, at least, not disproved by experiment. Our understanding is constantly evolving as the sophistication of our tools and instruments improves and our scientific knowledge increases. Many long held theories have eventually failed the test of experiment and have been modified or discarded entirely. Thus, chemistry is a dynamic science that continues to build upon past observations and theories by exploring new discoveries and hypotheses. The struggle of the earliest scientists to understand and explain the nature of things around them is an amazing journey of discovery. In this chapter, we examine some of the experiments that brought us from the birth of modern chemistry at the end of the 18th century to the discovery of subatomic particles near the end of the 19th century.

1.2 LAVOISIER AND THE BIRTH OF MODERN CHEMISTRY

Controlling fire was a major factor in the rise of humans, so it is not surprising that one of the first theories dealt with burning objects. We can make two obvious observations about fire: it is hot; and the flame leaps from the fuel. **Phlogiston theory** was born from little more than this kind of fireside observation. According to phlogiston theory, materials that burned contained a substance called phlogiston, and burning was thought to be the release

* Quantitative observations involve numbers, while qualitative observations do not. For example, “the mass of the object is 3.2 g” is a quantitative observation, while “the object is black” is a qualitative observation.

of phlogiston (the flame leaping from the fuel). The residue that remained after burning was called calx. A phlogistonist would view the brilliant white light that is produced when magnesium burns as the escape of phlogiston and represented the burning as



Thus, it was believed that the metal lost phlogiston when it burned. Early in the eighteenth century, however, Antoine Lavoisier, a French chemist, showed that the mass of the calx was greater than the mass of the metal. Scientists that supported the phlogiston theory reasoned that either mass was not relevant to chemistry or that phlogiston had negative mass, but most scientists realized that phlogiston theory had failed an important test, and it was eventually discarded.

Lavoisier measured the mass of many reactions and observed that the total mass does not change. He summarized his results in the law of conservation of mass.

Law of Conservation of Mass: during a chemical reaction, the total mass (reactants + products) remains constant; that is, mass is neither created nor destroyed during a chemical reaction.

After careful and repeated experiments, he realized that burning a metal was the combination of the metal with oxygen, not the release of phlogiston. Lavoisier introduced a new way of thinking about chemistry and is known as the father of modern chemistry. He viewed the calx of a metal as the metal oxide and the reaction as



Lavoisier was also the first to classify matter as elements or compounds. An **element** is a pure substance that cannot be broken down by chemical means to a simpler substance. Magnesium and oxygen are examples of elements. Today, there are over 100 known elements. A **compound** is a pure substance that consists of more than one element. Magnesium oxide is a compound that is formed by the combination of two elements (magnesium and oxygen).

The scientists of the early 19th century had a new system and a new way of thinking about matter as the field of chemistry was born. They began testing the concept that matter consisted of elements and compounds and that mass was indeed relevant to chemistry. After a great number of measurements of relative masses had been performed, two more laws that summarized the results were accepted.

Law of Definite Proportions: the elements of a compound are present in definite (fixed) proportions by mass. For example, the mass of table salt (sodium chloride) is always 39% sodium and 61% chlorine and that of water is always 11% hydrogen and 89% oxygen.

Law of Multiple Proportions: when two different compounds are formed from the same two elements, the masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers. For example, water and hydrogen peroxide are both compounds that are composed only of the elements hydrogen and oxygen. There are eight grams of oxygen for each gram of hydrogen in water, but there are 16 g of oxygen for each gram of hydrogen in hydrogen peroxide. For a specified mass of hydrogen (one gram), the mass ratio of oxygen in the two compounds is 8:16 or 1:2, a ratio of small whole numbers.

Example 1.1

Sodium (Na) and oxygen (O) form two different compounds that are 59% and 74% Na by mass. Show that these compounds obey the law of multiple proportions.

First, determine the mass of sodium that is combined with a specified mass of oxygen. Percents can be converted easily into grams by assuming a total mass of 100 g. For example, 59% of a 100 g sample is 59 g. The compounds consist only of Na and O, so the sum of the percents must be 100. Consequently, %O = 100 - %Na.

Next, specify a fixed mass of one of the substances, which is usually set at 1 g. In the following, it is the mass of oxygen that is fixed. The mass of Na combined with 1 g of O is obtained by dividing the mass of Na by the mass of O with which it is combined. The following table shows the results.

Compound	%Na	%O	grams Na/1 gram O
I	59	41	$\frac{59 \text{ g Na}}{41 \text{ g O}} = \frac{1.4 \text{ g Na}}{1 \text{ g O}}$
II	74	26	$\frac{74 \text{ g Na}}{26 \text{ g O}} = \frac{2.8 \text{ g Na}}{1 \text{ g O}}$

Finally, determine the ratio of the masses of Na combined with 1 g O in the two compounds. The ratio of compound II to compound I is

$$\text{ratio} = \frac{\frac{2.8 \text{ g Na in cmpd II}}{\text{g O}^*}}{\frac{1.4 \text{ g Na in cmpd I}}{\text{g O}^*}} = \frac{2.8 \text{ g Na in cmpd II}}{1.4 \text{ g Na in cmpd I}} = \frac{2.0 \text{ g Na in cmpd II}}{1.0 \text{ g Na in cmpd I}}$$

The ratio is a ratio of small whole numbers (2:1), so these compounds obey the law of multiple proportions. The ratio implies that there is twice as much Na per gram of O in compound II as there is in compound I. In fact, compound I is Na_2O_2 (sodium peroxide) and compound II is Na_2O (sodium oxide).

* Note that the units "g O" are in the denominators, so they cancel in the ratio to yield the desired ratio of masses of Na. Units are very important and their use in solving problems will be examined in more detail later in the chapter.

1.3 JOHN DALTON AND ATOMIC THEORY (1804)

Laws hold the key to understanding nature's secrets, and theories are our attempt to unlock the secrets. The chemists of the early 19th century had three laws to explain: conservation of mass, definite proportions, and multiple proportions. Elements and compounds were the accepted forms of matter; but what were the mass relationships telling them? In 1804, John Dalton, an English chemist, suggested an answer: elements consisted of tiny spheres, called atoms, which he likened to billiard balls with hooks on them. He assigned the following properties to atoms to assure that they behaved in a manner consistent with the laws of conservation of mass, definite proportions, and multiple proportions:

1. An element is composed of extremely small particles called **atoms**. The atoms of a given element all exhibit identical chemical properties,* but atoms of different elements have different chemical properties.
2. In the course of a chemical reaction, no atom disappears or is changed into another atom. This property explains The *law of conservation of mass* and is the basis for writing *balanced chemical equations*. In a balanced chemical equation, the number of each kind of atom must be the same on both sides of the equation.
3. Compounds are formed when atoms of different elements combine. In a given pure compound, the relative numbers of atoms of each element present will be definite and constant, and their ratios can be expressed as integers or simple fractions. This property explains the *laws of definite proportions and multiple proportions*.

Atoms combine with one another to form **molecules**, which are the smallest units of a substance that have the chemical properties of the substance. Dalton assumed that the simplest form of an element was an atom, while the simplest form of a compound was a molecule; but we shall soon see that this assumption is not quite correct because some elements exist as molecules.

Dalton developed a list of symbols to represent the different atoms. Hydrogen was ☺ and oxygen was O. Lacking any information to the contrary, he assumed water contained one hydrogen atom and one oxygen atom and was therefore represented as ☺O. Fortunately, his system was discarded for one in which the symbol of the element was formed from one or two letters of its name, usually the first one or two. Thus, a hydrogen atom is now represented by H and an oxygen atom by O. A water molecule would have been HO, but we now know that a water molecule contains two hydrogen atoms and one oxygen atom, so it is H₂O. The story of how the formula of this simple molecule was determined is fascinating and instructive, and it is presented in the next section.

* **Chemical properties** indicate how a substance can be changed into another substance. "Hydrogen reacts with oxygen to produce water" is a statement of a chemical property. **Physical properties** are independent of other substances and involve no change in the identity of the compound. Melting and boiling points, conductivity, hardness, and color are physical properties.

1.4 ATOMS AND MOLECULES

Dalton recognized that mass was an important property of atoms and molecules, so he introduced the concepts of atomic and molecular mass.* Hydrogen is the lightest of the known atoms, so Dalton assigned it a relative mass of one (no units). He assumed that the atom ratio in water was 1:1, so the reaction of hydrogen with oxygen to produce water was thought to be $\text{H} + \text{O} \rightarrow \text{HO}$. He also knew that 8 g of oxygen reacted for each 1 g of hydrogen to produce 9 g of water. Therefore, he reasoned that the mass of one oxygen atom was eight times that of one hydrogen atom, which meant that oxygen had a relative mass of 8. Water, which he assumed was HO, had a relative mass of $1 + 8 = 9$.

At about the same time that Dalton was formulating his atomic theory, the French chemist, Joseph Gay-Lussac, was measuring the volumes of reacting gases. In 1808, he published his results, now known as the law of combining volumes.

Law of Combining Volumes: Volumes of reacting gases are in simple whole number ratios.

Experiment showed that the volumes of hydrogen and oxygen that react are in a 2:1 ratio.



The law of combining volumes was soon explained in terms of Dalton's atomic theory, but the explanation rested on the assumption that *equal volumes of gases measured at the same temperature and pressure must contain equal numbers of particles!* The volume of hydrogen is twice that of oxygen in the reaction, so it was concluded that a water molecule contained twice as many hydrogen atoms as oxygen atoms. The formula of water had to be H_2O . The reaction was then thought to be $2\text{H} + \text{O} \rightarrow \text{H}_2\text{O}$.

The change in the formula of water meant that the *relative* masses that Dalton had determined for hydrogen and oxygen were wrong. One oxygen atom was eight times more massive than *two* hydrogen atoms and the atomic mass scale was changed accordingly. In the new scale, H = 1, O = 16, and $\text{H}_2\text{O} = 18$. The new scale was still consistent with the observation that 1 gram of hydrogen reacted with 8 grams of oxygen to produce 9 grams of water. However, one gram of hydrogen contained twice as many atoms as did 8 grams of oxygen.

The formula of water and the relative masses of hydrogen and oxygen had finally been determined, but the reaction of hydrogen and oxygen still had something to teach us. Consider that the equation $2\text{H} + \text{O} \rightarrow \text{H}_2\text{O}$ predicts that 2 volumes of hydrogen combine with 1 volume of oxygen to produce 1 volume of water vapor, but experiment was soon to show that the reaction produces 2 volumes of water!

* The terms atomic and molecular weights are commonly used, but the numbers represent masses not weights.

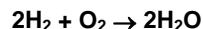
2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of water

The apparent dilemma was explained in 1811 by Amadeo Avogadro. His hypothesis became known as Avogadro's law.

Avogadro's law: Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Avogadro reasoned that elements, like compounds, can also occur as molecules, and it was the reaction of hydrogen and oxygen molecules, not atoms, that produced water molecules. His suggestion was contrary to Dalton's assertion that the atom is the simplest form of an element. Thus, an **element** is a substance that consists of only one type of atom, and a **compound** is a substance that contains more than one type of atom.

The relative volume of water produced in the reaction of hydrogen and oxygen could be explained if elementary hydrogen and oxygen each existed as diatomic (two atom) molecules, which means that the balanced reaction should be written as follows:



The above chemical equation is consistent with the experimental observations of both mass and volume ratios, and it is the way the reaction is written today. Hydrogen and oxygen are not the only elements to exist as diatomic molecules.

Common diatomic elements: H₂, N₂, O₂, F₂, Cl₂, Br₂, and I₂.

Some elemental molecules, such as P₄ and S₈, contain more than two atoms.

The atomic mass scale was constructed by measuring relative masses of combining substances and assuming or determining the formula of the compound they produced. However, the modern system of atomic masses is not based on the hydrogen atom; rather it is based on the most common form of carbon, called carbon-12, which is *assigned* an atomic mass of exactly 12. The mass of an oxygen atom is $\frac{4}{3}$ that of a carbon-12 atom, so oxygen's atomic mass is $(\frac{4}{3})(12) = 16$.

Example 1.2

Classify the following as elements or compounds and as atoms or molecules.

a) S_8

S_8 contains only one type of atom and is therefore an *element*. However, it contains eight chemically bound atoms, so it is also a *molecule*.

b) Ar

Ar contains only one type of atom and is therefore an *element*. In addition, it contains no chemical bonds and is an *atom*.

c) N_2O_5

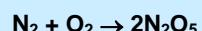
N_2O_5 contains two types of atoms, so it is a *compound*. The nitrogen and oxygen atoms are bound together to form a *molecule*.

Example 1.3

Balance the following chemical equations.

a) $N_2 + O_2 \rightarrow N_2O_5$

The number of atoms of each element in a balanced equation are made the same on both sides by placing coefficients in front of each species. Subscripts in the formula must not be changed as that would change the identity of the molecules. Note that N_2 and O_2 are both diatomic molecules, so the number of oxygen and nitrogen atoms will each be even on the left side if integer coefficients are used. We therefore start by placing a 2 in front of the N_2O_5 to assure an even number of oxygen atoms on the right side.



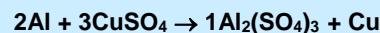
The right side now shows four nitrogen atoms, which means that two N_2 molecules must appear on the left. The right side also indicates ten oxygen atoms, so five O_2 molecules are required on the left. Thus, we write



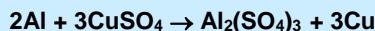
The above equation shows four nitrogen atoms and ten oxygen atoms on each side. The number of each atom is the same on both sides, so the equation is balanced.

b) $Al + CuSO_4 \rightarrow Al_2(SO_4)_3 + Cu$

The S and O atoms remain bound to one another in SO_4 , so we can balance the SO_4 as a unit rather than individual sulfur and oxygen atoms. We start by placing a one in front of the molecule with the greatest number of atoms, $Al_2(SO_4)_3$. That fixes the number of Al atoms and SO_4 units on the right side, so we must balance them on the left as follows:



The number of Cu atoms is now fixed on the left at 3, so we balance them on the right. Finally, coefficients of one are not usually shown, so the balanced equation is



1.5 THE MOLE AND MOLAR MASS

The last equation balanced in the preceding exercise shows that Al atoms react with CuSO₄ molecules in a 2:3 ratio, so we would like to mix the reactants in a ratio that is close to that. Unfortunately, individual atoms and molecules are much too small to see, and the numbers of atoms and molecules in reactions carried out in the laboratory are far too large to count, so we must measure the ratio of reacting atoms and molecules indirectly from their relative masses and their atomic or molecular masses.

If the masses of two pure substances are in the same ratio as their atomic or molecular masses, then the substances contain the same number of atoms or molecules.

The number of atoms or molecules in 12.0 g C, 16.0 g O, and 18.0 g H₂O is identical. While Dalton had no idea what that number was, it was still a very useful concept because chemists could mix ingredients in the desired atom or molecule ratios using masses. The number of atoms or molecules in each of the above examples is called the *mole*. We count atoms and molecules in moles just as we count our shoes in pairs and our eggs in dozens.

A **mole**, which is abbreviated *mol*, is the number of atoms or molecules present in a sample of an element or a compound with a mass equal to its atomic or molecular mass expressed in grams. The number of items in a mole is called **Avogadro's number (N_A)**, which has been determined to be N_A = 6.022 × 10²³ mol⁻¹.

Just as *dozen* means 12 items, *mole* means 6.022 × 10²³ items. Avogadro's number is a huge number, and its size is an indication of just how small atoms and molecules are. Consider that a mole of dice, each die $\frac{1}{2}$ inch on a side, would cover the 48 contiguous states of the United States to a height of 100 miles, while a mole of water has a volume of only 18 mL. Yet, a mole of dice and a mole of water contain the same number of items.

A mass of a pure substance equal to its atomic or molecular mass expressed in grams contains one mole of the substance, so it is referred to as the **molar mass (M_m)** of the substance. Alternatively, *the molar mass equals the atomic or molecular mass expressed in g·mol⁻¹*. The atomic mass of O is 16, so its molar mass is 16.0 g·mol⁻¹, while the molecular mass of O₂ is 32.0, so its molar mass is 32.0 g·mol⁻¹. The mass of an individual atom or molecule is its atomic or molecular mass expressed in **atomic mass units (amu)**. Thus, the mass of a single oxygen atom is 16.0 amu, the mass of one oxygen molecule is 32.0 amu, and the mass of one water molecule is 18.0 amu. Consequently, there are Avogadro's number of amu in one gram: 1 g = N_A amu = 6.022 × 10²³ amu, which means that 1 amu = (1/N_A) g = 1.661 × 10⁻²⁴ g.

Example 1.4

- a) What is the mass of 0.137 mol CaCO₃?

Mass \leftrightarrow mole conversions are very important in chemistry, and are most easily done by multiplying the given quantity by the appropriate **conversion factor** that converts the given quantity into the desired quantity. The molar mass is the conversion factor in this problem.

$$M_m(\text{CaCO}_3) = M_m(\text{Ca}) + M_m(\text{C}) + 3M_m(\text{O}) = 40 \text{ g/mol} + 12 \text{ g/mol} + 3(16 \text{ g/mol})$$

$$M_m(\text{CaCO}_3) = 100 \text{ g/mol}$$

We now multiply the given quantity by the conversion factor so that the given units are converted into the desired units (mol CaCO₃ cancel). Using units and conversion factors to solve a problem is called the **factor label method**.

$$\cancel{0.137 \text{ mol CaCO}_3} \times \frac{100 \text{ g CaCO}_3}{\cancel{1 \text{ mol CaCO}_3}} = 13.7 \text{ g CaCO}_3$$

- b) How many moles of CaCO₃ are present in 5.36 g of CaCO₃?

We determined the molar mass of CaCO₃ in Part a, so we multiply the given mass (5.36 g) by the conversion factor (100 g CaCO₃/mol CaCO₃) such that g CaCO₃ cancel and the result is the desired quantity.

$$\cancel{5.36 \text{ g CaCO}_3} \times \frac{1 \text{ mol CaCO}_3}{\cancel{100 \text{ g CaCO}_3}} = 0.0536 \text{ mol CaCO}_3$$

- c) How many moles of oxygen atoms are present in 2.69 g of CaCO₃?

Two conversion factors must be used in this example: one to convert grams of CaCO₃ to moles of CaCO₃ and one to convert moles of CaCO₃ to moles of oxygen atoms.

$$\cancel{2.69 \text{ g CaCO}_3} \times \frac{1 \text{ mol CaCO}_3}{\cancel{100 \text{ g CaCO}_3}} \times \frac{3 \text{ mol O}}{\cancel{1 \text{ mol CaCO}_3}} = 0.0807 \text{ mol O}$$

Note that the units of the denominator of the second conversion factor cancel the units of the numerator of the first conversion factor (mol CaCO₃). Using the units of the conversion factors to decide the order and manner of multiplication of the factors in a problem is a powerful tool. Refer to Appendix A for a review of how to use conversion factors in mass \leftrightarrow mole conversions.

See Appendix A for more examples.

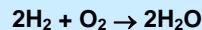
Ratios of atoms or molecules are equal to ratios of moles of atoms or molecules, and chemists usually use moles rather than numbers of individual particles in the laboratory. The reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ shows us that 2 mol H₂ react with every 1 mol O₂ and are required to produce every 2 mol H₂O. The ratio of the coefficients is the conversion factor, called the **stoichiometric factor**, that allows us to convert from one substance to another in a balanced chemical equation. The following stoichiometric factors and their reciprocals relate to the reaction of hydrogen and oxygen:

$$\frac{2 \text{ mol H}_2}{1 \text{ mol O}_2}, \frac{2 \text{ mol H}_2}{2 \text{ mol H}_2\text{O}}, \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}}$$

Example 1.5

How many moles of H₂ are required to react with 8.0 g O₂ to produce H₂O?

First, write the balanced chemical equation for the reaction.



The first thing that must always be done when solving a stoichiometry problem is to convert the masses into moles by dividing by the molar mass, which is 32.0 g·mol⁻¹ for O₂.

$$8.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} = 0.25 \text{ mol O}_2$$

The given number of moles is then converted into the chemically equivalent number of desired moles with the stoichiometric factor that contains both substances. The balanced equation indicates that 2 mol H₂ are required for every 1 mol O₂, so we write

$$0.25 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 0.50 \text{ mol H}_2 \text{ required}$$

This is an example of *reaction stoichiometry*, the topic of Appendix D.

Chemists seldom add chemicals in the exact stoichiometric ratio, so the amount of product that forms depends upon the amount of the reactant, called the **limiting reactant**, that is consumed first. Consider the reaction of 5 mol S and 6 mol O₂ to produce SO₃. There are 5 mol S, and each mole of SO₃ requires one mole of S, so there is enough S to produce 5 mol SO₃. There are 12 mol O atoms in 6 mol O₂, and each mole of SO₃ requires 3 mol of O, so there is enough O to make only 4 mol SO₃. After 4 mol SO₃ are produced, all of the O₂ is gone, and no more SO₃ can be made. Making 4 mol SO₃ requires only 4 mol S, so there is 1 mol S left over. Thus, O₂ is the limiting reactant, while S is in excess.

Example 1.6

How much Al₂O₃ can be produced from 10.0 mol Al and 9.0 mol O₂?

The balanced chemical equation is 4Al + 3O₂ → 2Al₂O₃.

To find the limiting reactant, we must determine how much Al₂O₃ can be made from each reactant.

$$10.0 \text{ mol Al} \times \frac{2 \text{ mol Al}_2\text{O}_3}{4 \text{ mol Al}} = 5.0 \text{ mol Al}_2\text{O}_3$$

$$9.0 \text{ mol O}_2 \times \frac{2 \text{ mol Al}_2\text{O}_3}{3 \text{ mol O}_2} = 6.0 \text{ mol Al}_2\text{O}_3$$

There is enough Al to make 5.0 mol Al₂O₃, and enough O₂ to make 6.0 mol Al₂O₃.

Therefore, Al is the limiting reactant and 5.0 mol Al₂O₃ is produced.

How many moles of excess reactant remain?

The number of moles of O₂ consumed in the reaction with 10.0 mol Al is

$$10.0 \text{ mol Al} \times \frac{3 \text{ mol O}_2}{4 \text{ mol Al}} = 7.5 \text{ mol O}_2$$

7.5 of the 9.0 moles of O₂ react, so there are 9.0 – 7.5 = 1.5 mol O₂ left over.

Dalton's atomic theory proved successful in predicting the experimental results of his time and became the accepted way to think about matter. His ideas on atomic masses also proved to be very useful, although some of the atomic masses had to be changed as new data became available. All in all, chemists of the day were quite comfortable with the idea that the smallest unit of matter was the 'billiard ball' atom proposed by Dalton. Then, near the end of the 19th century, new and more sophisticated experiments were performed that caused scientists to change their view. However, before we examine these experiments, we need to understand the roles of energy and charge in the study of chemistry.

1.6 ENERGY

Energy plays an important role throughout chemistry. Indeed, there is hardly a chapter in this text in which energy considerations are not required. In simple terms, energy is the capacity to move something. The energy of a substance is the sum of its kinetic energy and its potential energy. **Kinetic energy (KE)** is energy of motion; an object that is moving has the capacity to make another object move simply by colliding with it. The kinetic energy of a particle of mass m moving with a velocity v is given in Equation 1.1.

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

Eq. 1.1

If mass is expressed in kg and speed in m·s⁻¹, then the kinetic energy is in joules (J).

Potential energy is energy due to position. Some examples of objects with potential energy are a truck at the top of a hill, a stretched rubber band, and a stick of dynamite. In each case, the potential energy can be converted into kinetic energy. For example, releasing the brake of the truck causes the truck to gain speed as it rolls down the hill; and, because it is moving, it has kinetic energy. The stretched rubber band flies (moves) across the room as soon as it is released. The potential energy stored in a stick of dynamite is the result of the relative positions of the atoms in the molecules; that is, the energy is stored in the chemical bonds. The potential energy stored in the chemical bonds of the molecules in the dynamite is transformed into kinetic energy during the explosion.

A change in energy is represented by ΔE . The sign of the energy change is a significant consideration, so it is important to calculate it in the same manner each time. The convention used is that energy change equals the final energy, E_f , minus the initial energy, E_i , as shown in Equation 1.2.

$$\Delta E = \text{final energy} - \text{initial energy} = E_f - E_i$$

Eq. 1.2

$\Delta E > 0$ means that the energy of the object increases, while $\Delta E < 0$ means that the energy of the object decreases.

Example 1.7

a) What is the kinetic energy of a 2200 lb car moving at 40 mph?

This example serves as a basis by which to compare other energies we determine throughout the text. Clearly, the typical car moving at 40 mph has the capacity to move many objects, so it is representative of an object with substantial kinetic energy. All other energy considerations in this text are in joules, so we will calculate this kinetic energy in joules as well. Consequently, the mass must be in kilograms, and the speed must be in meters per second. We use the following equalities 1 kg = 2.2 lb and 1 km = 0.62 mi and the conversion-factor method to obtain the desired units.

$$2200 \text{ lb} \times \frac{1 \text{ kg}}{2.2 \text{ lb}} = 1000 \text{ kg}$$

$$\frac{40 \text{ mi}}{\text{hr}} \times \frac{1 \text{ hr}}{3600 \text{ s}} \times \frac{1 \text{ km}}{0.62 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} = 18 \text{ m} \cdot \text{s}^{-1}$$

Equation 1.1 can now be applied to obtain the kinetic energy of an object with this mass and speed.

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}(1000 \text{ kg})(18 \text{ m}\cdot\text{s}^{-1})^2 = 1.6 \times 10^5 \text{ J} = 160 \text{ kJ}$$

How does this energy compare to the energy released in chemical reactions? To obtain 160 kJ of energy, one would have to burn only about 3 g of gasoline or 10 g of sugar.

b) What energy change would the car undergo when it stops?

The final kinetic energy is zero, and the initial kinetic energy is 160 kJ.

$$\Delta E = E_f - E_i = 0 - 160 \text{ kJ} = -160 \text{ kJ}$$

Thus, ΔE indicates that the car loses 160 kJ of energy.

Why does the truck roll down hill, the rubber band fly, and the dynamite explode? All three processes occur because *systems in nature seek the position of lowest energy; i.e., nature favors processes for which $\Delta E < 0$.** Chemical processes can be understood in terms of this fundamental tendency and the fact that energy changes in chemistry are the result of interactions between charged particles. The relationship between energy and the charge on interacting particles is the topic of the next section.

1.7 ELECTROMAGNETISM AND COULOMB'S LAW

A great deal of research in the 1800's was centered on electricity and magnetism. Scientists recognized that there was a force of interaction, called the **electromagnetic force**, between charged particles when they were brought close to one another. The force could be either attractive or repulsive. Charles Augustus Coulomb measured this force and stated his observations in what is now called Coulomb's law.

Coulomb's Law: Two particles of charge q_1 and q_2 separated by a distance r experience a force F as shown in Equation 1.3.

$$F = \frac{kq_1q_2}{\epsilon r^2}$$

Eq. 1.3

$k = 8.9875 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2$ and is called **Coulomb's constant**. q_1 and q_2 are the charges in Coulombs, and ϵ is the **dielectric constant** of the medium separating the charges. The dielectric constant is a measure of how well the medium insulates the two charges. $\epsilon = 1$ in a vacuum, but it is 79 in water, which means that the interaction between charges in water is only about 1.3% of that in a vacuum for the same charges and separation. This decrease in the interaction results because the intervening water molecules have the ability to effectively shield the two charges from one another. When F is negative (q_1 and q_2 have

* As we will see in Chapter 9, $\Delta E < 0$ is indeed an important driving force, but it is not the only one.

opposite signs), the force is attractive. When \mathbf{F} is positive (q_1 and q_2 have the same signs), the force is repulsive. This is summarized by the statement that *opposite charges attract while like charges repel*. The force of attraction or repulsion between two particles is very small at large separation but gets stronger as the distance between the particles decreases. The force also becomes stronger as the charges on the particles increase.

In Section 1.5, energy was defined as the capacity to move something, but in order for something to be moved, a force (push or pull) must be exerted. Energy is defined as a force exerted through a distance ($E = F \times r$). Consequently, the change in potential energy that results when two charged particles interact can be obtained by multiplying Equation 1.3 by r . The result is given by Equation 1.4:

$$E = \frac{kq_1 q_2}{\epsilon r} \quad \text{Eq. 1.4}$$

E is the potential energy of the two particles separated by distance r *relative to their potential energy when they are not interacting** ($r = \infty$). E , which we will call the *energy of interaction* between the two particles, depends upon the charges on the particles (q), the distance between them (r), and the intervening medium (ϵ). A graph of the energy of interaction of two charged particles as a function of the distance between them is shown in Figure 1.1. At large separations, the charged particles do not interact and $E \sim 0$. As their separation decreases, however, their energy of interaction changes. If the charges are of the same sign, their energy of interaction increases (red line), but if the charges are of opposite sign, their energy of interaction (green line) becomes increasingly negative. Thus, particles of opposite charge are attracted because their potential energy decreases as they get closer to one another, while particles with charges of the same sign are repelled because their potential energy decreases as they move apart.

Coulomb's law, in combination with the fact that systems seek the position of lowest energy, is exceedingly important in the study of chemistry because interactions in chemistry can be viewed as interactions between charged particles. *We conclude that particles of opposite charge move closer and particles of like charge move apart to minimize their energy.* If particles of like charge are forced together or particles of opposite charge are pulled apart, the potential energy of the system rises and the process is unfavorable.

* E is actually the difference between the energy of interaction at a separation r and the energy when the charges at infinite separation; i.e., $\Delta E = E(r) - E(\infty)$, but $E(\infty) = 0$, so $\Delta E = E(r) - 0 = E(r)$. Hence, the Δ is often dropped and the energy of interaction is simply expressed as E .

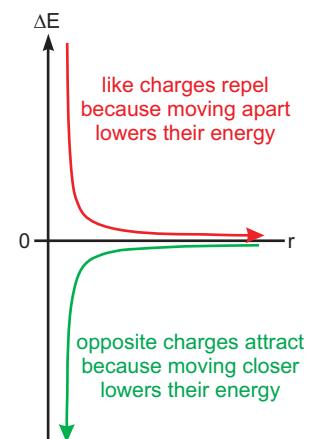


Figure 1.1 Electrostatic or Coulombic energy of interaction

Opposite charges are attracted because their energy decreases as they get closer to one another (green line). Like charges repel because moving apart lowers their energy (red line).

Example 1.8

- a) The particles shown in the margin are in the same medium and the numbers are their relative charges. Arrange the particles from most attractive to most repulsive.

The relative forces can be obtained from $F \propto q_1 q_2 / r^2$ because both k and ϵ in Equation 1.3 are constant in this example. The units of q and r are not important so long as they do not change from one system to the next.

$$F_a \propto \frac{(+1)(-2)}{(1)^2} = -2; F_b \propto \frac{(+3)(+2)}{(3)^2} = +0.67; F_c \propto \frac{(+3)(-3)}{(4)^2} = -0.56; F_d \propto \frac{(-3)(-2)}{(2)^2} = +1.5$$

Negative values are attractive, so the order from most attractive to most repulsive is
(most negative) a, c, b, d (most positive)

- b) Arrange the systems in order of energy of interaction.

Use $E \propto q_1 q_2 / r$ for the reasons outlined in Part a to find the relative energies

$$E_a \propto \frac{(+1)(-2)}{(1)} = -2; E_b \propto \frac{(+3)(+2)}{(3)} = +2; E_c \propto \frac{(+3)(-3)}{(4)} = -2.25; E_d \propto \frac{(-3)(-2)}{(2)} = +3$$

(most attractive) c, a, b, d (most repulsive)

The charges in system a have the lowest potential (interaction) energy.

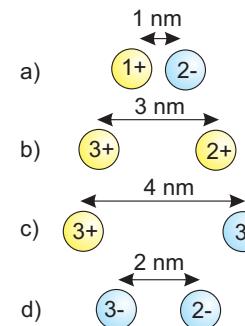
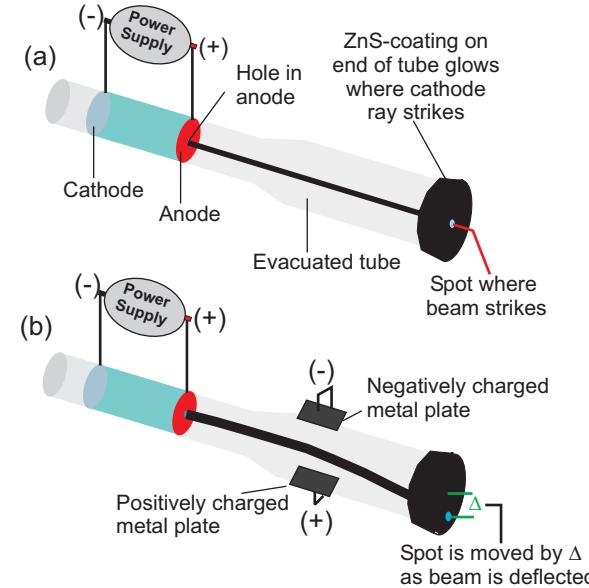
**Example 1.8**

Figure 1.2 Schematic of a cathode-ray tube

(a) In the absence of an electric or magnetic field, the ‘ray’ travels in a straight line from the cathode to the end of the tube where it strikes ZnS, causing it to glow. (b) The ‘ray’ is bent toward the + plate by an electric field. The amount of deflection is given by Δ .

Observation: The rays were deflected by the electric and magnetic fields.

Conclusion: Cathode rays were not light rays, because light is not deflected by electric or magnetic fields. He concluded that the rays had to be charged particles.

Observation: The direction of the deflection was away from the negative plate and toward the positive plate.

Conclusion: The particles were negatively charged.

Observation: The extent of the deflection (Δ in Figure 1.2) varies directly with the strength of the applied external field and the magnitude of the negative charge on the particles, but inversely with the mass of the particle (a bowling ball would be deflected far less than a Ping-Pong® ball when struck with the same force).

Conclusion: By measuring how far the particle was deflected, Thomson determined that the charge-to-mass ratio of the particle was $q/m = -1.76 \times 10^{11} \text{ C}\cdot\text{kg}^{-1}$.*

The charge-to-mass ratio (q/m) as determined by Thomson was much larger than had been determined for any other charged particle known at the time. In order for the ratio to be so large, either q (the charge) was very large, or m (the mass) was very small. He assumed that the magnitude of the charge on the particles could not be that much greater than that measured for other charged particles, which meant that the mass of the particles must be much smaller. Indeed, he estimated the mass to be less than 1/1000th the mass of the hydrogen atom; contrary to Dalton's atomic theory, a hydrogen atom was not the smallest particle. Thomson was shocked! These negatively charged particles were later named 'electrons' because they were found to be the source of electricity.

Although Thomson had determined the charge-to-mass ratio and estimated a probable mass for this new particle, another experiment was needed to determine the charge and mass separately. This experiment would be performed fourteen years later.

R. A. MILLIKAN AND THE CHARGE OF THE ELECTRON (1909)

Robert Millikan, an American physicist, was the first to determine accurately the charge on the electron. In an experiment at the University of Chicago, he welded two plates into an oil drum (Figure 1.3). The upper plate had a small hole drilled into it. Above the hole, he created a fine mist of oil droplets. Individual oil droplets passed randomly through the hole one-by-one to descend toward the lower plate. He used a microscope to observe the fall of an individual droplet. Initially, the drop accelerated due to gravity, but eventually the resistance due to the air stopped its acceleration and the drop began to fall at a constant speed called its *terminal speed*. He determined the droplet's terminal speed and used it to

* The minus sign results because the charge is negative.

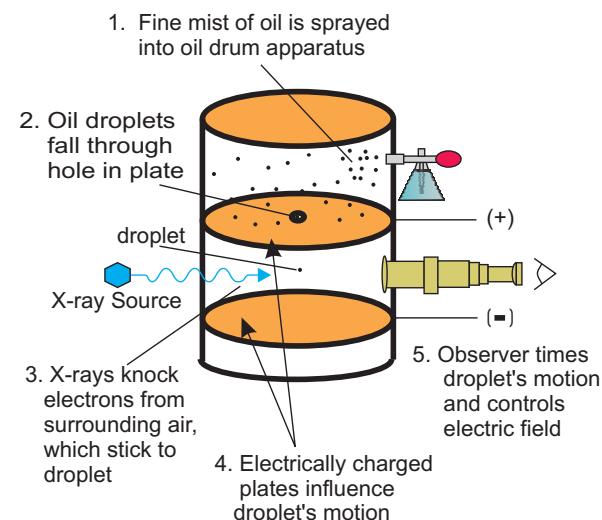


Figure 1.3 Millikan's oil drop experiment

determine the mass of the droplet. He then fired X-rays into the drum, which removed electrons from some of the molecules in the air. Some of the released electrons attached to the oil droplet creating a negative charge (q) on its surface. Next, he applied an electric field (\mathcal{E}) across the two plates creating a positive charge on the top plate and a negative charge on the bottom plate. As the electric field increased, the rate of descent of the droplet slowed as it was increasingly attracted to the positive upper plate and repelled by the lower plate.

Millikan adjusted the voltage across the two plates until the droplet became suspended, moving neither up nor down. At this point, the electrostatic force ($q\mathcal{E}$) that pulled the droplet up equaled the gravitational force (mg^*) that pulled it down, so $q = mg/\mathcal{E}$. m , and \mathcal{E} were all known, so he was able to determine the charge on the droplet. Various experiments yielded different values of q for different droplets, but all of the measured charges were multiples of the same number, $-1.6 \times 10^{-19} \text{ C}^\dagger$. Millikan reasoned that the charges on the droplets were different because each droplet had a different number of electrons; *i.e.*, $q = nq_e$, where n is the number of electrons and q_e is the charge on each electron. In this way he was able to determine that the charge on an electron must be $q_e = -1.6 \times 10^{-19} \text{ C}$. He then used Thomson's charge-to-mass ratio $q/m = -1.76 \times 10^{11} \text{ C}\cdot\text{kg}^{-1}$, and his charge determine that *the mass of the electron was $m_e = -1.6 \times 10^{-19} \text{ C}/-1.76 \times 10^{11} \text{ C}\cdot\text{kg}^{-1} = 9.1 \times 10^{-31} \text{ kg}$, which is approximately 1/1800 the mass of the hydrogen atom.*

Clearly, it was time to refine Dalton's atomic model. One proposed model was the 'raisin pudding' model of Lord Kelvin and J. J. Thomson. They reasoned that because atoms are uncharged themselves, they must contain enough positive charge to balance the negative charge of the electrons. In the Kelvin-Thomson model, the atom resembled *raisin pudding* with the negatively-charged electrons (the raisins) embedded in a mass of diffuse positive charge (the pudding).

E. RUTHERFORD AND THE NUCLEAR ATOM (1911)

A new model called for a new test, and the test of the Kelvin-Thomson model was not long in coming. In another classic experiment, a British physicist, Ernest Rutherford, tested the 'raisin pudding' model by bombarding a very thin gold foil with alpha (α) particles (particles with atomic masses of four and charges of +2) moving at 10,000 mi/s (Figure 1.4). If the Kelvin-Thomson model was correct and the positive charge in the atom was diffuse, then these particles should pass straight through the foil with, at most, only minor deflections.

* g is the acceleration due to gravity. $g = 9.8 \text{ m}\cdot\text{s}^{-2}$ on earth.

† C is the abbreviation for the Coulomb, the basic unit of electrical charge.

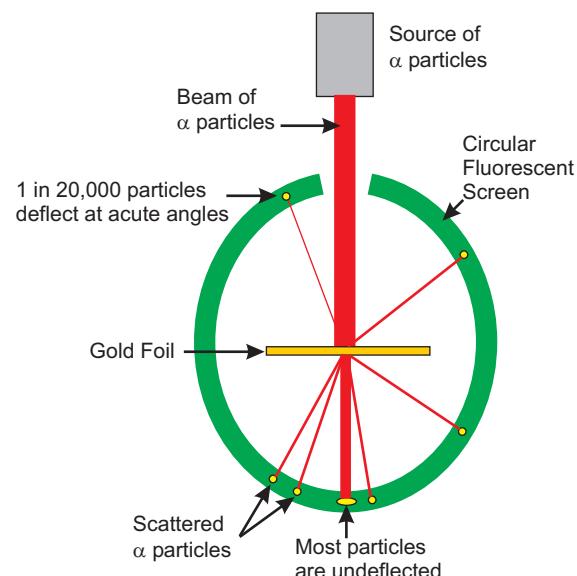


Figure 1.4 Rutherford's 'gold foil' experiment

A thin gold foil was bombarded with positively charged α -particles. The path of the particles (red lines) through the foil was determined by noting where the particles struck a fluorescent screen.

Indeed, Rutherford observed that most of the α -particles did pass through the gold foil, and some were deflected slightly, yet one in 20,000 was deflected at a sharp angle. This one particle in 20,000 was totally unexpected, but it provided the information that Rutherford needed. “It was as if you fired a 15-inch shell at a piece of tissue paper, and it came back to hit you!” he would later exclaim. Rutherford proposed a new model of the atom that was consistent with his observations.

Observation: Most of the α -particles passed through undeflected.

Conclusion: Most of the volume of the atom is empty space.

Observation: Some minor deflections were observed.

Conclusion: A very large force would be required to repel these high-energy particles. α -particles are positively charged, so he assumed that the deflections were due to collisions with another positively-charged and massive particle.

Observation: Only one α -particle in 20,000 experienced acute deflections.

Conclusion: Only one α -particle in 20,000 collided with the positively-charged particle in the atom, so the cross-sectional area of this particle must be less than 1/20,000th that of the atom; yet it must also contain almost all of the mass!

Rutherford’s model of the atom (Figure 1.5) placed the positive charge and essentially all of the mass of the atom in a very small particle, which he called the **nucleus**. The nucleus occupies almost none of the volume of the atom. He suggested that the electrons orbit the nucleus much as the planets orbit the sun.

Rutherford’s model was another giant step in our understanding of matter, but there were still dramatic changes to come over the next ten years that would revolutionize the way we would think about atoms and molecules. Nevertheless, the Rutherford model had identified an essential feature of the atom: electrons with negative charge surround a nucleus with positive charge. In fact, the electrons in an atom, as well as their interactions with the electrons and nuclei of other atoms, are the focus of chemistry. The electrons, their location about the nucleus, and their number relative to the number of positive charges in the nucleus dictate the chemistry of an element.

To appreciate just how small and dense the nucleus is, consider the following two analogies:

- If the nucleus of an atom were the size of a baseball, the atom would be a sphere with a one-mile diameter.
- A matchbox filled with nuclei (not atoms) would weigh 2.5 billion tons.

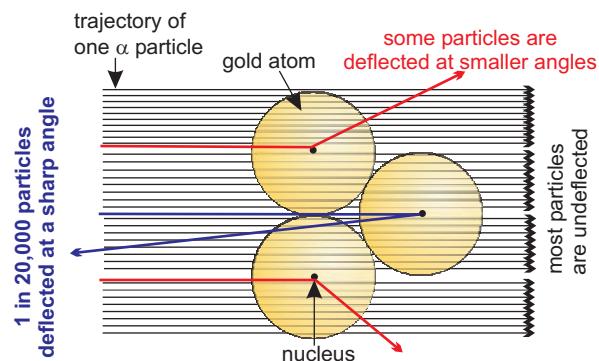


Figure 1.5 Rutherford’s model of the atom used to explain the gold foil experiment

The positive charge and most of the mass resides in the nucleus, which is represented as a small black dot in the center of the atom. Particles that were deflected at acute angles collided with the nucleus. If drawn to proper scale, the nucleus would be too small to be seen.

1.9 SUBATOMIC PARTICLES, ISOTOPES, AND IONS

As summarized in Table 1.1, scientists have discovered that atoms are composed of three subatomic particles: protons, neutrons, and electrons. The number of protons identifies the nucleus, and the number of protons and neutrons determines its mass.

Atomic number, Z, is the number of protons in the nucleus. It is the number that characterizes an element. If the atomic number of an element is known, then the identity of the element is known and *vice versa*.

Mass number, A, is the sum of the number of protons and the number of neutrons in the nucleus. Because the mass of each of these particles is nearly 1 amu, the mass number is an integer that closely approximates the nuclear mass in atomic mass units (amu).

The atomic mass is sometimes included with the symbol of the element. For example, the notation ^{63}Cu (read copper-63) indicates that the mass number of Cu is 63. There is no reason to include Z because it is implied in the element's symbol. Cu means Z = 29 because Cu always has 29 protons. Note that the number of neutrons is A minus Z. Thus, ^{63}Cu has $63 - 29 = 34$ neutrons.*

Isotopes are different forms of the same element that have the same atomic numbers (Z) but different masses (A). Consequently, they differ only in the number of neutrons (A - Z). For example: ^{35}Cl and ^{37}Cl , chlorine-35 and chlorine-37, are two isotopes of chlorine. Both contain 17 protons because both are chlorine atoms. They differ in that ^{35}Cl contains 18 neutrons ($35 - 17$) while ^{37}Cl contains 20 neutrons ($37 - 17$). Naturally occurring chlorine is 75.8% ^{35}Cl and 24.2% ^{37}Cl . It is this combination of the two that gives a mole of chlorine a mass of 35.5 grams (the molar mass of chlorine).

Charge is not continuous; it comes in bundles[§] of $1.6 \times 10^{-19} \text{ C}$. Electrons are bundles of negative charge and protons are bundles of positive charge. All charge is comprised of an integral number of these bundles, and the net charge on a particle at the atomic and molecular level is usually given as the difference between the positive and negative charge carriers rather than the actual charge in coulombs.

$$\text{charge on particle} = \text{number of protons} - \text{number of electrons}$$

Atoms have no charge because the number of protons and electrons are equal. Thus, Al (Z=13) contains 13 protons, 13 electrons, and no net charge. While the number of protons in an atom is fixed, electrons can be added or removed to produce charged particles called **ions**. Positively charged ions, which are called **cations**, are produced when electrons are lost, and negatively charged ions, which are called **anions**, are produced when electrons

Table 1.1 Subatomic particles

Particle	Mass (amu)	Charge [†]
electron	5.49×10^{-4}	-1
proton	1.00728	+1
neutron	1.00867	0

[†] Charge at the atomic and molecular level is usually expressed as multiples of the fundamental unit of charge as determined by Millikan. Thus, the charge on the electron is designated as -1, which means that it carries a charge of $(-1)(1.6 \times 10^{-19} \text{ C})$. The charge on the proton is then $(+1)(1.6 \times 10^{-19} \text{ C})$.

* A and Z are sometimes shown in the atom's symbol. Thus, the element whose symbol is X and whose atomic number and mass are Z and A, respectively would be represented as follows:

$${}_{\text{Z}}^{\text{A}}\text{X} \Rightarrow \frac{(\# \text{ protons} + \# \text{ neutrons})}{\# \text{ protons}}\text{X}$$

This notation is redundant because the symbol (X) identifies the element and its atomic number (Z). However, the notation is used when balancing nuclear equations.

[§] Quantities that are not continuous but come in discrete units are said to be **quantized**, and the bundles that carry the units are called quanta. Thus, electrons and protons are quanta of negative and positive electrical charge. In Chapter 2, we show that electromagnetic energy is also quantized.

are gained. Al^{3+} is a cation with a charge of +3. An Al atom must lose three electrons to form Al^{3+} , so Al^{3+} contains 13 protons and 10 electrons. Similarly, an O atom has 8 protons, so the O^{2-} anion must have 10 electrons.[†]

Example 1.9

Indicate whether the energy of the system would increase, decrease, or remain the same during each of the following processes.

a) An anion approaches a cation.

An anion is negatively charged and a cation is positively charged. According to Coulomb's law (Equation 2.4) opposite charges lower their energy when they approach.

b) One cation is moves away from another.

Cations are positively charged. Moving like charges away from one another lowers their energy.

c) A neutron moves toward an electron.

Neutrons carry no charge, so there is no interaction and the energy remains the same.

1.10 DIMITRI MENDELEEV AND THE PERIODIC LAW (1869)

Well after Dalton's atomic theory had been accepted, but before Thomson's experiments, Dimitri Mendeleev, a Russian chemist, was writing a chemistry book describing the reactions and properties of the elements. However, he could not decide on a good way to organize the chapters. As he sought to arrange and label the elements in an orderly fashion, he decided to use their atomic masses because that was the only known sequential number that was available. Consequently, he arranged the elements in order of increasing atomic masses. As Mendeleev studied the elements in this arrangement, he noticed that their chemical and physical properties seemed to cycle (Figures 1.6 and 1.7).

He arranged the elements in rows of a length such that elements of similar properties fell directly beneath one another to form chemical **families** or **groups** (see the caption to Figure 1.6). The rows are referred to as **periods** (see the caption to Figure 1.7). Thus, the properties of the elements change gradually as you progress across a period, but they remain similar as you progress down a group. The elements on the left side of any period tend to be lustrous solids (have a luster or shine) that are malleable (can be beaten into a form), ductile (capable of being drawn into wires), and good conductors of heat and

[†] Note: +1 and -1 charges are normally indicated as simply '+' and '-' as in Na^+ and Cl^- . However, the charge is easily overlooked when written in this manner, so 1+ and 1- are used for emphasis in this book. Thus, $\text{Na}^{1+} = \text{Na}^+$ and $\text{Cl}^{-1} = \text{Cl}^-$.

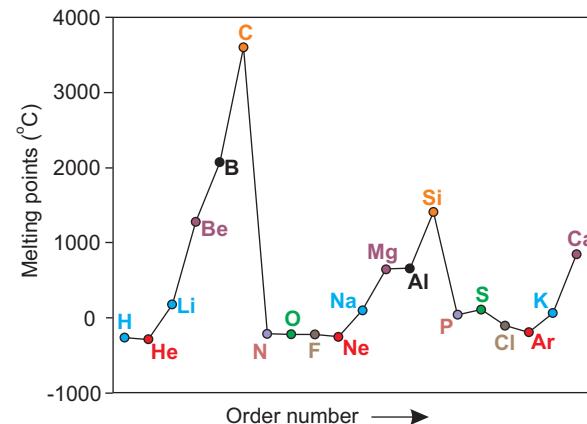


Figure 1.6 Periodic behavior of a physical property

The melting points of the first 20 elements in order of increasing atomic mass. Atoms that are shown in the same color are in the same chemical group.

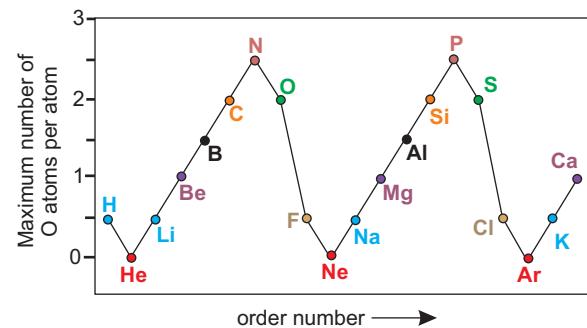


Figure 1.7 Periodic behavior of a chemical property

The maximum number of oxygen atoms that bind to an atom is given as a function of the order number of the atom. Elements shown in the same color, such as N (N_2O_5) and P (P_2O_5), are in the same chemical group, while elements between the atoms in red are in the same chemical period.

electricity. These are the typical properties of **metals**. The elements on the right side of a period tend to be gases or dull, brittle solids that are poor conductors of electricity or heat. These are the typical properties of **nonmetals**. Thus, the properties of the elements gradually go from metallic on the left side of a period to nonmetallic on the right side of a period. Those elements that have some properties of both metals and nonmetals and lie between the two broader classes are called **metalloids**.

Mendeleev published his observations as the periodic law in 1869: The elements, if arranged in an order that *closely approximates that of their atomic masses*, exhibit an obvious periodicity in their properties. The phrase in italics was used because Mendeleev had so much confidence in his periodic law that he reversed the order of some elements in order to maintain the periodicity even though it meant reversing the order of their atomic masses. Thus, tellurium with an atomic mass of 128 was placed before iodine, which has an atomic mass of 127. He did not understand why the properties of the elements did not exactly follow the order of the atomic masses, but he was confident that the concept of periodicity was correct!

Had Mendeleev blindly used a rigid atomic mass ordering of the elements, he also would have placed arsenic (atomic mass = 75) next to zinc (atomic mass = 65) because gallium and germanium had not yet been discovered. This would have placed arsenic directly under aluminum, yet he knew their properties were quite different. Instead, he placed arsenic directly under phosphorus because arsenic and phosphorus have similar properties. Thus, he left two holes in his chart, which he correctly predicted would someday be filled by two new elements. He even went so far as to predict the properties of these two new elements. While other scientists were defining similar ordering schemes for the elements, it was Mendeleev's faith in the underlying principle of periodicity that made him leave room in his table for undiscovered elements. The confidence displayed by Mendeleev set him above others who were trying to construct similar relationships. For this reason, he is given credit for the periodic law.

We now realize that the parameter that characterizes an atom is its atomic number (Z), but Mendeleev did not know about electrons or protons, so he had no atomic number to reference. He had only the atomic mass. We now understand why tellurium comes before iodine in the periodic order. Although tellurium is heavier than iodine, its atomic number is smaller. Today, the **periodic law** is stated as:

Arranged in the order of their atomic numbers, the elements exhibit periodicity in their chemical and physical properties.

Mendeleev's arrangement of the elements has become known as the **periodic chart** or the **periodic table** and is the source of a great deal of information about the physical and chemical properties of the elements. The columns define **groups**, which consist of elements with similar properties. The rows define **periods**, which contain elements whose properties change gradually. There has been some controversy over the numbering of the groups in the periodic table. The American method, 1A - 8A and 1B - 8B, and the newer method, which numbers the groups as 1 - 18, are both shown on the periodic tables in this book (Figure 1.8 and the back cover). Both methods are in use today, but the older method is still more common, and we will use the older method in the remainder of this text.

The elements in the groups 1A - 8A, the 'A' groups, are the **main group elements**, and groups 1B - 8B are the **transition metals**. The two rows at the bottom of the periodic table are the lanthanides and the actinides, which are also known as the **inner transition metals**.

The periodic table contains a great deal of information about the elements. Each box in the table presented in Figure 1.8 contains (from top to bottom) the atomic number, the chemical symbol, and the atomic mass of the element. As shown in the margin, the atomic number of hydrogen is 1, its symbol is H, and its atomic mass is 1.0079.

The properties of an element are dictated by its position in the periodic table. In the table on the following page, they are also indicated by the background color as follows:

metal	The metals occupy the left side of the periodic table. They represent about 75% of the elements. All metals are solids under ordinary conditions, with the exception of mercury (Hg), which is a liquid, and most are lustrous. Metal atoms lose electrons to form cations in their compounds with nonmetals.
nonmetal	The nonmetals lie on the right side of the Periodic Table and represent about 20% of the elements. Many of the nonmetals occur as gases (nitrogen, oxygen, fluorine, chlorine, and the 8A's); only bromine is a liquid at room conditions, and the remaining five (carbon, phosphorus, sulfur, selenium and iodine) are solids. Nonmetal atoms gain electrons to become anions in their compounds with metals.
metalloid	The metalloids or semimetals lie on a diagonal between the metals and nonmetals and have characteristics that are intermediate between metals and nonmetals. Metalloids are shiny like metals, but brittle rather than malleable. Metalloids are neither good conductors nor nonconductors of electricity. Instead they are semiconductors (their conductivity changes with temperature), with silicon being a well-known example.

1	Atomic Number
H	Atomic Symbol
1.0079	Atomic Mass (Weight)

3 Li 6.941	4 Be 9.0122																		
11 Na 22.990	12 Mg 24.305																		
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Tl 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80		
37 Rb 85.478	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29		
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Uun (269)	111 Uuu (272)	112 Uub (277)								
58 Ce 140.11	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97						
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	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 (262)						

Figure 1.8 Modern periodic table

See text on previous page for descriptions of metals, metalloids, and nonmetals

The chemical properties of an element can be determined from its group:

- Hydrogen** is unique as shown by its position in the periodic table in Figure 1.8. It normally forms a +1 ion, which would put it into Group 1A, where it is placed in the periodic table on the back cover. However, it is a nonmetal and can also form compounds in which it is a -1 ion, which is more consistent with the Group 7A elements.
- Group 1A** elements are known as the **alkali metals**. All members of this family are very reactive, readily losing one electron to form +1 ions.
- Group 2A** elements are known as the **alkaline earth metals**. They are also very reactive but not as reactive as the 1A's. They occur as +2 ions in their compounds.
- Groups 1B - 8B** elements are the **transition metals**. Most form a +2 ion, but +1 and +3 ions are also found. Unlike the 1A and 2A metals, many transition metals can form more than one type of ion, such as Fe^{2+} and Fe^{3+} .
- Group 3A** elements are metals, except for boron, which is a metalloid. They typically form +3 ions. Thallium (Tl) forms both +3 and +1 ions.
- Group 4A** elements demonstrate that metallic character also increases in going down a group. Carbon is a nonmetal and does not typically form ions. Silicon and germanium are metalloids, but tin and lead are metals that form +2 ions.
- Group 5A** elements also progress from nonmetallic at the top to metallic at the bottom. Nitrogen and phosphorus are nonmetals, which can form -3 ions. Arsenic, antimony, and bismuth increase in their tendency to form +3 ions.
- Group 6A** elements display only gradual changes in their chemistry, except for the chemistry of oxygen, which differs substantially from the other members. Oxygen, sulfur, and selenium are nonmetals; tellurium is a metalloid, and polonium is a radioactive metal.
- Group 7A** elements are known as the **halogens**. They are very reactive, readily forming -1 ions. In fact, they are found in nature only in compounds such as NaCl and MgF_2 .
- Group 8A** elements are known as the **noble gases** because they show little tendency to react with other substances. There are no known compounds of helium, neon or argon and only a very few of krypton and xenon. Radon is radioactive.

Example 1.10

Identify each of the atoms or ions below based on the number of protons and electrons they contain.

	Protons	Electrons
a)	11	10
b)	16	18
c)	26	26

- a) This element contains 11 protons, so it must be Na (sodium). The fact that it contains only 10 electrons means that it carries a charge of $11 - 10 = +1$. Thus, the species is Na^{1+} , a cation or positively-charged ion.
- b) An atomic number of 16 signifies sulfur. It has gained two electrons to carry a charge of $16 - 18 = -2$. It is the S^{2-} anion or negatively-charged ion.
- c) Fe (iron) has an atomic number of 26 and, because the number of electrons equals the number of protons, this species is the Fe atom.

Example 1.11

How many protons, neutrons, and electrons are in each of the following?



Chlorine's atomic number is 17, so it has 17 protons. The number of neutrons (N) in an element is the difference between mass number (A) and the atomic number (Z): $N = A - Z = 37 - 17 = 20$ neutrons. $^{37}\text{Cl}^{-1}$ has a charge of -1. Charge equals (the number of protons) – (the number of electrons), so $-1 = 17 - x$ for this ion. Solving for x, we find that there are $x = 18$ electrons in the ion.



Z = 20 for calcium, so it must have 20 protons. A = 40, so N = 40 - 20 = 20 neutrons for this isotope. The +2 charge means that the number of electrons is two less than the number of protons. Thus, there are 18 electrons in this ion.



There is no charge, so the number of electrons equals the number of protons. Z = 53, so the atom contains 53 protons and 53 electrons. In addition, A = 127, so this isotope of iodine contains $127 - 53 = 74$ neutrons.

1.11 CHAPTER SUMMARY AND OBJECTIVES

Early scientists used the scientific method to study the chemical and physical properties of matter. Their experiments led to the classification of pure substances as elements or compounds. Initially, they identified atoms as very small spheres characterized by mass. By the early 20th century, scientists had arrived at the nuclear model of the atom. In this model, the atom has a very small, dense, positively charged nucleus that contains the protons and neutrons and is orbited by even smaller, negatively charged electrons. The number of protons in the nucleus, which is the atomic number, characterizes the atom, while the number of electrons that surround the nucleus dictates the charge on the species. If the number of electrons exceeds the number of protons, the substance is negatively charged and called an anion. If the number of protons exceeds the number of electrons, the species is positively charged and called a cation.

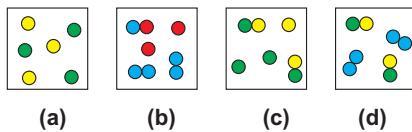
The periodic table is one of the greatest classifying systems in science. It orders logically a great deal of information about an element's chemical and physical properties, such as its atomic number, whether it is a metal, nonmetal, or metalloid, and the ease with which it undergoes chemical reaction.

After studying the material presented in this chapter, you should be able to:

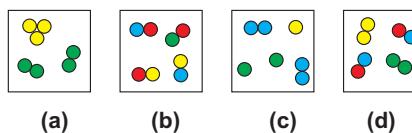
1. explain the scientific method (Section 1.1);
2. distinguish between atoms, molecules, elements, and compounds (Sections 1.2 - 1.4);
3. determine molar mass of elements and compounds and determine the number of moles present in a sample (Section 1.5);
4. define kinetic energy and potential energy (Section 1.6);
5. use Coulomb's law to explain how the energy of two particles varies with the charge of, the distance between, and the medium that separates them (Section 1.7);
6. describe the experiments that led to the discovery of the electron and to the determination of its charge and mass (Section 1.8);
7. describe the nuclear atom and the experiments that led to its discovery (Section 1.8);
8. list the common subatomic particles with their mass numbers and charge; distinguish between atomic number (Z) and mass number (A); and determine the number of protons, neutrons, and electrons in an ion or atom (Section 1.9); and
9. describe the meaning of all numbers and symbols given on the periodic table and determine whether an element is a metal, nonmetal, or metalloid from its position on the periodic table (Section 1.10).

1.12 EXERCISES

- Distinguish between a qualitative observation and a quantitative observation. Give two examples of each.
- Distinguish among the terms element, compound, atom and molecule. Give an example of an element that is a molecule and an example of an element that is an atom.
- Indicate whether each of the following represents a mixture of atoms, a mixture of molecules, or a mixture of atoms and molecules. Is each a mixture of elements, compounds, or elements and compounds?



- Indicate whether each of the following represents a mixture of atoms, a mixture of molecules, or a mixture of atoms and molecules. Is each a mixture of elements, compounds, or elements and compounds?



- Classify each of the following as an element or compound:
 - P_4
 - Fe
 - C_3H_6O
 - SO_2
 - O_3
- Classify each of the following as an element or compound:
 - H_2O
 - C_{60}
 - Au
 - CO
 - N_2
- Classify each of the following as an atom or a molecule:
 - P_4
 - Fe
 - C_3H_6O
 - SO_2
 - O_3
- Classify each of the following as an atom or a molecule:
 - H_2O
 - C_{60}
 - Au
 - CO
 - N_2
- Classify each of the following as an atom, molecule, anion, or cation:
 - NH_3
 - NH_4^{1+}
 - N^{3-}
 - CH_3COO^{1-}
 - Si
- Classify each of the following as an atom, molecule, anion, or cation:
 - Na^{1+}
 - NO_3^{1-}
 - Na
 - Cl^{1-}
 - Al^{3+}
- Give the name of each of the following elements:
 - Na
 - Br
 - Hg
 - Fe
 - Ag

- Give the name of each of the following elements:
 - Pb
 - Au
 - F
 - Ca
 - P
- Write the symbol for each of the following elements:
 - copper
 - lead
 - strontium
 - silicon
 - tin
- Write the symbol for each of the following elements:
 - potassium
 - iron
 - nickel
 - cadmium
 - selenium
- Determine the number of moles of atoms that are present in each of the following samples:
 - 5.0 g K
 - 17 g Mg
 - 3.0 g C
 - 2.2 kg Fe
 - 14 mg Ag
- How many moles are in a 5.0-g sample of each of the following elements? How many moles of atoms are in each sample?
 - Ca
 - F_2
 - O_2
 - S_8
 - P_4
- How many moles of molecules are in a 10.0-g sample of each of the following compounds? How many moles of atoms are in each sample?
 - SF_6
 - CCl_4
 - C_6H_{14}
 - SO_3
 - BF_3
- Determine the number of moles of carbon that are present in each of the following samples:
 - 1.0 g of aspirin, $C_9H_8O_4$
 - 3.0 g of ibuprofen, $C_{13}H_{18}O_2$
 - 12 mg of acetaminophen (Tylenol), $C_8H_9NO_2$
- Determine the mass of the following samples:
 - 2.5 mol $CaCl_2$
 - 0.75 mol C_6H_{12}
 - 1.8 mol CO_2
- Determine the mass of the following samples:
 - 4.6×10^{-3} mol $Al(NO_3)_3$
 - 3.6 mol $C_{12}H_{22}O_{11}$
 - 220 mol H_2
- Consider a 5.00 g sample of Ca_2S_3 .
 - How many moles of Ca_2S_3 does it contain?
 - How many moles of sulfur does it contain?
 - How many grams of sulfur does it contain?
- A sample of $Al(NO_3)_3$ contains 0.90 moles of nitrogen.
 - How many moles of $Al(NO_3)_3$ are present in the sample?
 - What is the mass of the sample in grams?
 - How many moles of oxygen are in the sample?
 - How many aluminum atoms are in the sample?
 - How many grams of aluminum are in the sample?

23. Balance the following equations using the smallest integer coefficients:

- a) $\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$
- b) $\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- c) $\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$
- d) $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2$
- e) $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4$
- f) $\text{Ca} + \text{O}_2 \rightarrow \text{CaO}$

24. Balance the following equations using the smallest integer coefficients:

- a) $\text{P}_4 + \text{H}_2 \rightarrow \text{PH}_3$
- b) $\text{Cl}_2 + \text{O}_2 \rightarrow \text{Cl}_2\text{O}_7$
- c) $\text{Al} + \text{S}_8 \rightarrow \text{Al}_2\text{S}_3$
- b) $\text{H}_3\text{PO}_4 + \text{KOH} \rightarrow \text{K}_3\text{PO}_4 + \text{H}_2\text{O}$
- e) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$
- f) $\text{Al} + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{H}_2$

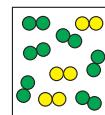
25. Consider the reaction of 0.30 mol K with O_2 , $4\text{K} + \text{O}_2 \rightarrow 2\text{K}_2\text{O}$

- a) How many moles of molecular oxygen are required?
- b) How many moles of potassium oxide would form?
- c) What mass, in grams, of potassium oxide would form?

26. Consider the reaction of 6.5 g of iron with O_2 , $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$

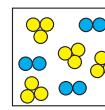
- a) How many moles of iron react?
- b) How many moles of oxygen must react?
- c) How many moles of Fe_2O_3 are formed?
- d) What is the mass, in grams, of the Fe_2O_3 ?

27. The green molecules (G_2) react with the yellow molecules (B_2) to form G_3B as shown to the right. Each circle represents one mole of the atoms. Atomic masses: $\text{G} = 10$ and $\text{B} = 30$.



- a) How many grams of G_2 and B_2 are in the container?
- b) How many G_3B molecules can be produced?
- c) What is the balanced chemical equation for the reaction?
- d) How many grams of G_3B would be produced?
- e) What mass of G_2 or B_2 molecules would be left over?

28. The yellow molecules (Y_3) react with the blue molecules (B_2) to form Y_2B as shown to the right. Each circle represents one mole of the atoms. Atomic masses: $\text{Y} = 20$ and $\text{B} = 25$.



- a) How many grams of Y_3 and B_2 are in the container?
- b) How many Y_2B molecules can be produced?
- c) What is the balanced chemical equation for the reaction?
- d) How many grams of Y_2B would be produced?
- e) What mass of Y_3 or B_2 molecules would be left over?

29. Consider the reaction of 6 mol Fe and 6 mol O_2 to produce Fe_3O_4 .

- a) Write the balanced chemical equation.

b) How many moles of Fe_3O_4 could be produced?

c) How many moles of excess reactant remain after the reaction is done?

30. Consider the reaction of 3 mol P_4 and 10 mol O_2 to produce P_2O_5 .

a) Write the balanced chemical equation.

b) How many moles of P_2O_5 could be produced?

c) How many moles of excess reactant remain after the reaction is done?

31. Use Coulomb's law to explain why Na^{+} ions and Cl^{-} ions exist as separated ions in liquid water ($\epsilon = 79$) but form ion pairs (NaCl units) in liquid carbon tetrachloride ($\epsilon = 2$).

32. Explain what happens to the energy of an electron and a proton as the distance between them decreases. Explain how the energy of two protons changes as the distance between them decreases.

33. What is the charge in coulombs of a mole of electrons?

34. List the following systems of charged particles from most negative to most positive energies of interaction. Also list the forces from most attractive to most repulsive.

- a) +2 and -3 charges separated by 10 nm
- b) -2 and -1 charges separated by 8 nm
- c) -2 and +2 charges separated by 8 nm

35. List the following systems of charged particles from most negative to most positive energies of interaction. Also list the forces from most attractive to most repulsive.

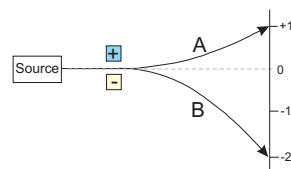
- a) +2 and +2 charges separated by 10 nm
- b) -2 and +3 charges separated by 11 nm
- c) +2 and +1 charges separated by 6 nm

36. Consider Thomson's experiments with cathode rays.

- a) What conclusion was drawn because the "rays" were deflected by electric and magnetic fields?
- b) What information about the rays was deduced from the fact that the "rays" moved toward the positive plate of the electric field?
- c) What two factors dictated the extent of deflection of the rays?

37. Why didn't the oil droplets in Millikan's experiment all have the same charge? What did the charges all have in common?

38. What conclusions did Rutherford draw from the following observations?
- Most α -particles passed through the foil with little or no deflection.
 - Some α -particles were deflected at very sharp angles.
 - The fraction of α -particles that was deflected at sharp angles was very small.
39. The deflection of an X^{1+} ion in an electric field is 14% of that of an α -particle. What is the identity of X? An α -particle is ${}^4\text{He}^{2+}$.
40. The paths of two particles, A and B, which pass between the plates of an electric field designated by '+' and '−', are shown below. One is a cation with a +1 charge, and the other is an anion with a -1 charge. The line in the center represents the path of an uncharged particle.



- Identify each particle as an anion or a cation.
 - What is the approximate ratio of the masses of the two particles?
Express your answer as the ratio (mass of B)/(mass of A).
41. Use Figure 1.7 and the periodic law to determine the formulas of the oxides of the following elements:
- | | | |
|---------------|------------|-------------|
| a) phosphorus | b) arsenic | c) selenium |
| d) carbon | e) cesium | |
42. Use Figure 1.6 and the periodic nature of the elements to predict which element in each pair has the higher boiling point.
- Rb or Ca
 - Si or Sn
 - C or Pb
 - Cs or Xe
 - He or Xe
43. Use periodic behavior and the given chemical formulas to predict the formulas of the compound formed between the following elements:
- Pb and Cl, given the formulas TiCl and BiCl_3
 - Sc and Br, given the formulas KBr and CaBr_2
44. Use periodic behavior and the given chemical formulas to predict the formulas of the compound formed between the following elements:
- Al and S, given the formulas Na_2S and MgS
 - Na and N, given the formulas NaF and Na_2O

45. Determine the number of protons, neutrons and electrons in
- ${}^{16}\text{O}^{2-}$
 - ${}^{27}\text{Al}^{3+}$
 - ${}^{25}\text{Mg}$
 - ${}^{19}\text{F}$
 - ${}^{48}\text{Ti}^{4+}$
46. Determine the number of protons, neutrons and electrons in
- ${}^{75}\text{As}^{5+}$
 - ${}^{31}\text{P}^{3-}$
 - ${}^{195}\text{Pt}$
 - ${}^{235}\text{U}$
 - ${}^{207}\text{Pb}^{2+}$
47. Write the symbol for the species with the number of protons and electrons shown below.
- 34 protons and 36 electrons
 - 26 protons and 23 electrons
 - 47 protons and 47 electrons
48. Write the symbol for the species with the number of protons and electrons shown below.
- 30 protons and 28 electrons
 - 81 protons and 78 electrons
 - 7 protons and 10 electrons
49. Distinguish between a group and a period. How are the properties of the elements in each related?
50. Identify each of the following elements:
- the alkali metal in the same period as bromine
 - the lightest alkaline earth metal
 - the noble gas in the same period as silicon
 - the transition metal in the same family as iron and the same period as antimony
51. Identify each of the following elements:
- the metalloid in the same family as gallium
 - the nonmetal in the same family as germanium
 - the only gas in the fifth period
 - the halogen in the same period as lead
 - the only metal in the same group as sulfur
52. Group the following elements in pairs that are likely to have similar chemical properties: Li, N, F, P, K, and Br.
53. Group the following elements in pairs that are likely to have similar chemical properties: Ca, S, Sr, He, O, Ar.

Chapter 2

Quantum Theory

- | | |
|---|---|
| <p>2.0 <i>Introduction</i></p> <p>2.1 <i>The Nature of Light</i></p> <p>2.2 <i>Quantization</i></p> <p>2.3 <i>Bohr Model</i></p> <p>2.4 <i>Quantum Theory</i></p> <p>2.5 <i>Quantum Numbers</i></p> | <p>2.6 <i>Orbital Shapes, Signs, and Sizes</i></p> <p>2.7 <i>Electron Configurations</i></p> <p>2.8 <i>Quantum Theory and the Periodic Table</i></p> <p>2.9 <i>Chapter Summary and Objectives</i></p> <p>2.10 <i>Exercises</i></p> |
|---|---|
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2.0 INTRODUCTION

Quantum theory, the theory that explains our world at the atomic and molecular levels, is one of humanity's greatest intellectual achievements. A few brilliant scientists, trying to explain experiments that could not be understood in terms of classical theory, launched a theory that initially defied but later defined our understanding of our universe. In this chapter, some of the key experiments leading to quantum theory are described. In Chapter 3, we apply the theory to the structure of the atom.

THE OBJECTIVES OF CHAPTER 2 ARE TO:

- describe how we learn about the nature of atoms and molecules by investigating their interaction with light;
- explain color;
- discuss the wave nature of matter;
- introduce quantum theory and demonstrate how it accounts for the behavior of electrons;
- use quantum numbers to describe the electronic structure of the atom; and
- demonstrate how quantum theory successfully explains the arrangement of the elements in the periodic table.

2.1 THE NATURE OF LIGHT

Much of what we understand about atoms and molecules is based on the way they interact with light. To understand what those interactions tell us about matter, we must first understand something of the nature of light. Light is **electromagnetic radiation**, oscillating electric and magnetic fields that travel through space at a speed of $2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$, the **speed of light (c)**. Figure 2.1a represents a ‘snapshot’ of the amplitude of the electric field in 2800 nm region of space at the moment that two different colors of light, red and violet, are passing through. Although the two waves pass through the region at the same speed, the speed of light, they differ in their **wavelength (λ)**, which is the distance between two adjacent maxima or minima in their electric fields. The top wave in Figure 2.1a has a wavelength of 700 nm ($7 \times 10^{-7} \text{ m}$), while the bottom wave has a wavelength of 400 nm. Light with a wavelength near 700 nm would be perceived as red light by the human brain, while light with a wavelength close to 400 nm would be seen as violet. All visible light lies between these two wavelengths. **White light** is the sum of all of the colors that comprise visible light.

The two light waves can also be represented by showing the variation in their electric field at some point over a period of time (Figure 2.1b). The red wave makes four oscillations during $9.33 \times 10^{-15} \text{ s}$, while the violet wave makes seven oscillations. The number of oscillations of the electric or magnetic field of a light wave during one second is called its **frequency (v , nu)**. $v = 4 \text{ oscillations}/9.33 \times 10^{-15} \text{ s} = 4.29 \times 10^{14} \text{ s}^{-1}$ for the red wave and $7.50 \times 10^{14} \text{ s}^{-1}$ for the violet wave. Comparing Figures 2.1a and b, we note that the shorter the wavelength of a light wave, the higher is its frequency. The relationship between the speed, frequency, and wavelength of a light wave is given in Equation 2.1.

$$c = v\lambda$$

$$\text{Eq. 2.1}$$

The table in the margin characterizes the two light waves shown in Figure 2.1.

A **spectrum** is a display of the component colors of a light beam, separated by their wavelengths. Raindrops can sometimes separate the component colors of white light by their wavelengths to produce a rainbow, which is a display of the spectrum of white light. This spectrum is produced when each wavelength (color) of light is bent at a different angle as it passes through the water droplets. Because the colors all merge into one another *continuously*, the resulting spectrum is called a **continuous spectrum**. A continuous spectrum can also be obtained by dispersing white light through a prism or from a grating.

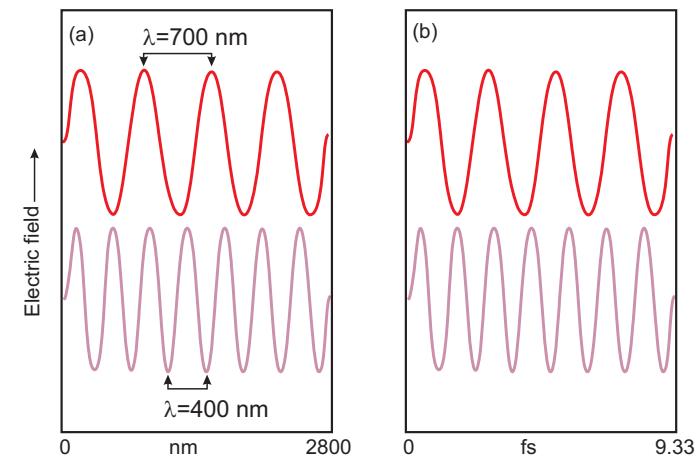


Figure 2.1 Two electromagnetic waves

Only the electric field is shown. The magnetic field oscillates perpendicular to the electric field. The red wave would be perceived as visible red light and the violet wave as visible violet light.

(a) Snapshot of the electric field over a 2800 nm range as the two waves pass through.

(b) The variation of the electric field at one position during a 9.33 fs ($9.33 \times 10^{-15} \text{ s}$) interval of time, the time required for light to move the 2800 nm used in (a).

Color	λ	c	$v = c/\lambda$
Red	700 nm^\dagger	$3.0 \times 10^8 \text{ m}\cdot\text{s}^{-1}$	$4.3 \times 10^{14} \text{ s}^{-1}$
Violet	400 nm	$3.0 \times 10^8 \text{ m}\cdot\text{s}^{-1}$	$7.5 \times 10^{14} \text{ s}^{-1}$

[†] $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$

We can see only a very small fraction of the entire electromagnetic spectrum. Other forms of electromagnetic radiation include radio wave, microwave, ultraviolet, x-ray and γ -ray. Figure 2.2 shows the electromagnetic spectrum and defines each of these regions by its range of wavelengths.

2.2 QUANTIZATION

At the end of the 19th century, a number of experiments were reported that could not be understood in terms of the physics of the day, known now as classical physics. One flaw of classical physics was the assumption that the energy of tiny particles such as electrons, atoms, and molecules, varied continuously, just as for large objects. For example, a bowling ball's energy can be varied continuously by changing its speed to any desired value; *i.e.*, there are no energy values that are not allowed. Some experiments performed at the turn of the century, however, showed that the energy of a system *at the atomic or molecular level* could not take on continuous values; *i.e.*, energies at the atomic/molecular level are **quantized** or **discrete**.^{*} In this section, we discuss some of these early experiments and introduce the concept of quantization.

THE PARTICLE NATURE OF LIGHT

All objects emit electromagnetic waves, and as their temperature increases, so too do the total intensity and the average frequency of the radiation. At sufficiently high temperatures, a significant portion of the radiation is in the visible region of the spectrum. For example, a burner in an electric oven emits infrared radiation on a low setting, but it becomes ‘red hot’ on a high setting as it emits both infrared and visible radiation. Similarly, the tungsten filament of a light bulb becomes ‘white hot’ because all of the colors in the visible region are being emitted. This emission of electromagnetic waves from a warm body is called **blackbody radiation**. Physicists of the late 1800’s tried to model the energy emitted by a blackbody radiator by assuming that the energy of each wave depended only upon its amplitude (intensity), and that all light waves had the same amplitude and therefore the same energy. Although there were some restrictions on the waves, there were still an infinite number of waves allowed. Each wave had the same energy, so the model predicted that there should be an infinite amount of energy given off!

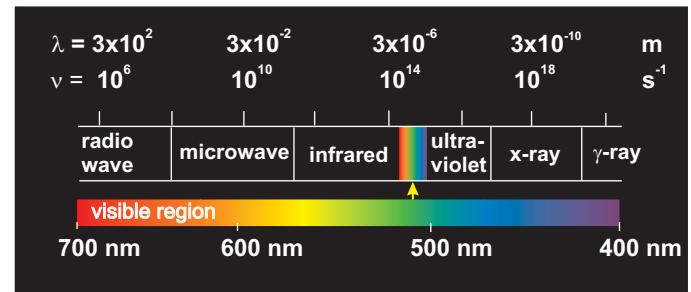


Figure 2.2 The electromagnetic spectrum

The region of the spectrum visible to the human eye is a very small portion of the spectrum and has been expanded in this figure to better display the wavelengths of the different colors.

* Recall that electrical charge is also quantized and that electrons and protons are the discrete bundles of charge.

Clearly an infinite amount of energy presents a dilemma, and Max Planck, a German physicist, addressed the problem in 1900. He proposed that the energy of a wave is **quantized**. That is, the total energy of a wave could not be varied continuously because it is composed of many tiny bundles of energy called **quanta**. Planck proposed that the energy of one quantum of light is proportional to its frequency,

$$E = h\nu$$

Eq. 2.2

h, which has the value 6.626×10^{-34} J·s, is a proportionality constant called **Planck's constant**. The amount of energy in a wave is then $E = nh\nu$, where n is the number of quanta in the wave. Thus, increasing the intensity of light increases the number of energy quanta it contains, not the energy of each quantum. Planck's model using light waves with quantized energy correctly accounted for blackbody radiation, but the only reason he could offer for this remarkable behavior was that it worked.

Another observation of the late 1800's that could not be understood with the classical picture of light was that when certain metals were irradiated with light, they ejected electrons with a kinetic energy (speed) that depended only upon the metal and the frequency of light. Increasing the intensity of the light increased the number of electrons ejected, but not their kinetic energy. For these metals, there is a minimum frequency below which no electrons are ejected, no matter how intense the light. This minimum frequency is called the **threshold frequency** of the metal, ν_0 . A plot of the ejected electron's kinetic energy versus the frequency of the light striking the metal is a straight line with a slope equal to Planck's constant (Figure 2.3).

In order to explain this phenomenon, a German physicist named Albert Einstein used Planck's hypothesis. He assumed that each electron that was ejected had interacted with a single quantum, which had an energy $E = h\nu$. He proposed that the electron is bound to the metal by an energy, W , and the threshold frequency for electron ejection is that frequency for which $h\nu_0 = W$. When the frequency of the light is greater than the threshold frequency, the energy of the quantum is greater than W , and the excess energy is converted into the kinetic energy of the ejected electron: $KE_{\text{electron}} = h\nu - W = h\nu - h\nu_0$.

Einstein reasoned that light consisted of a stream of tiny packets or quanta, which were later named **photons**. The energy of each photon is $h\nu$. The intensity of a light wave reflects the number of photons that it contains. A beam that contains n photons has a total energy of $nh\nu$, but when light interacts with matter, it does so one photon at a time. Thus, it is the energy of each photon that dictates the energy of the process that can be initiated

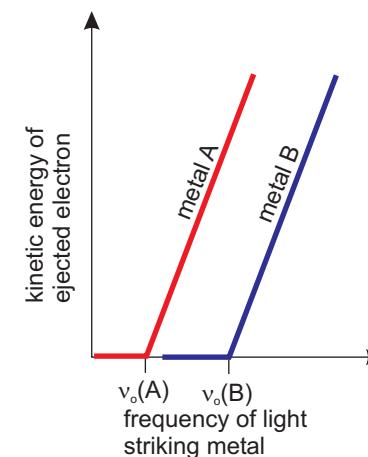


Figure 2.3 The photoelectric effect

The kinetic energy of electrons ejected by two different metals is shown as a function of the frequency of the light striking them. The threshold frequency, ν_0 , is the lowest frequency at which electrons are ejected. The fact that the threshold frequency of metal B is greater than that of metal A means that the electrons are more tightly bound to metal B.

by the light, while the intensity of the light dictates the number of events that can occur in a given time, that is, the rate at which the process takes place.

Planck and Einstein had shown that light consisted of particles of energy called photons, but classical experiments showed that light was also a wave. This property of behaving as both a particle and a wave is called *wave-particle duality*.

Example 2.1

A He-Ne laser produces light with a wavelength of 633 nm. What are the frequency (ν) and the energy (E) of a photon of this light?

Light can be characterized as both a wave and a photon. Its wave properties dictate that $c = \lambda\nu$, which can be solved for ν

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{633 \times 10^{-9} \text{ m}} = 4.74 \times 10^{14} \text{ s}^{-1}$$

The energy of each photon is proportional to its frequency:

$$E = h\nu = (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(4.74 \times 10^{14} \text{ s}^{-1}) = 3.14 \times 10^{-19} \text{ J}$$

What would be the energy of a mole of these red photons?

The energy of a mole of photons is the energy of one red photon times Avogadro's number, $E = N_A h\nu$

$$(3.14 \times 10^{-19} \text{ J/photon})(6.02 \times 10^{23} \text{ photons/mol}) = 1.89 \times 10^5 \text{ J/mol} = 189 \text{ kJ/mol}$$

ATOMIC SPECTRA

When you take a picture of an object with a camera, you simply capture on film the reflection of light from the object, but what do you do when the object is too small to be seen? That was the problem faced by scientists trying to ‘picture’ atoms and molecules. The solution turned out to be not so different from using a camera. With the work of Planck and Einstein, a new understanding of light had been achieved, and application of this understanding to the interaction of light with matter led to the present picture of the atom. The manner in which matter interacts with light depends upon the frequency of the light. For example, a ‘snapshot’ taken with visible light yields different information from one taken with infrared radiation. Taken together, ‘snapshots’ from a variety of electromagnetic waves provided new understanding of atoms and molecules. This is similar to a doctor using visible light (physical exam), x-rays, and radio waves (magnetic resonance imaging or MRI). Each of the three spectral regions gives the doctor different

information, each of which must be analyzed to get the best picture possible.

The ‘picture’ that scientists obtain is called the **spectrum** of the atom or molecule: a plot of how much light is absorbed or emitted *versus* the wavelength or frequency of the light. Scientists analyze the spectrum of a substance to determine its composition or to better understand its properties. For example, scientists have long used atomic spectra to determine the composition of a mixture and to identify the presence of elements in distant stars. The study of atomic and molecular spectra is called **spectroscopy**.

Let us begin our discussion of atomic spectra with the observation that high-energy electrons in a gas discharge tube can cause certain gases contained in the tube to glow with characteristic colors. For example, neon, a colorless gas in the absence of the high-energy electrons, glows bright red when a voltage is applied across a discharge tube containing neon (*i.e.*, a neon light). Recall that white light consists of all colors, so it produces a continuous spectrum, similar to the one shown at the top of Figure 2.4, as the colors merge continuously into one another. However, the light observed from the gas in a discharge tube consists of only a few colors, which are separated from one another, to produce a **line spectrum**. Each *line* of a line spectrum represents one of the component *colors* of the observed glow.

Figure 2.4 represents the experiment in which the visible line spectrum from a hydrogen discharge tube could be obtained. A narrow beam of light from the discharge tube is passed through a prism, where the different wavelengths of light present in the beam are separated. The line spectrum of hydrogen consists of many different lines, but only four are observed in the visible region. These four beams strike the photographic plate at different positions that depend upon their wavelengths (color). The plate is exposed at these positions, and the wavelength of each beam can be determined very precisely from the position of the exposure (line). If white light were used instead of the hydrogen discharge, the entire photographic plate would be exposed because all wavelengths would strike the plate.

The visible line spectrum of hydrogen gas was first observed in 1885. Similar line spectra for hydrogen have been observed in the ultraviolet and the infrared, resulting in over 40 spectral lines for the hydrogen atom. Some atoms can have hundreds of such lines.

Johannes Rydberg discovered a single mathematical expression that allowed scientists to calculate the frequency of every line in the hydrogen spectrum. The expression, now known as the Rydberg equation, is shown in Equation 2.3a:

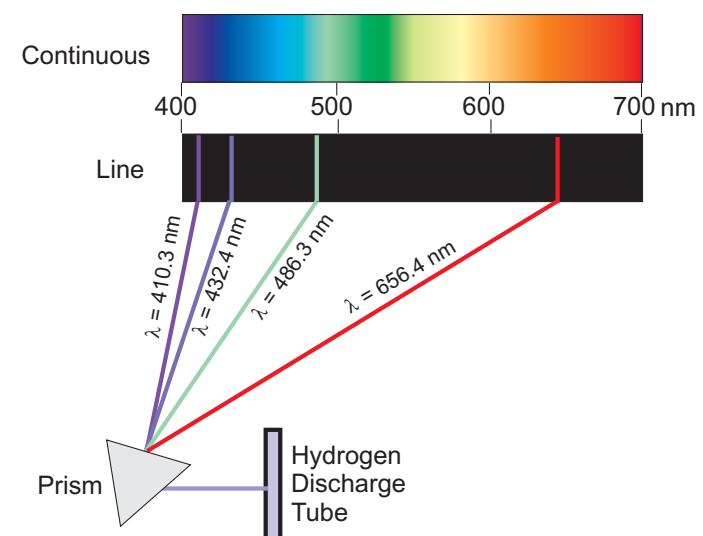


Figure 2.4 A continuous and a line spectrum

The spectrum at the top is a continuous spectrum that would be obtained with white light, while the line spectrum below it would be obtained from a hydrogen discharge tube.

$$v = R_H \left(\frac{1}{n_{lo}^2} - \frac{1}{n_{hi}^2} \right) \quad \text{Eq. 2.3a}$$

$n_{hi} > n_{lo}$ are *integers* and $R_H = 3.290 \times 10^{15} \text{ s}^{-1}$ is the Rydberg constant for the hydrogen atom. The Rydberg constant had no theoretical basis at the time; it was simply the number that made the equation work! Multiplication of Equation 2.3a by Planck's constant yields the energy of the *emitted* photon ($E = hv$) as shown in Equation 2.3b,

$$E_{\text{photon}} = h\nu = hR_H \left(\frac{1}{n_{lo}^2} - \frac{1}{n_{hi}^2} \right) = 2.180 \times 10^{-18} \left(\frac{1}{n_{lo}^2} - \frac{1}{n_{hi}^2} \right) \text{ J} \quad \text{Eq. 2.3b}$$

Example 2.2

What are the wavelength and the frequency of the $n_{hi} = 3 \rightarrow n_{lo} = 2$ emission transition in hydrogen?

We use the values $n_{lo} = 2$ and $n_{hi} = 3$ in the Rydberg Equation (Eq 2.3a) to obtain the emitted wavelength.

$$v = 3.290 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 4.569 \times 10^{14} \text{ s}^{-1}$$

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{4.569 \times 10^{14} \text{ s}^{-1}} = 6.562 \times 10^{-7} \text{ m} = 656.2 \text{ nm}$$

This is the red line in the visible spectrum, the lowest energy (frequency) line in the visible region of the hydrogen spectrum.

According to Rydberg, the frequency of each emitted photon obeyed a relatively simple mathematical expression; it is proportional to the difference of the reciprocals of two squared integers! Scientists had another simple relationship, and understanding its origin would unlock yet another of nature's secrets. It was time for a new model of the atom, one that would explain 40 different lines in the hydrogen spectrum and account for the relatively simple relationship of their frequencies. Rutherford's model of electrons orbiting the nucleus like planets around the sun would serve as the starting point for the new model, but the new model had to incorporate the ideas of quantization.

2.3 BOHR MODEL

In the Rutherford model, electrons moved in circular orbits, but particles tend to move in straight lines not circles, so circular orbits require a force, called the centripetal force,* to pull the orbiting particle toward the center. Earth is kept in its orbit by the gravitational attraction of the sun, and *the electron is kept in its orbit by the Coulombic attraction of the nucleus*. However, there was one major flaw with these orbiting electrons: the orbit would be unstable because a charged particle moving in this way would radiate energy, which would cause it to spiral into the nucleus. Clearly that was not the case in the hydrogen atom! Niels Bohr, a Danish physicist, postulated the reason for the stability of the atom: the electron remains in its orbit because its angular momentum[†] is quantized. He proposed that the angular momentum was proportional to an integer, called the **principal quantum number**, **n** ($n = 1, 2, 3, 4, \dots \infty$). By forbidding $n = 0$, he assured that the electron always had some angular momentum, which stabilized the orbit and kept the electron moving in its circular path! Using Coulomb's law to evaluate the electron-nuclear attraction and the quantized angular momentum to determine the centripetal force, he determined the stable radii of rotation to be

$$r_n = 5.292 \times 10^{-11} \left(\frac{n^2}{Z} \right) \text{ m} = 52.92 \left(\frac{n^2}{Z} \right) \text{ pm} \quad \text{Eq. 2.4}$$

The n^2 dependence of the radius is shown in Figure 2.5. The constant was calculated from known physical constants, such as Planck's constant, and the mass and charge of the electron and the proton. Z is the atomic number (number of positive charges in the nucleus). For a hydrogen atom, $n = 1$ and $Z = 1$, so the distance between the electron and the proton was determined to be $r_1 = 52.92 \text{ pm}$, which is called the **Bohr radius**.

The total energy of the electron (E) is the sum of its kinetic energy (KE) and its potential energy (U); *i.e.*, $E = KE + U$. The potential energy of the electron arises from its Coulombic energy of interaction with the nucleus, and its kinetic energy from its circular motion about the nucleus. However, the fact that the centripetal force resulted from the Coulombic force required that the kinetic energy be one-half of the Coulombic energy but opposite in sign; *i.e.*, $KE = -\frac{1}{2}U$. The total energy is then $E = KE + U = -\frac{1}{2}U + U = \frac{1}{2}U$. The Coulombic energy of interaction between the nucleus and the electron is given by Equation 1.4, so the total energy of an electron in the n^{th} orbit is

$$E_n = \frac{1}{2}U_n = \frac{1}{2} \left(\frac{kq_e q_N}{\epsilon r_n} \right)$$

* As you rotate an object that is attached to a rope about you, you must pull on the rope with a force equal to the centripetal force. If you release the rope, there is no more centripetal force, and the object flies away in a straight line.

[†] Angular momentum (L) is a property of a rotating object. For a circular orbit, it is the product of the mass, velocity, and the orbital radius of the particle ($L = mv r$). Bohr quantized the angular momentum in bundles of $h/2\pi$; *i.e.*, $L = nh/2\pi$. h is Planck's constant.

[§] pm is the picometer. $1 \text{ pm} = 1 \times 10^{-12} \text{ m}$

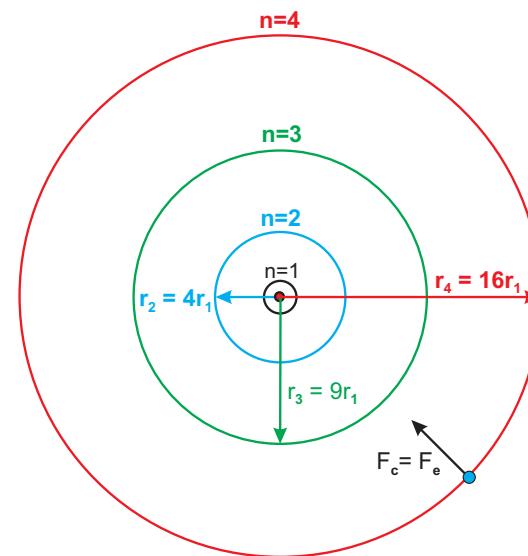


Figure 2.5 Four electron orbits in the Bohr model

The red dot in the center represents the nucleus. The blue dot represents an electron in the 4th orbit, which is $4^2 = 16$ times farther from the nucleus than in the $n = 1$ orbit. The arrow labeled $F_c = F_e$ shows the direction of the centripetal force (F_c) caused by the electromagnetic force (F_e), which maintains the circular motion.

The basic unit of charge is $q = 1.602 \times 10^{-19}$ C, so the charge on an electron is $q_e = -q$ and the charge on a nucleus with Z protons is $q_N = +Zq$. $\epsilon = 1$ in a vacuum, and r is the radius of the nth orbit as given in Equation 2.4. Substitution of these known quantities into the preceding energy expression yields the total energy of an electron in the nth orbit in terms of the n quantum number.

$$E_n = -2.180 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) J \quad \text{Eq 2.5a}$$

The constant determined by Bohr, 2.180×10^{-18} J, was the same as the experimental value determined by Rydberg in Equation 2.3a, which was strong support for the Bohr model. Thus, the energy of the electron in the nth orbit is also expressed as

$$E_n = -hR_H \left(\frac{Z^2}{n^2} \right) \quad \text{Eq. 2.5b}$$

Equations 2.5 show that the energy of an electron in an atom is *quantized*; i.e., it can have only discrete values that are dictated by the value of the n quantum number. The allowed energies are called **energy levels**, and Figure 2.6 shows an energy level diagram for the hydrogen atom as determined with Equation 2.5. Each horizontal line represents an allowed energy level. Note how the energy levels get closer with increasing n.

Example 2.3

What are the orbital radius and energy of an electron in the n = 1 level of a Li²⁺ ion?

Li²⁺ has one electron, so we use Equations 2.4 and 2.5 and the fact that Z = 3 for Li.

$$r_1 = 5.292 \times 10^{-11} \left(\frac{n^2}{Z} \right) = 5.292 \times 10^{-11} \left(\frac{1^2}{3} \right) = 1.764 \times 10^{-11} \text{ meters} = 17.64 \text{ pm}$$

$$E_1 = -2.180 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) = -2.180 \times 10^{-18} \left(\frac{3^2}{1^2} \right) = -1.962 \times 10^{-17} \text{ J}$$

Note how the increased nuclear charge draws the electron closer to the nucleus and lowers its energy. We will use this trend in the next chapter to describe atomic properties.

Atomic spectra can be understood in terms of the electron moving from one energy level into another, which is referred to as an **electronic transition**. If n_{hi} is the higher quantum number and n_{lo} is the lower quantum number, then the energy difference between

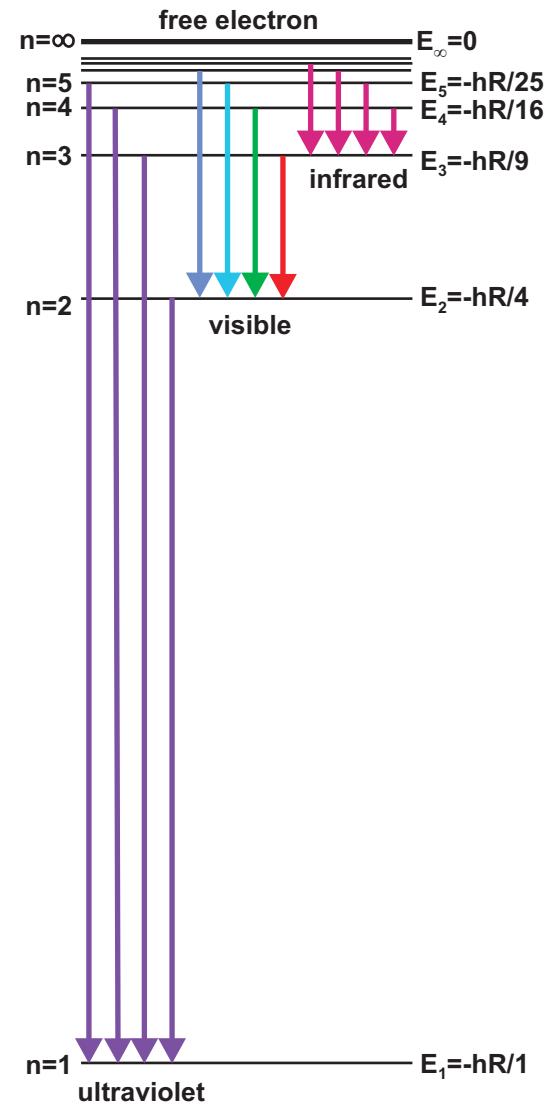


Figure 2.6 Energy level diagram of the H atom

Arrows represent the transitions that produce some of the observed lines in the emission spectrum of a hydrogen atom. The length of each line is proportional to the energy (photon frequency) of the transition. Reversing the direction of the arrows would result in absorptions rather than emissions. Note that it is the value of n_{lo} that dictates the series.

the two energy levels is $\Delta E = E_{n_{hi}} - E_{n_{lo}}$, which can be determined with Equation 2.5[†] to be

$$\Delta E_{atom} = E_{n_{hi}} - E_{n_{lo}} = -hR_H Z^2 \left(\frac{1}{n_{hi}^2} - \frac{1}{n_{lo}^2} \right) = hR_H Z^2 \left(\frac{1}{n_{lo}^2} - \frac{1}{n_{hi}^2} \right) \quad \text{Eq. 2.6}$$

Equation 2.6 is identical to the empirical Equation 2.3b. The energy change can be accomplished with light when a photon of energy ΔE_{atom} is either absorbed or emitted:

- a photon must be absorbed if the energy of the electron increases (n_{lo} is the initial level)
- a photon must be emitted if the energy of the electron decreases (n_{hi} is the initial level)

The electronic transitions resulting in some of the 40 lines in the *emission spectrum** of a hydrogen atom are represented with the vertical arrows in Figure 2.6. The lowest energy line in the visible series occurs for $n_{lo} = 2$ and $n_{hi} = 3$, which is designated as the $n = 3$ to $n = 2$ transition ($3 \rightarrow 2$). The violet line in the H atom spectrum is the highest energy line in the visible region; it results from the $6 \rightarrow 2$ transition. Note that the lines would correspond to absorptions if the arrows were pointed in the opposite direction. For example, the $2 \rightarrow 3$ transition is an absorption because the initial level is n_{lo} .

In a gas discharge tube, a high energy electron collides with an atom and transfers some of its energy to an electron in the atom, exciting the electron into a higher energy level (energy is absorbed). However, electrons always seek the lowest energy level, so the excited electron soon returns to a lower energy level. When it does so, it must give up all or some of the energy that it absorbed initially. Many of the electrons that are excited in this manner give up their energy by emitting photons. Only a fraction of the emitted photons fall in the visible region of the spectrum, but they are the ones that produce the glow in the tube.

Light is a form of energy that results from changes that occur during atomic and molecular processes, and its frequency depends upon the type of process. For example, molecules absorb microwave radiation when they rotate, and they absorb infrared radiation when their atoms vibrate back and forth against their bonds. Visible light originates in electronic transitions; *all color is the result of these transitions*. A red shirt appears red because it reflects the red portion of white light and absorbs the green portion. The fabric of the shirt contains dye molecules that have electrons that absorb green light when they undergo electronic transitions between energy levels. The levels, however, are not separated by an energy equal to the energy of red photons, so the red photons are reflected and not absorbed. Our eyes perceive the reflected red photons but not the green ones that are absorbed by the shirt.

[†] Electron-electron interactions have been ignored in this section, so Equations 2.5 and 2.6 apply only to one-electron systems such as the H atom and any ion formed by removing all but one electron from the atom. He^{1+} , Li^{2+} , and Be^{3+} are some examples of one-electron systems.

* It is an emission spectrum because n_{hi} is the initial level in each case. The electron must therefore give up energy during the transition. The released energy is in the form of an emitted photon.

2.4 QUANTUM THEORY

The Bohr model explained the main features of the atomic spectrum of hydrogen, but it could not explain the spectrum of hydrogen in a magnetic field, nor could it account for the spectra of atoms with more than one electron. Moreover, scientists did not yet understand the basis of quantization. Why were the electron energies quantized? There had to be a reason! An answer was suggested in 1923 by a French physics graduate student, Louis deBroglie, who reasoned that, if light could behave as both a wave and a particle, so might an electron. deBroglie recognized the analogy between quantized energy levels and vibrating strings, a system that was both macroscopic and quantized.

Figure 2.7 shows a taut string of length L that is tied at both ends. When the string is plucked, standing waves with wavelengths (λ) that obey the relationship $L = n(\lambda/2)$ can be produced. The wavelength of each wave is $\lambda = 2L/n$, so *the integer n must be positive and nonzero*, which is the same restriction placed on the n quantum number in the Bohr model. The various values of the integer n define the harmonics. The points where the waves have zero amplitude (indicated by dotted arrows in Figure 2.7) are called **nodes**. Each wave has $(n - 1)$ nodes, not counting the two ends where the string is attached. The motion of the vibrating string was well understood by classical physicists and could be described very precisely by an equation, known as the *wave equation* for a vibrating string, that also employs an integer n .

deBroglie concluded that the explanation for the quantization proposed by Bohr resulted from the fact that the electron, which is a particle, also has wave properties. His hypothesis was later confirmed by experiment. Like light, the electron had to be treated as both a particle and a wave! This was a perplexing concept. Is the electron a wave or is it a particle? The answer depends upon the experiment: In some experiments, the electron behaves like a wave; in other experiments, it behaves like a particle. Although we will usually refer to the electron as a small, negatively charged particle, it has some properties that are definitely wavelike. Thus, the *wave-particle duality* applies to the electron just as it does to light.

Both the position and the velocity of macroscopic objects, such as the earth, can be known very precisely. If both are known, then the exact position of the object at any given time in the future can be predicted - we know exactly where the earth will be at any given time and where it was at anytime in the past. However, an important principle (the **uncertainty principle**) in quantum theory states that the precise position and velocity of an electron cannot be known because the more precisely you know one, the less precisely

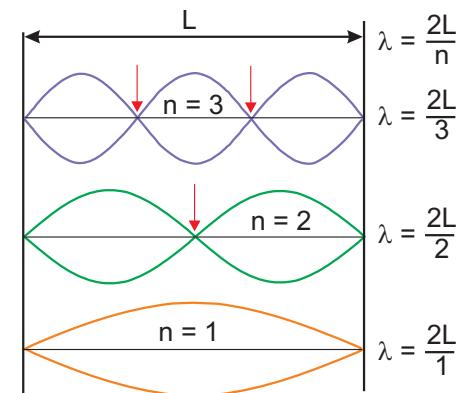


Figure 2.7 Standing waves of a string of length L

The wavelength of each wave must obey the relationship $\lambda = 2L/n$, where n is an integer. The red arrows indicate nodes, points where the amplitude of the wave is zero.

you know the other. Consequently, future positions and velocities cannot be predicted because, if you know where the electron is, you cannot know how it is moving. Although the Bohr model was a giant step forward in our understanding of atomic structure, ***the notion of electrons moving in predictable orbits the way planets do was wrong.*** Instead, we deal in terms of *probability*; we cannot know exactly where the electron is, but we can predict the probability that it will be found in some region of space. Sometimes we can say where an electron cannot be, but we can never say precisely where it will be.

2.5 QUANTUM NUMBERS

In 1926, Erwin Schrödinger applied the wave equation of a vibrating string to the electron. The result has come to be known as the Schrödinger wave equation, or simply the **wave equation**. Solving the wave equation produces mathematical functions, called **wave functions**, which contain all of the information pertinent to the electron in an atom. In modern quantum theory, an electron is treated mathematically like a vibrating string, and its full description requires four quantum numbers:

1. **n** , the principal quantum number,
2. **l** , the angular momentum quantum number,
3. **m_l** , the magnetic quantum number, and
4. **m_s** , the spin quantum number.

With these four quantum numbers and their relationships to one another, a convincing picture of the electronic structure of the atom can be drawn, one that explains both atomic spectra and chemical periodicity.

n , the principal quantum number: n is restricted to being an integer that is greater than zero [$n = 1, 2, 3, \dots$]. It designates the level or shell in which the electron can be found and is the *primary* (not the sole) indicator of the electron's energy. It also dictates the electron's *average* and *most probable* distances from the nucleus. Electrons in the $n = 1$ level are, on the average, the closest to the nucleus and have the strongest interaction with the nucleus. Thus, they have the lowest (most negative) energy.

l , the angular momentum quantum number: Each level, n , contains one or more *sublevels*, which differ in their value of l , an integer that can take values from zero through $(n - 1)$; i.e., $0 \leq l < n$. Consequently, there are n sublevels in the n th level [$l = 0, 1, 2, \dots (n-1)$].

Historically, the physical appearance of each spectral line was characterized as sharp, principal, diffuse, or fundamental. These classifications were carried over into the following designations of the sublevels: $l = 0$ is an s sublevel; $l = 1$ for a p sublevel; $l = 2$

for a d sublevel; and $l=3$ for an f sublevel. For values of l greater than three, the letters *g*, *h*, *i*, etc., are used. The sublevels are summarized in Table 2.1.

Together, n and l define the **sublevel** or **subshell**. A sublevel is specified by its n quantum number and the letter equivalent of its l quantum number as given in Table 2.1. Thus, the sublevel in which $n = 2$ and $l = 1$ is designated as the 2p sublevel, while the 4f sublevel is the one in which $n = 4$ and $l = 3$. The energy of a sublevel increases with increasing $(n + l)$ with l being of secondary importance as discussed in Example 2.4. Recall from the Bohr model that the energy of an electron in a hydrogen atom depends only on the n quantum number (Equation 2.5). However, this is only true for systems with a single electron. Interaction between electrons introduces the l dependence.

Example 2.4

a) Which sublevel is higher in energy, a 4s or a 3d?

$n = 4$ and $l = 0$ for the 4s sublevel, so $n + l = 4 + 0 = 4$.

$n = 3$ and $l = 2$ for the 3d sublevel, so $n + l = 3 + 2 = 5$.

Because $n + l$ is greater for the 3d, it is higher in energy.

b) Which sublevel is higher in energy, a 4p or a 3d?

$n = 4$ and $l = 1$ for the 4p sublevel, so $n + l = 4 + 1 = 5$.

From the first example, $n + l = 5$ for a 3d sublevel. Thus, the 4p and 3d sublevels have the same value of $n + l$. However, l is secondary to n in determining the energy, so the sublevel with the higher value of n has the greater energy, and we conclude that the 4p sublevel is higher in energy than the 3d sublevel.

m_l is the magnetic quantum number. Each sublevel has one or more *orbitals* that are completely defined by n , l and m_l . The **n quantum number** dictates the size of the orbital while the **l and m_l quantum numbers** dictate its shape and orientation in space. The **m_l quantum number** can take all integer values (including zero) from $-l$ to $+l$, i.e., $-l \leq m_l \leq +l$. There are $2l + 1$ orbitals in an l sublevel (l positive values plus l negative values plus one for $l = 0$).

Electrons reside in orbitals that are characterized by a unique set of three quantum numbers (n , l and m_l). The restrictions on the quantum numbers dictate the number of orbitals in a sublevel and the number of sublevels in a level. Consider the case of the $n = 3$ level shown in Figure 2.8, where each line represents one orbital. Because $n = 3$, there are three sublevels: $l = 0$, 1, and 2, which correspond to the 3s, 3p and 3d sublevels, respectively. In an $l = 0$ sublevel, there can be only one value of m_l and, therefore, only one orbital ($m_l = 0$). This is the 3s orbital. In an $l = 1$ sublevel, there are three allowed

Table 2.1 Letter symbols of the l quantum numbers

l	notation
0	s (sharp)
1	p (principal)
2	d (diffuse)
3	f (fundamental)

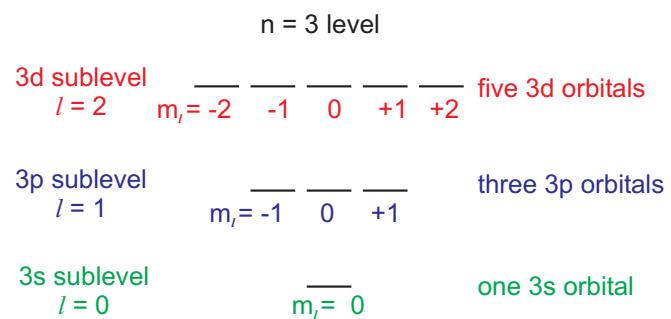


Figure 2.8 Sublevels (l) and orbitals (m_l) of the $n=3$ level

values of m_l (-1, 0, +1) and, consequently, three orbitals. These three orbitals are the 3p orbitals. In the $l = 2$ sublevel, $m_l = -2, -1, 0, +1$, and +2 for the five orbitals in the 3d sublevel. Thus, in the $n = 3$ level, there are three sublevels and nine orbitals.

The wave equation developed by Schrödinger required only the n , l and m_l quantum numbers, but many details of the emission spectra of the atoms could not be explained using only this set of quantum numbers. In addition, silver atoms that are passed through a magnetic field divided into two beams. All of these problems could be explained only if the electron had magnetic properties, which required a new quantum number, the electron spin. *Electron spin is a quantum mechanical effect* that is as much a property of the electron as is its charge. However, a simple macroscopic analogy is often used to describe this quantum mechanical effect. In the analogy (Figure 2.9), electron spin results from the rotation of the electron about its axis (analogous to the 24 hour rotation of the earth about its axis). The rate of rotation is the same for all electrons, but there are two different directions of rotation, which are distinguished by the spin quantum number, m_s .

m_s , the spin quantum number, has only two possible values: $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. All magnetic properties are attributed to electron spin, so it is often represented as the spin of the electron about its own axis in a clockwise ($m_s = +\frac{1}{2}$) or counterclockwise ($m_s = -\frac{1}{2}$) direction because a magnetic field is produced by a charge moving in a circular path. Thus, the 'spinning charge' can be thought to generate a magnetic field as indicated by the arrows in Figure 2.9. The arrow representing the magnetic field is often used to represent the m_s quantum number of the electron. ↑ ('up spin') is used to indicate an electron with $m_s = +\frac{1}{2}$ and ↓ ('down spin') indicates an electron with $m_s = -\frac{1}{2}$.

Example 2.5

Identify the incorrect quantum number and change it to an acceptable value.

- | | n | l | m_l | m_s | |
|----|-----|-----|-------|----------------|--|
| a) | 0 | 1 | 0 | $\frac{1}{2}$ | n cannot be 0. Any integer above 0 would be acceptable. |
| b) | 3 | 3 | 3 | $-\frac{1}{2}$ | l cannot equal n , so n must be increased or l decreased. Decreasing l is not acceptable because m_l cannot be greater than l . n must be increased to 4 or above. |
| c) | 8 | 0 | -1 | $\frac{1}{2}$ | m_l must lie between $+l$ and $-l$, so either l must be increased to 1 or above, or m_l must be reduced to 0. |
| d) | 6 | 5 | 0 | 0 | m_s must be $+\frac{1}{2}$ or $-\frac{1}{2}$ |

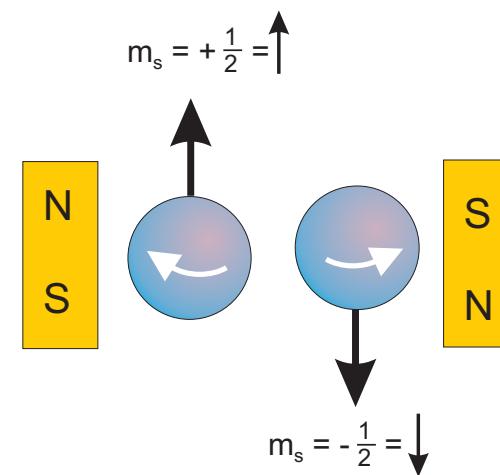


Figure 2.9 Classical analog of electron spin

The 'spinning' electron generates a magnetic field represented by the vertical arrows. The two possible values of m_s are often referred to as the 'up-spin' ($m_s = +\frac{1}{2}$) and the 'down-spin' ($m_s = -\frac{1}{2}$) due to the direction of the arrows. The north and south poles of the corresponding permanent magnet are shown next to each spinning electron.

2.6 ORBITAL SHAPES, SIGNS, AND SIZES

Solutions of the wave equations for the electrons in atoms result in mathematical functions that can be plotted and whose sign depends upon where in space the function is evaluated. Plots of the functions describe the regions in space in which the electrons are most likely to be found. These regions of space are called ‘**orbitals**’, and orbitals lie at the heart of chemistry. It is the interactions of orbitals and the electrons in them that lead to chemical bonding. Indeed, our discussion of bonding in Chapters 5 and 6 will rely on a good understanding of both the shape and sign of atomic orbitals.

l and m_l dictate the shape and orientation of the orbital, respectively. The shapes represent regions of space around the nucleus in which the electron can be found some large fraction of the time (typically 90 - 95%). These **electron clouds** or regions of **electron density** are useful when considering interactions between atoms. The sign of the function in a given region is designated by its shading. In this text, we use blue shading in regions where the sign is positive and red shading in regions where it is negative.

s orbitals ($l = 0$)

$l = 0$, so $m_l = 0$ and there is only one s orbital in an s sublevel. An s orbital is spherical, which means that the electron has equal probability of being found in any direction and that its charge is distributed equally in all directions. As shown in Figure 2.10, l dictates the spherical shape of the orbital, but n dictates its size. There are no nodal planes, so the function has the same sign everywhere as indicated by the blue shading in Figure 2.10.

p orbitals ($l = 1$)

$l = 1$, so there are three values of m_l (-1, 0, +1) and three orbitals in a p sublevel - the p_x , p_y and p_z orbitals. The shape of a p orbital is best represented by Figure 2.11a, but it is more common to represent it as a “figure 8” as shown in Figure 2.11b. The electron density in each orbital is distributed in two lobes, which are of opposite sign. Where the sign changes, the value of the function is zero, which means that there is no electron density in the plane that lies between the two lobes. This plane of zero electron density is called a **nodal plane**. The number of nodal planes in an orbital is equal to the l quantum number: s orbitals have no nodal planes ($l = 0$), p orbitals have one ($l = 1$), d orbitals have two ($l = 2$), etc.

d orbitals ($l = 2$)

There are five possible values of m_l in an $l = 2$ sublevel (-2, -1, 0, +1, +2), so there are five d orbitals. Figure 2.12 shows a representation of these orbitals. The d_{z^2} (or simply z^2) orbital is directed along the z-axis, but there is a donut shaped region of electron density in the xy plane. The $d_{x^2-y^2}$ (or x^2-y^2) orbital is directed along both the x- and the y-axes in both the positive and negative directions. Much of the d_{xz} (xz) orbital electron cloud lies in the xz plane 45° from either axis. The shapes of the d_{yz} (yz) and d_{xy} (xy) are identical to that of the d_{xz} , only the labels of the axes change.

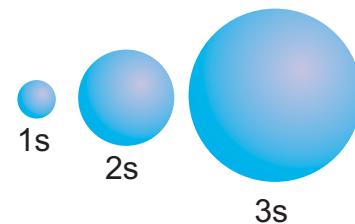


Figure 2.10 Relative sizes of 1s, 2s, and 3s orbitals

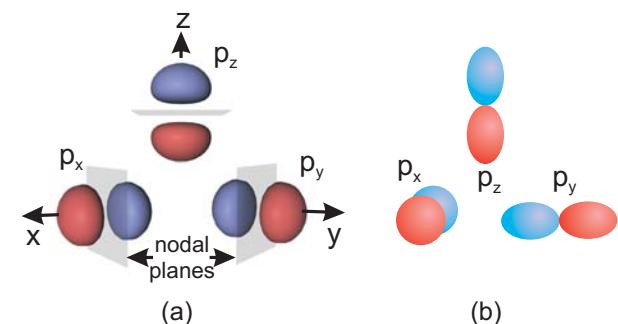


Figure 2.11 p orbitals

- (a) Truer representation of the shape
(b) Commonly used representation

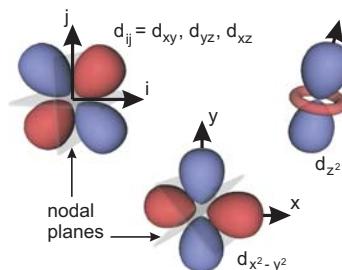


Figure 2.12 d orbitals

2.7 ELECTRON CONFIGURATIONS

Neither the orbital quantum number (m_l) nor the spin quantum number (m_s) can be determined unambiguously for a particular electron in an atom. However, the sublevel in which the electron resides can be determined because the energy of an electron can be determined. For example, we can determine that an electron is a p electron, but we cannot distinguish between p_x , p_y and p_z . Consequently, the electronic structure of an atom is normally given as a list of its occupied sublevels and the number of electrons in each of those sublevels. This list is called the atom's **electron configuration**. The notation used for a sublevel is $n l^{\#}$, where n is the n quantum number, l is the letter of the sublevel (s, p, d, ...), and $\#$ is the number of electrons in the sublevel. For example, $1s^2\ 2s^2\ 2p^1$ implies that there are two electrons in the $1s$ ($n = 1$; $l = 0$) sublevel, two electrons in the $2s$ ($n = 2$, $l = 0$) sublevel, and one electron in the $2p$ ($n = 2$; $l = 1$) sublevel.

The orbitals of an atom are filled in such a way as to satisfy the following three rules:

1. The electrons in atoms and molecules strive toward the lowest energy electron configuration known as the **ground state**. Electron configurations that do not yield the lowest energy represent **excited states**. Atoms and molecules have many excited states but only one ground state.
2. **The Pauli Exclusion Principle** states that no two electrons in an atom can have the same set of four quantum numbers. Two electrons in the same orbital have the same values of n , l and m_l , so they must have opposite spins (Figure 2.13). Thus, *an orbital can accommodate no more than two electrons*, one with $m_s = +\frac{1}{2}$ and one with $m_s = -\frac{1}{2}$. An orbital with two electrons is filled while one with a single electron is a half-filled orbital. When two electrons occupy the same orbital, they are said to be *paired*; that is, their spins are opposed and their magnetic fields cancel.
3. **Hund's rule** states that the electrons in a sublevel that is less than half-filled must occupy different orbitals within the sublevel and have the *same spin* (Figure 2.14). This is because electrons with the same spin tend to stay away from one another, which minimizes the electrostatic repulsion between them. Paired electrons, on the other hand, spend more time close to one another, which increases their electrostatic interaction. Consequently, the energy of two electrons in a sublevel is lower if the electrons have the same spin.

The atomic orbitals, in order of increasing energy ($n + l$), are shown in Figure 2.15. The electron configuration of the ground state of an atom is obtained by placing its electrons into the lowest energy orbitals in a manner consistent with the Pauli exclusion principle and Hund's rule.

The two electrons of He are in the $1s$ sublevel, so He has a $1s^2$ configuration. Neon's

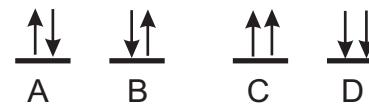


Figure 2.13 The Pauli exclusion principle

A and B are acceptable, but C and D are not because they violate the Pauli Exclusion Principle.

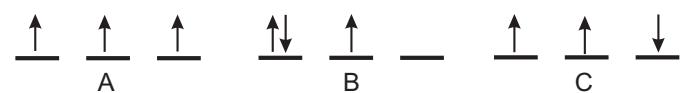


Figure 2.14 Hund's rule

A is the lowest energy configuration because it obeys Hund's rule. The energies of B and C are greater than that of A because the three spins are not the same in B and C.

4p	— — — — —	Ga, Ge, As, Se, Br, Kr
3d	— — — — —	Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
4s	—	K, Ca
.....	Fourth Period
3p	— — —	Al, Si, P, S, Cl, Ar
3s	—	Na, Mg
.....	Third Period
2p	— — —	B, C, N, O, F, Ne
2s	—	Li, Be
.....	Second Period
1s	—	H, He
.....	First Period

Figure 2.15 Atomic orbitals in order of increasing energy

The atoms to the right of each sublevel are the atoms whose highest energy electrons reside in that sublevel. Atoms between dotted lines are in the same period.

ten electrons have a $1s^2 2s^2 2p^6$ configuration, which is sometimes abbreviated as [Ne], while the $1s^2 2s^2 2p^6 3s^2 3p^6$ configuration of Ar is abbreviated as [Ar]. The symbol of the preceding noble gas in a square bracket is often used to abbreviate electron configurations. K has 19 electrons, so its configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, but it is often written [Ar]4s¹. Similarly, the configuration of the 34 electrons of selenium is [Ar]4s²3d¹⁰4p⁴. To the right of each sublevel in Figure 2.15 is a list of those elements whose highest energy electrons are in that sublevel. Thus, the elements aluminum ($Z = 13$) through argon ($Z = 18$) are filling the 3p sublevel while scandium ($Z = 21$) through zinc ($Z = 30$) are filling the 3d sublevel.

2.8 QUANTUM THEORY AND THE PERIODIC TABLE

The periodic table contains four distinct blocks (Figure 2.16): two columns on the left; six columns on the right; ten columns in the middle; and fourteen columns inserted in the bottom. One of the major accomplishments of modern quantum theory is that electron configurations explain this arrangement of the periodic table.

- The column specifies the l quantum number of the sublevel of the highest energy electrons in an atom. The highest energy electrons in elements in the first two columns are in s sublevels, those in the last six are in p sublevels, those in the 10 columns in the middle (transition elements) are in d sublevels, and those in the 14 columns at the bottom are in f sublevels.
- The period (row) number equals the principle quantum number of the outermost shell (n). The principle quantum number s and p sublevels equals n , but it is $n-1$ for the d sublevels and $n-2$ for the f sublevels.

Thus, the first two columns (Groups 1A and 2A) are called the **s block**, last 6 columns on the right (Groups 3A through 8A) comprise the **p block**, the 10 columns in the middle (the B groups or transition metals) form the **d block**, and the 14 columns at the bottom make up the **f block**. The position of the element in a block equals the number of electrons that element has in that sublevel. Example 2.6 shows how to determine the electron configuration of an atom from its position in the periodic table.

Example 2.6

Use the periodic table to determine the electron configurations of Ti and Bi.

Ti is the second element in the d block of the 4th row. For the d block, $n = \text{row} - 1 = 4 - 1 = 3$, so it has two electrons in the 3d sublevel. The previous noble gas is Ar, and only the 4s block (K and Ca) lies between Ar and the 3d sublevel. Thus, Ti is [Ar]4s²3d².

Figure 2.16 Quantum numbers and the periodic table

The number at the top of each group is the number of electrons in the highest energy sublevel for that group. Thus, the '6' above Fe indicates that Fe has six 3d electrons ($3d^6$).

Bi is the third element of the p block of the 6th period, so the outermost sublevel is 6p³. The preceding noble gas is Xe. The 6s (Ca-Ba), 4f* (Ce-Lu), and 5d (La-Hg) blocks lie between Xe and Bi, so Bi is [Xe] 6s²4f¹⁴5d¹⁰6p³. Note that the number of electrons in the configuration is 54 (Xe) + 2 + 14 + 10 + 3 = 83, which is the correct number of electrons.

The method outlined above is based solely on the energies of the sublevels, but in multi-electron atoms, there is the added complexity of electron-electron repulsion. Energy is required to pair electrons and this **pairing energy** can influence orbital occupancies if the energy spacing between the sublevels is small. The separation between s and p sublevels is quite large, so main group elements always adopt the predicted configuration, but elements in the d and f blocks frequently deviate from the predicted configurations. However, those in the first d block are well behaved except for two elements.

- **Chromium** is predicted to have a [Ar]4s²3d⁴ configuration, but one of its 4s electrons is moved into the d sublevel resulting in a [Ar] 4s¹3d⁵ configuration. This removes all pairing and achieves two stable half-filled sublevels.
- **Copper** is predicted to be [Ar] 4s²3d⁹, but it moves one electron from the 4s into the 3d to attain a [Ar]4s¹3d¹⁰ configuration, which produces one half-filled and one completely filled sublevel.

Almost 50 years elapsed before scientists understood Mendeleev's pioneering arrangement of the elements, *in an order that closely approximated that of their atomic weights*, and the basis of the periodicity of the chemical and physical properties of the elements. His wonderful organization of the elements turned out to be a direct consequence of the wave nature of the electron!

2.9 CHAPTER SUMMARY AND OBJECTIVES

The current model of the atom is one in which particles behave like waves and waves like particles. The electrons in an atom are treated like vibrating strings and can have only certain discrete energies. Four quantum numbers with well-defined restrictions are required to characterize each electron in an atom:

- **n**, the principal quantum number, designates the level or shell of the electron. It must be an integer that is greater than zero.
- **l**, the angular momentum quantum number, designates the electron's sublevel or subshell. It must be an integer such that $0 \leq l < n$.
- **m_l**, the magnetic quantum number, designates the shape and orientation of the orbital. It must be an integer such that $-l \leq m_l \leq +l$.
- **m_s**, the spin quantum number, indicates the direction of the magnetic field generated by the spinning electron. It has two values: $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$.

The electron configuration of an atom indicates the electron population of the filled sublevels. It is determined by three rules:

- Electrons seek the lowest energy orbital.
- No two electrons can have the same set of quantum numbers (Pauli exclusion principle).
- Electrons in sublevels that are half-filled or less than half-filled remain unpaired and have the same spin (Hund's rule).

As a result of all of the above restrictions, the electron configurations of the atoms show the same periodicity as the periodic table. For the main group elements, the highest energy electron is in an s sublevel (Groups 1A and 2A) or a p sublevel (Groups 3A - 8A). The row or period of the main group element corresponds to the n quantum number of its highest energy electron. The highest energy orbitals for the transition elements lie in a d sublevel, with an n quantum number equal to its period minus one.

After studying the material presented in this chapter, you should be able to:

1. explain the relationships between wavelength, frequency, and energy (Section 2.1);
2. define the term 'quantized' and use it describe line spectra and color (Section 2.2);
3. explain Bohr's model of the atom and relate it to the atomic spectrum of hydrogen (Section 2.3);
4. explain how and why the electron is treated like a wave (Section 2.4);
5. distinguish between acceptable and unacceptable sets of quantum numbers (Section 2.5);
6. draw pictures of ns, np, and nd orbitals and describe their key features (Section 2.6); and
7. write electron configurations for atoms based on their position in the periodic table (Section 2.8).

2.10 EXERCISES

1. Which has more energy, a photon of microwave radiation or a photon of infrared radiation? Explain your answer.
2. Arrange the following in order of increasing photon energy:
 a) $\lambda = 0.2 \text{ cm}$ b) $\lambda = 1 \text{ mi}$ c) $v = 10^{16} \text{ s}^{-1}$ d) yellow light
3. Radiation from the sun can cause the decomposition of O_2 in the stratosphere: $\text{O}_2 \rightarrow 2\text{O}$. This requires 495 kJ/mol of energy. What is the longest wavelength of light in nm that can accomplish this process? In what region of the electromagnetic spectrum (*i.e.*, infrared, visible, ultraviolet, etc.) is light of this energy found?
4. Fill in the following table:

λ (nm)	v (s^{-1})	E/photon (J)	E/mol photons (kJ/mol)
900			
	8.00×10^{14}		
		8.50×10^{-20}	
			250
5. Fill in the following table:

λ (nm)	v (s^{-1})	E/photon (J)	E/mol photons (kJ/mol)
333			
	6.42×10^{15}		
		1.86×10^{-18}	
			108
6. The threshold frequency for the ejection of an electron from iron is $1.1 \times 10^{15} \text{ s}^{-1}$. Indicate whether each of the following photons has enough energy to eject an electron from iron.
 a) $\lambda = 1 \text{ mm}$ b) $\lambda = 1 \text{ nm}$ c) blue light d) an x-ray
7. Use the Bohr model to determine the radii of the $n = 2$ and $n = 4$ orbits of a He^{1+} ion.
8. Use the Bohr model to determine the radii of the $n = 2$ and $n = 4$ orbits of a Be^{3+} ion.

9. Determine the energies of the $n = 2$ and $n = 3$ levels of a He^{1+} ion. What region of the spectrum (*i.e.*, infrared, visible, ultraviolet, etc.) would the $n = 3 \rightarrow 2$ transition in He^{1+} ion occur? Is this transition an absorption or an emission?
10. Determine the energies of the $n = 6$ and $n = 8$ levels of a Be^{3+} ion. What region of the spectrum (*i.e.*, infrared, visible, ultraviolet, etc.) would the line $n = 6 \rightarrow 8$ transition occur? Is the transition an absorption or an emission?
11. A 20 cm string, which is fastened at both sides, is plucked. What is the wavelength of the $n = 5$ standing wave? How many nodes does it contain? Draw the wave.
12. Consider the transitions shown in the following energy level diagram:

a) Which transitions absorb and emit photons of highest frequency?
 b) Which transitions absorb and emit photons of longest wavelength?
 c) Which transition involves the greatest energy change?
13. Which restriction on the quantum numbers is violated in the following:

n	l	m_l	m_s
a) 2	1	-1	1
b) 3	-2	0	$1/2$
c) 2	2	0	$-1/2$
d) 3	2	3	$-1/2$
14. Which restriction on the quantum numbers is violated in the following:

n	l	m_l	m_s
a) 3	3	-3	$1/2$
b) 75	74	-68	0
c) 6	-5	-5	$-1/2$
d) 4	0	-1	$-1/2$

15. What is the maximum number of electrons that can be accommodated in an $n = 7$ level?

16. Indicate whether each of the following transitions would be an emission or an absorption. The notation ‘ $4p \rightarrow 6s$ ’ means the transition from a $4p$ orbital to a $6s$ orbital.

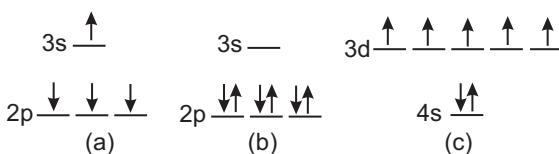
- a) $4p \rightarrow 6s$ b) $3d \rightarrow 3p$ c) $8s \rightarrow 6f$ d) $4p \rightarrow 4s$

17. Sketch the p orbitals. Be sure to label the axes.

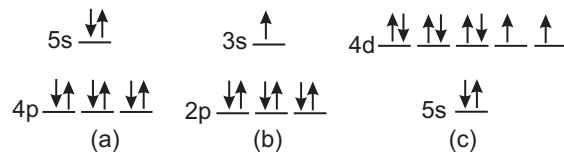
18. Sketch the d orbitals. Be sure to label the axes.

19. How many orbitals are in an h sublevel? What is the lowest n quantum number for a level with an h sublevel? How many electrons could occupy this level?

20. Write short hand notations for each of the following orbital occupancies. Arrows are used to represent the electron spin quantum number; that is, ↑ represents $m_s = +\frac{1}{2}$, and ↓ represents $m_s = -\frac{1}{2}$.



21. Write short hand notations for each of the following orbital occupancies. Arrows are used to represent the electron spin quantum number; that is, ↑ represents $m_s = +\frac{1}{2}$ and ↓ represents $m_s = -\frac{1}{2}$.



22. Give the n and l quantum numbers for the highest energy electrons in each of the following atoms:

- a) strontium b) indium c) zinc d) fluorine

23. Give the n and l quantum numbers for the highest energy electrons in each of the following atoms:

- a) ruthenium b) antimony c) barium d) silicon

24. Write electron configurations for the following:

- a) phosphorus b) cobalt c) lead d) strontium

25. Write electron configurations for the following:

- a) manganese b) thallium c) sulfur d) bromine

26. If an electron is brought closer to the nucleus, the force of attraction between the electron and the nucleus _____ and the potential energy of the electron _____. Fill in each blank with increases or decreases.

27. How many of the following are populated by at least one electron in an atom of cobalt?

- a) levels b) sublevels c) orbitals

28. How many unpaired electrons are present in each of the following?

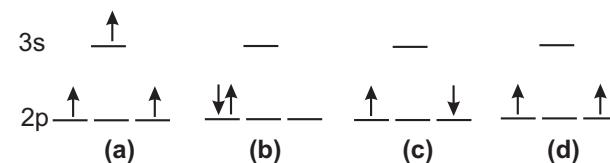
- a) phosphorus b) cobalt c) lead d) strontium

29. How many unpaired electrons are present in each of the following?

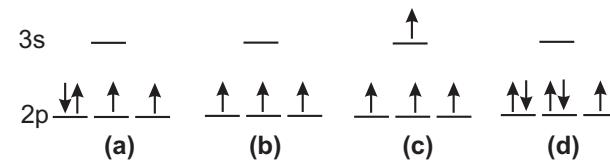
- a) manganese b) thallium c) sulfur d) bromine

30. How many p electrons does an atom of Te ($Z = 52$) have? How many of the p electrons are in the outermost shell?

31. Indicate whether each of the following orbital occupancies is a ground state, an excited state or not allowed. If it is a ground state occupancy, identify the atom. If it is not the ground state, explain why. Assume the 1s and 2s sublevels are full.



32. Indicate whether each of the following orbital occupancies is a ground state, an excited state, or not allowed. If it is a ground state occupancy, identify the atom. If it is not the ground state, explain why. Assume the 1s and 2s sublevels are full.



33. What is the common feature of the electron configurations of elements in a given group (family) of the periodic table?

- 34.** What two atoms have two unpaired electrons in the 3p sublevel?
- 35.** Identify the atom that
- contains five electrons in the $n = 3$ level
 - has nine electrons in the $n = 3$ level?
- 36.** Indicate which transition in a hydrogen atom would emit the photon of greater frequency.
- $n = 3 \rightarrow 2$ or $n = 6 \rightarrow 3$
 - $n = 8 \rightarrow 4$ or $n = 8 \rightarrow 6$
- 37.** Indicate which transition in a hydrogen atom would emit the photon of longer wavelength.
- $n = 4 \rightarrow 3$ or $n = 6 \rightarrow 3$
 - $n = 2 \rightarrow 1$ or $n = 12 \rightarrow 2$
- 38.** Is the energy difference between the outermost s and p orbitals greater for carbon or for silicon? Explain.
- 39.** Give a set of quantum numbers for all of the electrons in the outermost shell of Ga.
- 40.** Give a set of quantum numbers for all of the electrons in the outermost shell of P.
- 41.** Draw an orbital energy diagram similar to Figure 2.8 that describes the electrons in the outermost shell of Si and place electrons (arrows) to show the orbital occupancy.
- 42.** Draw an orbital energy diagram similar to Figure 2.8 that describes the electrons in the outermost shell of Br and place electrons (arrows) to show the orbital occupancy.
- 43.** Give the number of s, p, d, and f electrons in each of the following atoms.
- Na
 - Fe
 - Pb
 - Se
- 44.** Give the number of s, p, d, and f electrons in each of the following atoms.
- Ba
 - Hg
 - I
 - Ga
- 45.** What are the n and l quantum numbers for the electrons with the highest energy in the following atoms?
- Na
 - Fe
 - Pb
 - Se
- 46.** What are the n and l quantum numbers for the electrons with the highest energy in the following atoms?
- Ba
 - Hg
 - I
 - Ga
- 47.** Identify the element with each of the following electron configurations:
- [Ne]4s²3d¹⁰4p³
 - [Ar]4s²3d⁶
 - [Kr]5s¹
 - [Xe]6s²4f¹⁴5d¹⁰
- 48.** Identify the element with each of the following electron configurations:
- [Ar]4s²
 - [He]2s²p⁴
 - [Ar]4s²3d¹
 - [Kr]5s²4d¹⁰5p²
- 49.** A hydrogen atom in its ground state absorbs a photon of frequency $\nu = 3.084 \times 10^{15} \text{ s}^{-1}$. To what level is the electron promoted?
- 50.** A hydrogen atom in an excited state emits a photon of frequency $\nu = 2.924 \times 10^{15} \text{ s}^{-1}$. If the electron returns to the ground state, in which level was it before the photon was emitted?
- 51.** How many orbitals have each of the following designations?
- 3p
 - $n = 7$ and $l = 3$
 - $n = 3$
 - $n = 2, l = 1$ and $m_l = 1$

Chapter 3

Atomic Structure And Properties

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- | | | | |
|-----|---|-----|---------------------------------------|
| 3.0 | <i>Introduction</i> | 3.5 | <i>Ionization Energy</i> |
| 3.1 | <i>Valence Electrons</i> | 3.6 | <i>Electronegativity</i> |
| 3.2 | <i>Shielding and Effective Nuclear Charge</i> | 3.7 | <i>Magnetic Properties</i> |
| 3.3 | <i>Relative Sizes of Atoms</i> | 3.8 | <i>Chapter Summary and Objectives</i> |
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3.0 INTRODUCTION

In the previous chapters, we constructed a model of the atom. However, for this model to be useful, it must be able to account for atomic properties, and it must form a basis upon which predictions can be made. In this chapter, we test some predictions based on the quantum model and discuss atomic properties in terms of quantum theory.

THE OBJECTIVES OF CHAPTER 3 ARE TO USE THE QUANTUM THEORY DEVELOPED IN CHAPTER 2 TO:

- explain the periodicity in the chemical properties of the elements;
- predict relative sizes of atoms;
- predict relative orbital energies;
- predict the relative ability of atoms to lose or gain electrons; and
- describe the magnetic properties of atoms.

3.1 VALENCE ELECTRONS

Most of the remainder of this text is concerned more with molecules than with atoms. However, molecules are built from atoms that bond to one another through an exchange or sharing of electrons. Indeed, most atomic properties are dictated by the nature of the electron cloud and how strongly the electrons interact with the nucleus. Sublevels that are full are generally very stable and closer to the nucleus, so electrons can neither be added to nor removed from them. The outermost s sublevel is the only exception: electrons can be removed from a filled, outermost s sublevel because it is very high in energy and contains only two electrons. Consequently, electrons in filled sublevels (other than the outermost s) are not involved in bonding and are referred to as **core electrons**. The chemical properties of an atom are dictated by the electrons and orbitals that are involved in bonding. These high-energy electrons are called **valence electrons**, and the orbitals they occupy are called **valence orbitals**.

The valence electrons are those in the outermost s and in any partially filled sublevels.

Valence electrons can be donated to or shared with other atoms to produce bonds, while the valence orbitals are used to accept electrons from or to share electrons with other atoms. Thus, the number and location of the valence electrons are important characteristics of the atom, and they are given in an atom's **valence electron configuration**. As shown in Table 3.1, the number of valence electrons of a main group element is equal to its group number, so valence electron configurations vary periodically through the periodic table. Indeed, *the periodicity of the chemical properties of the elements is the result of the periodicity of their valence electron configurations.*

The valence electrons are *frequently*, but not always, those electrons beyond the previous noble gas. For example, the electron configuration of Al is [Ne]3s²3p¹, and its valence electron configuration is 3s²3p¹. However, *electrons in filled d sublevels are not valence electrons* even though they come after the previous noble gas and the outermost s electrons in the electron configuration. Thus, the valence electron configurations of elements in the p block (Groups 3A - 7A) do not include the d electrons. For example, the electron configuration of Ga is [Ar]4s²3d¹⁰4p¹, but the 3d sublevel is full so the 3d electrons are not valence electrons. The valence electron configuration of gallium is 4s²4p¹, consistent with the fact that it is a Group 3A nonmetal with three valence electrons.

The valence electrons of the transition metals are in the outermost s and d sublevels, so their valence electron configurations are typically of the form ns²(n - 1)d^x where n is the period and x is usually determined from the position of the element in the transition metal block. For example, the valence electron configuration of Mn, the fifth element in the block is 4s²3d⁵. However, there are three transition elements in the first d block that can be confusing. In Section 2.8, we saw that the electron configurations of Cr and Cu were exceptions and those exceptions are found in their valence electron configurations.

- Cr is 4s¹3d⁵
- Cu is 4s¹3d¹⁰. The 3d sublevel of copper is full and Cu is in Group 1B, so it would be easy to omit the 3d electrons. However, much of copper's chemistry involves its 3d orbitals, so they are considered to be valence orbitals.
- Zn is 4s². The 3d sublevel of Zn is filled and not used in bonding. This is not an exception, it is pointed out here only because Zn has no d electrons even though it is in the d-block.

We now apply our knowledge of the electronic structure of the atoms to the valence electrons in order to predict those atomic properties that will help us in our study of chemical bonding.

Table 3.1 Valence electron configurations of the elements by chemical group and examples from the 2nd period

1A	2A	3A	4A	5A	6A	7A
ns ¹	ns ²	ns ² np ¹	ns ² np ²	ns ² np ³	ns ² np ⁴	ns ² np ⁵
Li	Be	B	C	N	O	F
2s ¹	2s ²	2s ² 2p ¹	2s ² 2p ²	2s ² 2p ³	2s ² 2p ⁴	2s ² 2p ⁵

3.2 SHIELDING AND EFFECTIVE NUCLEAR CHARGE

The nuclear charge experienced by the valence electrons helps determine the atomic properties because the greater the nuclear charge a valence electron experiences, the more tightly it is bound to the atom and the lower is its energy. However, a valence electron is not exposed to the full positive charge of the nucleus because it is **shielded** or **screened** from the nuclear charge by intervening electrons, mainly the core electrons (Figure 3.1). Consider the case of Li ($1s^2 2s^1$). The nuclear charge is +3, but the 2s valence electron experiences a nuclear charge of only +1.3 because most of the electron density of the 1s core electrons lies between it and the nucleus. Thus, the 1s electrons shield the 2s electron from over half of the nuclear charge. The nuclear charge that is actually experienced by a valence electron is called the **effective nuclear charge**, Z_{eff} . The effective nuclear charge experienced by an electron is equal to the charge of the nucleus (Z) minus that portion of the nuclear charge that is shielded by the other electrons (σ) or

$$Z_{\text{eff}} = Z - \sigma$$

Eq. 3.1

We can apply Equation 3.1 to the 2s electron in Li and write $1.3 = 3 - \sigma$, or $\sigma = 1.7$. Thus, the two 1s electrons shield with only 85% of their full charge of -2.

Core electrons are closer to the nucleus, so they shield valence electrons better than do other valence electrons. Thus, in going from one atom to the next in a period, Z increases by one as one proton is added, but σ increases by less than one because the additional valence electron does not shield with its full charge. Therefore, as shown in Figure 3.2, *the effective nuclear charge experienced by the outermost electrons increases from left to right in a period*. As a result, Z_{eff} is low for metals and high for nonmetals.

Screening is the reason that the energy of an electron in a multi-electron atom depends upon both the n and l quantum numbers, while the energy of a one-electron atom or ion depends only upon n (Equation 2.5). An electron in an orbital screens other electrons best when its electron density is closer to the nucleus. Each nodal plane in an orbital reduces the electron density at the nucleus, and the number of nodal planes is equal to the l quantum number. Consequently, the shielding ability of electrons in a level decreases as their l quantum number increases; *i.e.*, *within a level*, the screening ability of the electrons is $s > p > d > f$. For example, $Z_{\text{eff}} = 6.12$ for the 3p electrons of chlorine, but it is 7.07 for the 3s electrons. The greater effective nuclear charge experienced by the 3s electrons lowers their energy to below that of the 3p electrons. Thus, orbital energies increase with the l quantum number because increasing l decreases Z_{eff} .

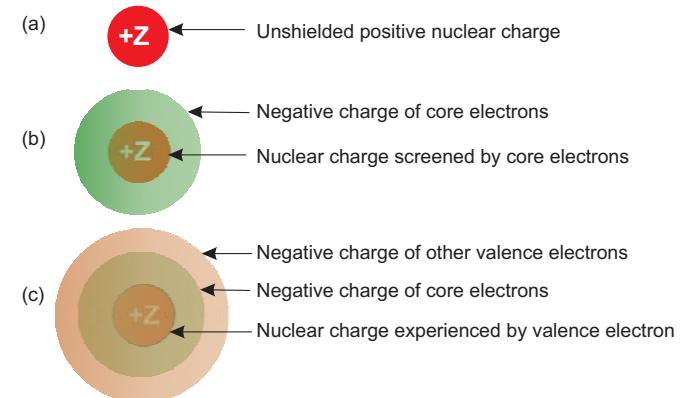


Figure 3.1 Shielding nuclear charge

(a) The unshielded positive charge of the nucleus. (b) The negative charge of the core electrons shields much of the nuclear charge. (c) The nuclear charge experienced by the outermost electrons is greatly reduced because it is shielded by both the core electrons and the other valence electrons.

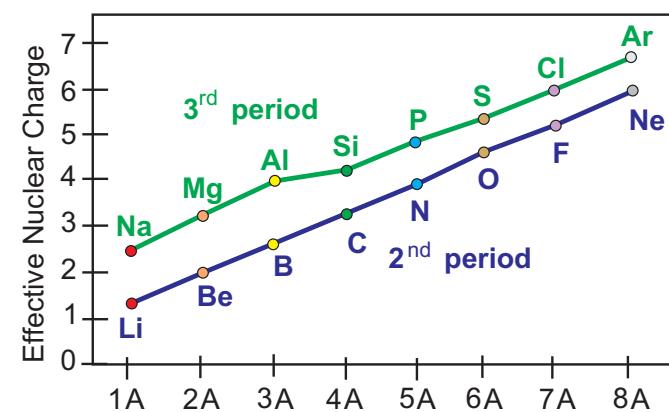


Figure 3.2 Effective nuclear charge

The effective nuclear charge experienced by the outermost electrons of the second and third period elements.

3.3 RELATIVE SIZES OF ATOMS

The size of an atom is represented by the size of its outermost (valence) shell, but electrons clouds are not hard spheres with well-defined boundaries, so the term “atomic radius” is somewhat vague. As a result, there are several definitions of the atomic radius, which are inferred from the distances between atoms in molecules or metals. Although these distances can be readily determined with several techniques, their determination requires knowledge of chemical bonding and the solid state. Consequently, we postpone a detailed discussion of atomic radii until Chapter 8. However, knowledge of *relative* atomic size will aid our discussion in future chapters, so we now apply our knowledge of the Bohr model, quantum theory, and effective nuclear charge to determine qualitative trends in atomic sizes. Although the idea of a fixed radius given in the Bohr model is incorrect, the Bohr equation for the radius (Equation 2.4) does reflect the appropriate terms. Thus, we will assume that $r_n \propto \frac{n^2}{Z_{\text{eff}}}$, so the size of an atom depends upon two factors:

- **n quantum number:** The average distance between an electron and the nucleus increases with its principle quantum number. The n quantum number of the valence electrons is constant within a period, but it increases in going down a group. We conclude that the sizes of the atoms increase in going down a group due to an increase in their n quantum number.
- **Z_{eff} :** An electron cloud is contracted by high effective nuclear charge, so increases in Z_{eff} result in smaller atomic radii. Z_{eff} increases in going across a period, so we conclude that the sizes of the atoms decrease in going left to right in a period due to an increase in Z_{eff} .

Rb (large n, low Z_{eff}) is a very large atom, while F (low n, high Z_{eff}) is very small. Figure 3.3 shows the relative atomic sizes of the main group elements.

3.4 ORBITAL ENERGY

Two important properties of an atom that are discussed in the following sections are the ease with which it gains and loses electrons. However, both depend upon the energy of the orbital from which it is removed or added, so we begin our discussion with a treatment of relative orbital energies.

The Bohr equation for the energy of an electron (Equation 2.5) does not apply to multi-electron atoms because it neglects interactions between electrons. However, it can provide insight into trends in atomic properties if the effective nuclear charge is used instead of the atomic number. Therefore, we use Equation 3.2 in our discussion.

$$E_x \propto -\frac{Z_{\text{eff}}^2}{n^2} \quad \text{Eq 3.2}$$

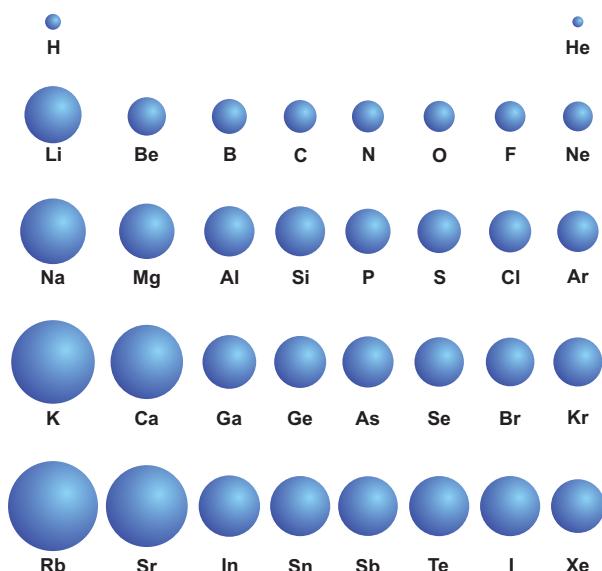


Figure 3.3 Relative sizes of the atoms of the main group elements

* As shown in Figure 3.3, Z_{eff} also changes within a group, but the differences in the properties of the elements within a group are dominated by the differences in the n quantum number.

E_x is the energy of a valence orbital on atom X, and n is the n quantum number of its valence shell. Equation 3.2 is only a very rough approximation and will be used only to order the orbital energies not to determine what the energies are. We begin by ordering the valence orbital energies of the following elements of the second period. They are in the second period, so n = 2, and Z_{eff} , which is obtained from Figure 3.2, is given in parenthesis after each element. Li (1.3), C (3.3), O (4.6), and F (5.2). Equation 3.2 produces the following: $E_{\text{Li}} \propto -0.4$; $E_{\text{C}} \propto -2.7$; $E_{\text{O}} \propto -5.3$, and $E_{\text{F}} \propto -6.8$. Based on these numbers, we conclude that the 2s orbital of lithium is the highest energy (least negative) orbital of the four, while the 2p orbitals of carbon, oxygen, and fluorine follow in order. These four atoms demonstrate one important rule:

Orbital energies decrease going across a period because the effective nuclear charge increases while the n quantum number of the valence electrons is unchanged.

Example 3.1

- a) Use Equation 3.2 and Figure 3.2 to determine the relative energies of the third period elements silicon, sulfur, and chlorine.

n = 3 for all four atoms, and Figure 3.2 shows that $Z_{\text{eff}} = 4.3$ for Si, 5.5 for S, and 6.1 for Cl. Substitution into Equation 3.2 yields $E_{\text{Si}} \propto -2.1$, $E_{\text{S}} \propto -3.4$, and $E_{\text{Cl}} \propto -4.1$. The 3p orbital of silicon is the highest and the 3p orbital of Cl is the lowest in energy of the three.

- b) What is E_{H} , the relative position of the hydrogen orbital?

Hydrogen is a one-electron atom, so Equation 2.5 can be used: $E_{\text{H}} \propto -(1^2/1^2) = -1$.

- c) Draw an energy diagram that shows the relative energies of the valence orbitals of the seven elements discussed thus far.

E_{Li} is the least negative, so the 2s valence orbital of Li is the highest energy orbital considered. Hydrogen follows with $E_{\text{H}} \propto -1.0$. Arranging the other elements in descending order, we arrive at Figure 3.4, which shows the relative orbital energies. Note that the orbital energy of hydrogen is higher than the other nonmetals, but it is lower than the metals. The fact that the valence orbital of H lies between those of the metals and the nonmetals is an important one that we will use in several of the later chapters.

Comparing the results of Equation 3.2 for the second and third periods, we note that the 3p orbital of sulfur is higher in energy than the 2p orbital of oxygen even though the effective nuclear charge experienced by the electrons is greater in sulfur. Similar conclusions can be drawn from comparisons of carbon and silicon and from fluorine and

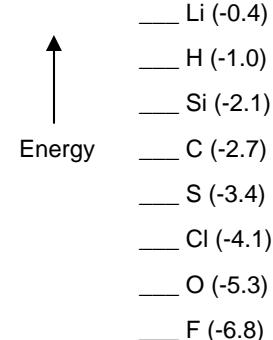


Figure 3.4 Relative valence orbital energies
Numbers in parentheses are $-Z_{\text{eff}}^2/n^2$.

chlorine. We conclude the following important rule

Orbital energies increase (become less negative) going down a group due to increases in the n quantum number even though the effective nuclear charge also increases slightly.

The energies of the valence orbitals of all atoms lie in a relatively narrow range due to the periodicity in Z_{eff} and an increasing n quantum number. Core electrons, on the other hand, continue to drop in energy as the number of protons increases because they are not shielded very efficiently by the valence electrons. Thus, the valence 2p orbitals of oxygen are at lower energy than the valence 3p valence orbitals on sulfur because valence orbital energies increase going down a group, but the 2p electrons in oxygen are much higher in energy than the 2p electrons on sulfur because sulfur has 16 protons while oxygen has only eight.

Example 3.2

Select the orbital at lower energy in each pair.

... the 2p orbital on N or the 2s orbital on N

$n+l$ is less for a 2s than for a 2p, so the 2s orbital is lower in energy. The reason is that s orbitals have no nodal planes, while p orbitals have one. Consequently, the s electrons screen the p electrons better than the p electrons screen the s.

... the 2p orbital on Br or the 2p orbital on F

$n = 2$ for both orbitals, but Z_{eff} is much greater in the vicinity of the 35 protons of a Br atom than around the nine protons of a F atom. Using Equation 3.2 and the relative magnitudes of Z_{eff} , we conclude that the 2p orbital of Br is much lower in energy. The 2p electrons in Br are core electrons, while those in F are valence electrons, and core electrons are always lower in energy than valence electrons.*

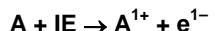
... the 2p orbital on N or the 2p orbital on O

$n = 2$ for both orbitals, but Z_{eff} increases in going from left to right in a period, so it is greater for O than for N. Thus, the 2p orbital on O is lower in energy because electrons in an O orbital experience a greater effective nuclear charge.

* The valence 2p electrons of F are lower in energy than the valence 4p electrons of Br due to the difference between the n quantum numbers and the number of shielding electrons.

3.5 IONIZATION ENERGY

Ionization energy (IE) is the energy required to remove the outermost electron from an atom or ion in the gaseous state. The process for atom A is described by the following:



The ionization energy is a measure of how tightly the electron is bound to the atom, so it measures essentially the same thing as does the orbital energy. We conclude that

The ionization energy is approximately equal to the negative of the orbital energy of the removed electron.

Thus, trends in ionization energies should be similar to those for orbital energies given in the previous section. Consider the cases for Li, C, O, and F shown in Figure 3.5. The order of their ionization energies is the same as that for their orbital energies given in Figure 3.4. Li is a 1A metal with a low Z_{eff} and a relatively high valence orbital energy, so it has a relatively low ionization energy of 520 kJ/mol. This places the energy of the 2s orbital in lithium at about -520 kJ/mol. Metals are characterized by low ionization energies, which means that they lose their valence electrons relatively easily, which is why they corrode. Oxygen and fluorine are nonmetals with high Z_{eff} , so their 2p orbitals are very low in energy, and their ionization energies are quite high. Indeed, the ionization energy of a fluorine atom, 1681 kJ/mol, is the highest ionization energy of any atom other than the noble gases. The energy of the 2p orbital in fluorine is approximately -1681 kJ/mol, which is the lowest energy valence orbital of any atom. Carbon lies between Li and O in the periodic table and in Figure 3.4, and its ionization energy also lies between those of Li and O.

Example 3.3

Use the relative orbital energies given in Figure 3.4 to order the ionization energies of silicon, sulfur, and chlorine.

The valence orbitals of silicon are higher than those of sulfur and chlorine, which means that the electrons are not bound as tightly. Therefore, the ionization energy of silicon is the lowest. The valence orbitals of chlorine are the lowest of the three, so they are bound most tightly. Consequently, chlorine has the highest ionization energy. We conclude that $IE_{\text{Si}} < IE_{\text{S}} < IE_{\text{Cl}}$. The observed ionization energies are 786, 999, and 1256 kJ·mol⁻¹, respectively. Comparing these values with those of C, O, and F, we conclude that ionization energies decrease in going down a group.

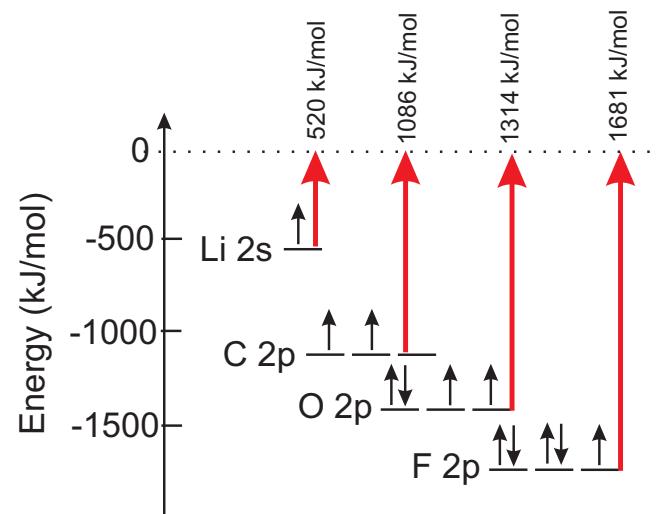


Figure 3.5 Ionization energy and orbital energy

The ionization energy is approximately equal to the negative of the orbital energy. The ionization energies of Li, C, O, and F are 520, 1086, 1314, and 1681 kJ/mol, respectively.

Figure 3.6 shows the periodic trend in ionization energies of the main group elements. Note that the rise in the ionization energies from left to right within a period follows that of the effective nuclear charge, while the steady decrease within a group is due to an increase in the n quantum number. In general,

Metals have low ionization energies because they have low effective nuclear charges. Consequently, they readily lose valence electrons to form cations. Nonmetals have high ionization energies, so they do not form cations in chemical processes.

Electron configurations in which sublevels are filled (Groups 2A and 8A) or half-filled (Group 5A) are unusually stable, so removing an electron from these elements is more difficult and results in deviations from the expected periodicity. For example, the effective nuclear charge of B is greater than that of Be, but the ionization energy of Be is greater than that of B because the electron must be removed from a filled 2s sublevel in Be. Similarly, the ionization energy of N is greater than that of O because the 2p sublevel of N is half-filled.

3.6 ELECTRONEGATIVITY

Electronegativity (χ) is a measure of an atom's ability to attract bonding electrons, so electron density in a bond accumulates near those atoms with higher electronegativities. Bonding electrons reside in orbitals involving the valence orbitals of the atoms, especially those that are unfilled, and electrons seek to minimize their energy, so an atom that is highly electronegative is simply one whose valence orbitals, especially those that are unfilled, are low in energy. $E_n \propto -(Z_{\text{eff}})^2/n^2$, so atoms with large Z_{eff} (nonmetals) and valence orbitals with low n quantum numbers have high electronegativities.

Electronegativity depends upon the energy of the valence orbitals. It increases as the energy of the valence orbitals decreases.

Consider the orbital energies of Li, C, and F shown in Figure 3.7. Li is a metal with a low Z_{eff} , so its orbital energy is high. The electron in it is readily lost (low ionization energy), but bonding electrons are not drawn to the high-energy orbital, so Li has a very low electronegativity. F is a nonmetal with a high Z_{eff} , so its orbital energy is low. Thus, it is very difficult to remove a 2p electron from F (high ionization energy), but bonding electrons are drawn to the low energy unfilled orbital, so F is highly electronegative. The 2p orbital energy of C is about half way between the valence orbital energies of Li and F, and its electronegativity is also about half way between these two extremes in the period.

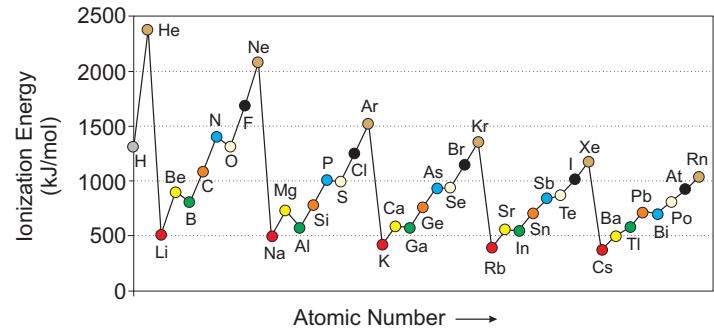


Figure 3.6 Ionization energies of the main group elements

Circles of the same color are used for elements in the same group.

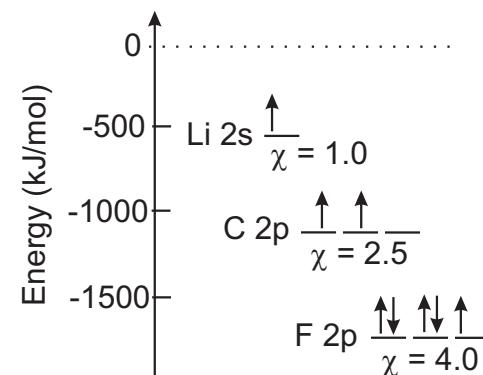


Figure 3.7 Electronegativity and orbital energy

Electronegativities of Li, C, and F. Atoms with lower energy valence orbitals have higher electronegativities.

Example 3.4

- a) Use the relative orbital energies given in Figure 3.4 to order the electronegativities of silicon, sulfur, and chlorine.

Silicon has the highest energy valence orbitals of the three, so it is the least electronegative, while the valence orbitals of chlorine are the lowest in energy, so Cl is the most electronegative: $\chi_{\text{Si}} < \chi_{\text{S}} < \chi_{\text{Cl}}$. Orbital energies increase going down a group, so we also predict the following: $\chi_{\text{Si}} < \chi_{\text{C}}; \chi_{\text{S}} < \chi_{\text{O}}; \chi_{\text{Cl}} < \chi_{\text{F}}$.

- b) Use Figure 3.4 to predict which is more electronegative, oxygen or chlorine.

The valence orbitals of oxygen are lower than those of chlorine, so oxygen is more electronegative.

The periodic behavior of electronegativity is shown in Figure 3.8. Electronegativity increases left to right in a period due to an increase in effective nuclear charge and decreases going down a group due to an increase in the n quantum number. Consequently, fluorine (high Z_{eff} and low n) is the most electronegative atom, while cesium (low Z_{eff} and high n) is the least electronegative element shown in Figure 3.8. In summary,

Nonmetals have high electronegativities, so they tend to gain electrons to form anions, but metals have low electronegativities, so they do not gain electrons to become anions.

An exception to the above generality about the electronegativities of metals arises from the fact that d and f electrons do not shield very well because they contain two and three nodal planes, respectively. Therefore, the effective nuclear charge experienced by the valence orbitals in late metals (metals that lie on the right side of the Periodic Table) can be quite large. For example, Pb has 27 more protons and electrons than does Cs, but 24 of those electrons are d and f electrons, which do not shield the 27 additional protons very well. Thus, the 6p electrons in Tl and Pb experience relatively high Z_{eff} (12.25 and 12.39, respectively), which makes both of these metals fairly electronegative. Indeed, the electronegativity of Pb is much greater than that of Si even though they are in the same Group, and the valence orbitals in Pb have a much higher n quantum number. We conclude that *due to their high effective nuclear charges, late metals have unusually high electronegativities (Table 3.2), which impacts significantly on their chemical properties*.

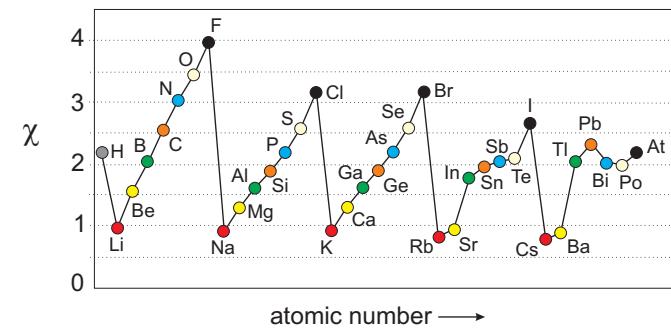


Figure 3.8 Electronegativities (χ) of main group elements

Elements within the same group are identified by circles with the same color.

Table 3.2 Electronegativities of some late metals*

Metal	Electronegativity
Ag	1.9
Sn	2.0
Hg	2.0
Tl	2.0
Pb	2.3

* Late metals, such as those listed in Table 3.2, are those that lie on the right side of the periodic table. Early metals, such as the Group 1A and 2A metals, lie on the left side of the table.

Example 3.5

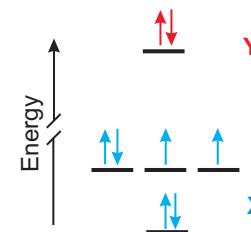
Use the energy level diagram for the valence orbitals of atoms X and Y in the margin to answer the following:

a) Which atom has the lower ionization energy?

The atom with the lower ionization energy is the one with the higher energy electrons. The two electrons on atom Y are at higher energy, which means that they are not attracted to the nucleus as strongly. Thus, atom Y has the lower ionization energy.

b) Which atom is more electronegative?

The more electronegative atom is the one whose valence orbitals are at lower energy. The valence orbitals on Atom X are much lower in energy than those on atom Y, so atom X is much more electronegative than atom Y.

**Example 3.5****3.7 MAGNETIC PROPERTIES**

Magnetic phenomena have been known since ancient times. For example, early Chinese, Greeks and Romans knew that the mineral lodestone or magnetite, Fe_3O_4 , has the property of attracting other iron particles. When lodestone is rubbed against a piece of iron, the iron acquires a similar ability to attract other magnetized materials. The magnets produced in this manner have two ends, the north (N) and south (S) poles. Furthermore, like-poles (N-N and S-S) repel one another, and unlike-poles (N-S) attract. Thus, by the 13th century, magnets were used to make directional compasses, which interacted with the earth's magnetic field.

In 1819, the Danish physicist Hans Christian Oersted found that a magnetic needle is deflected by an electric current flowing through a wire. In 1831, the English scientist Michael Faraday showed that electricity and magnetism were related when he discovered that moving a magnet near a wire induced an electric current in that wire.

In the 20th century, investigations on magnetism turned toward an understanding of its origins at an atomic-level. The origin of magnetism became apparent in the work of two American physicists, Samuel Goudsmit and George Uhlenbeck, who showed that the electron itself had *spin*, and the spinning electron behaved like a magnet (Section 2.5). Indeed, *all magnetic properties are due to the magnetic fields caused by spinning electrons*. However, no magnetic field is generated by paired electrons because the two different electron spins are opposed and their magnetic fields cancel. Consequently, *the magnetic properties of an atom are due solely to its unpaired electrons*. There are two

magnetic classifications for atoms:

1. **Paramagnetic atoms** have unpaired electrons and are attracted by an applied magnetic field. The attraction is due to the interaction of the magnetic fields of the unpaired electrons with the applied magnetic field. *The greater the number of unpaired electrons, the more paramagnetic is the atom.*
2. **Diamagnetic atoms** have no unpaired electrons and are not attracted by an applied magnetic field.*

Although *magnetism is the result of unpaired electrons, it is a bulk property of the material*; that is, magnetism is a property of large groups of atoms rather than individual atoms. It is important to realize that individual atoms typically occur only as gases because they interact with one another in the solid state so strongly that they lose their atomic identity and become part of a material. Thus, carbon is a paramagnetic atom with two unpaired electrons (valence electron configuration: $2s^22p^2$), but graphite and diamond, the common forms of elemental carbon, are diamagnetic because of the manner in which the carbon atoms interact in the solid. Iron atoms are also paramagnetic with four unpaired electrons ($4s^23d^6$), and they interact with one another in the solid. However, some of the unpaired electrons in iron align over many iron atoms to make iron a *magnetic material*. We discuss magnetic materials in more detail in Chapter 14.

* Diamagnetic atoms are actually repelled slightly by an applied field, but the reasons for the repulsion are beyond the scope of this discussion.

3.8 CHAPTER SUMMARY AND OBJECTIVES

Valence electrons and orbitals, which are those in the outermost s sublevel and any unfilled sublevels, are involved in bonding and determine the chemical properties of the element. Indeed, the periodicity of chemical properties is a result of the periodicity of valence electron configurations. The size and energy of a valence orbital both depend upon the n quantum number and the nuclear charge that it experiences, which is called the effective nuclear charge. The effective nuclear charge increases in going from left to right in the periodic table, while the n quantum number increases in going down a group. Thus, atoms that lie on the right side of the periodic table (nonmetals) at the top of their groups have low energy valence orbitals that are closer to the nucleus, while atoms on the left side (metals) and at the bottom of their group have high energy electrons that are far from the nucleus. Ionization energy is the energy that is required to remove an electron, so atoms on the left side of the periodic table (metals) have low ionization energies and lose their valence electrons easily. Electronegativity is a measure of an atom's ability to attract bonding electrons. Atoms with unfilled orbitals at low energy are highly electronegative,

so nonmetals have high electronegativities because they have high effective nuclear charges. The trends in atomic size, ionization energies, and electronegativities are summarized in Figure 3.9. Paramagnetic atoms are attracted by magnetic fields because they have unpaired electrons. In contrast, diamagnetic atoms are not attracted by magnetic fields because all of their electrons are paired.

After studying the material presented in this chapter, you should be able to:

1. distinguish between valence and core electrons (Section 3.1);
2. determine the number of valence electrons present in an atom (Section 3.1);
3. predict valence electron configurations (Section 3.1);
4. explain shielding and effective nuclear charge (Section 3.2);
5. predict trends in atomic radii from the periodic table (Section 3.3);
6. predict relative valence orbital energies of atoms (Section 3.4)
7. define ionization energy and predict trends in it from the periodic table (Section 3.5);
8. define electronegativity and predict trends in it from the periodic table (Section 3.6); and
9. predict whether an atom is paramagnetic or diamagnetic (Section 3.7).

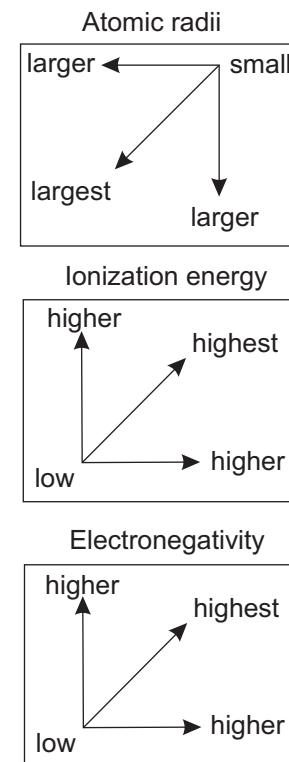


Figure 3.9 Periodic trends in the labeled properties

Arrows indicate direction in the periodic table of increasing atomic radii, ionization energy, and electronegativity.

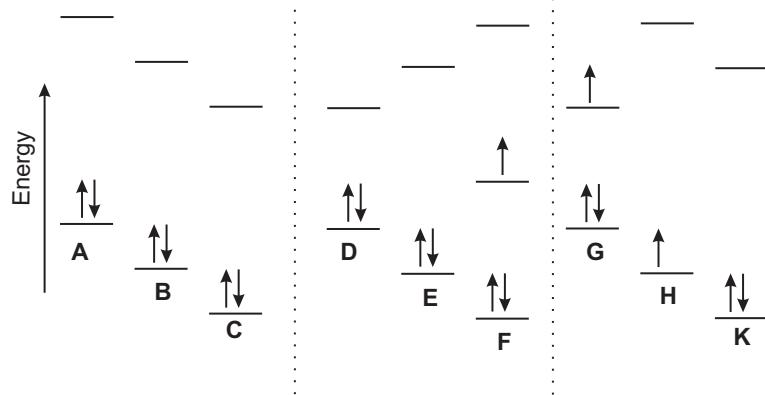
3.9 EXERCISES

1. Write valence electron configurations for each of the following:
a) carbon b) cobalt c) chlorine d) magnesium
2. Write valence electron configurations for each of the following:
a) copper b) calcium c) sulfur d) phosphorus
3. Which electron experiences the greater nuclear charge? Explain your reasoning in each case.
 - a) a 5p electron of In or a 5p electron of Sb?
 - b) a 5s electron of Sn or a 5p electron of Sn?
4. Which orbital is at *higher* energy? Explain your reasoning in each case.
 - a) a 4p orbital of Se or a 3d orbital of Se
 - b) a 3s orbital of S or a 3s orbital of Se
 - c) a 2p orbital of C or a 2p orbital of O
5. Use ionization energies to explain why +4 ions are very rare.
6. Use only the Periodic Table to order the elements in each of the following groups by increasing atomic radius.
a) N, F, B b) Ge, Pb, Sn c) K, Na, Li d) As, Sn, S
7. Use only the Periodic Table to order the elements in each of the following groups by decreasing atomic radius.
a) Na, K, Cl b) Al, C, B c) C, Ge, Sn d) Cs, Zn, O
8. Order the elements in each group of Exercise 6 by increasing first ionization energy.
9. Order the elements in each group of Exercise 7 by decreasing first ionization energy.
10. Order the elements in each group of Exercise 6 by increasing electronegativity.
11. Order the elements in each group of Exercise 7 by decreasing electronegativity.
12. Which is the *largest* atom in each of the following groups?
a) C, N, P, S b) N, O, F c) F, Cl, Br

13. Which is the *most electronegative* atom in each of the following groups?

- a) N, O, P b) O, S, Se c) Si, P, S

Refer to the following diagrams showing the highest energy electrons and lowest energy empty orbitals of some atoms to answer Exercises 14-16



Exercise 14

Exercise 15

Exercise 16

14. For atoms A, B, and C,

- a) list the atoms in order of increasing ionization energy,
- b) list the atoms in order of decreasing electronegativity, and
- c) identify each atom as either paramagnetic or diamagnetic.

15. For atoms D, E and F,

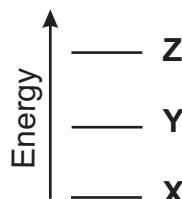
- a) list the atoms in order of increasing ionization energy,
- b) list the atoms in order of decreasing electronegativity, and
- d) identify each atom as either paramagnetic or diamagnetic.

16. For atoms G, H and K,

- a) list the atoms in order of increasing ionization energy,
- b) list the atoms in order of decreasing electronegativity, and
- e) identify each atom as either paramagnetic or diamagnetic.

17. The relative energies of the highest occupied orbitals of H, Li, and F are given to the right.

- Identify each atom as X, Y, or Z.
- Where would the energies of the 3p orbital of Cl and the 4s orbital of K be placed? (Below X, between X and Y, between Y and Z, or above Z)



18. How many of the electrons in each of the following are core electrons and how many are valence electrons?

- Na
- Xe
- S
- Ga

19. Use Equation 3.2 to explain why first ionization energies decrease going down a group and why electronegativities increase going from left to right in a period.

20. The first ionization energy of magnesium is 738 kJ/mol; its second ionization energy is 1451 kJ/mol; and its third ionization energy is 7733 kJ/mol.

- Write the chemical equations for the processes to which these numbers apply.
- Why is the second ionization energy so much greater than the first?
- Suggest a reason why the third ionization energy is over five times greater than the second, but the second is less than twice the first.

21. Use the following effective nuclear charges experienced by the outermost electrons to order their outermost orbitals from lowest to highest energy:

Element	P	Al	Br	Pb
Z _{eff}	4.89	4.07	9.03	12.39

22. Given the following n quantum numbers of the valence shells, and the effective nuclear charges experienced by their valence electrons:

Element	A	B	C
n	2	4	5
Z _{eff}	3.1	3.5	11.6

Arrange the elements in increasing electronegativity and size. The elements belong to Groups 1A, 4A, and 7A. To which group does each element belong?

23. Use Equation 3.2 to determine where in Figure 3.4 the energy of the valence orbitals of nitrogen ($Z_{\text{eff}} = 3.9$) would be found? Is the location consistent with its electronegativity of 3.04? ... with its ionization energy of 1402 kJ/mol? If not, explain why.

24. Use Equation 3.2 to determine where in Figure 3.4 the energy of the valence orbitals of boron ($Z_{\text{eff}} = 2.6$) would be found. Is the location consistent with its electronegativity of 2.04 and its ionization energy of 800 kJ/mol? If not, explain why.

Chapter 4

The Ionic Bond

- 4.0 Introduction
- 4.1 Ionic Bonding
- 4.2 Naming and Predicting Ions
- 4.3 Relative Sizes of Ions
- 4.4 Oxidation States

- 4.5 Polyatomic Ions
- 4.6 Naming Ionic Compounds
- 4.7 Structure of Ionic Compounds
- 4.8 Chapter Summary and Objectives
- 4.9 Exercises

4.0 INTRODUCTION

The valence electrons in metals are at relatively high potential energies, so metals have low ionization energies, while the unfilled valence orbitals in nonmetals are at relatively low potential energies, so nonmetals have high electronegativities. Electrons seek to lower their potential energy whenever possible, so when metal atoms combine with nonmetal atoms, the high-energy valence electrons of the metal are *transferred* to the low-energy orbitals of the nonmetal. The result is that the metal becomes a cation and the nonmetal becomes an anion. The oppositely charged ions are held together by an electrostatic force called an **ionic bond**, and the compounds between metals and nonmetals are called **ionic compounds**. Ionic compounds are not molecular because each cation in an ionic solid is surrounded by a number of anions, none of which is uniquely associated with the cation. The situation is quite different in the bonds between two nonmetals because the energy difference between the valence orbitals of two nonmetals is relatively small. Thus, when nonmetals bond to one another, the valence electrons are *shared* rather than transferred. The resulting bond is known as a **covalent bond**, and compounds composed only of nonmetals are called **covalent*** or **molecular**, as individual molecules are readily identified. The properties of ionic and molecular substances are quite different. In this chapter, we discuss the ionic bond and ionic compounds. The covalent bond and molecular compounds will be discussed in Chapters 5 and 6.

THE OBJECTIVES OF CHAPTER 4 ARE TO:

- discuss the properties of ions;
- define oxidation states and show how they are determined in ions and molecules;
- demonstrate how to name ionic compounds;
- explain how to predict the formulas of binary ionic compounds; and
- explain why ionic compounds are not molecular.

* Although covalent compounds are not discussed until the next chapter, we define them here so that we can compare ionic compounds to them in this chapter.

4.1 IONIC BONDING

The valence electrons in metals are at relatively high energy, so they have low ionization energies and lose their valence electrons readily. The unfilled valence orbitals in nonmetals are at relatively low energy, so they have high electronegativities and gain electrons easily. When a metal atom comes into contact with a nonmetal atom, the valence electrons of the metal are *transferred* to the low-energy orbitals of the nonmetal to produce a cation and an anion. The oppositely charged ions are then held together by an electrostatic force called an **ionic bond**, and the compound that forms is an **ionic compound**. Figure 4.1 considers the case of NaCl. When a sodium atom binds to a chlorine atom, the high-energy electron on sodium transfers to the low-energy orbital on chlorine. The loss of an electron by Na produces the Na^{1+} cation, and the gain of an electron by Cl produces the Cl^{1-} anion. In order for a bond to be ionic, the valence orbital of the cation must be very high in energy, but only metals have high-energy valence orbitals, so a good aid in identifying ionic compounds is that *ionic compounds almost always contain a metal**.

Some metals, such as Cu, Ag, Au, and Pt are not reactive in their elemental form, but most metals react with oxygen in the atmosphere and are found as their oxides. The metals of Group 1A are so reactive that they must be stored in oil to keep them away from oxygen and water. Sodium is a common element, but it is found in nature only as the Na^{1+} ion as in NaCl. Na metal must be prepared from its ion. Thus, most reactions involving metals, involve their ions, not the atoms, but ions and atoms are very different. For example, Na is a highly reactive solid, but Na^{1+} is an inert ion that cannot be isolated without a counterion.[†] The properties of Na and Na^{1+} are more different than are those of Na and K, which have similar physical properties and almost identical chemical properties! Na and Na^{1+} are totally different species, so *it is imperative that the charge on an ion be included whenever the ion is written alone*. Thus, we write the dissociation of sodium chloride into its ions as $\text{NaCl} \rightarrow \text{Na}^{1+} + \text{Cl}^{1-}$.

Example 4.1

Which of the following are ionic? CaCl_2 , SF_2 , KCl , CCl_4 , Na_2O , F_2O , N_2O_3 , FeCl_3

Ionic substances contain a metal and a nonmetal. Only CaCl_2 , KCl , Na_2O , and FeCl_3 contain metals, so only they are ionic. As discussed in the Chapter Introduction, bonds between nonmetals are covalent and their compounds are molecular. Thus, SF_2 , CCl_4 , F_2O , and N_2O_3 are molecular because they contain only nonmetals.

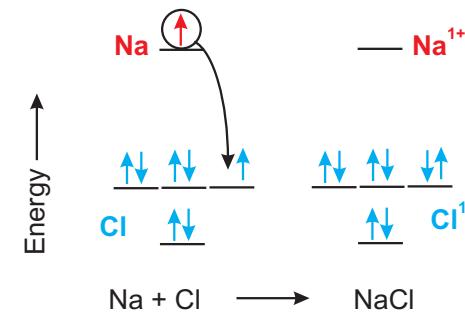


Figure 4.1 Electron transfer and ionic bonding

Na transfers an electron to Cl to produce Na^{1+} and Cl^{1-} ions. Coulombic attraction between the oppositely charged ions produces NaCl.

* We will see later in the chapter that there are also polyatomic cations that form ionic compounds. The ammonium ion (NH_4^{1+}) is the only such ion treated in this text.

[†] Cations and anions are charged species, but only neutral materials can be isolated. Therefore, cations must always be accompanied by anions and *vice versa*. That is, each ion must be accompanied by a counterion. Cl^{1-} is the counterion of Na^{1+} in NaCl.

4.2 NAMING IONS AND PREDICTING THEIR CHARGE

Anions: Filled sublevels are more stable than partially filled sublevels, so atoms react with one another to reduce the number of partially filled sublevels. Nonmetals tend to gain electrons, so they add electrons to fill their valence shell, which requires 8 electrons (ns^2 np^6) for a nonmetal. The number of valence electrons in a nonmetal atom equals its group number, so the number of electrons required to fill the valence shell is $(8 - \text{Group Number})$. Each added electron carries a charge of -1, so the charge on an anion equals the number of electrons added times -1. The resulting anion is named by replacing the ending of the atom's name with *-ide*. Oxygen is a Group 6A nonmetal and therefore gains $(8 - 6) = 2$ electrons to acquire a -2 charge, so the *oxide* ion is O^{2-} . Nitrogen, a Group 5A nonmetal, gains three electrons to form the *nitride* ion, N^{3-} . Monatomic anions^{*} are isoelectronic[†] with the next noble gas, so their electron configurations are all [noble gas].

Example 4.2

What is the charge on the anions formed by the halogens? What is the name of the ion formed from Cl, and what is its electron configuration?

The halogens are the elements in Group 7A, so they gain $(8 - 7) = 1$ electron to form -1 ions. Cl^{1-} is the chloride ion. It is isoelectronic with argon, so its configuration is [Ar].

Cations: Metals tend to lose electrons, so they eliminate partially filled sublevels by emptying them to produce cations. The charge on a cation equals the number of electrons lost, and the name of the cation is the same as the name of the atom. There are two rules that determine which electrons are lost.

1. The valence electrons with the highest *n* quantum number are lost first.
2. When the valence electrons are in more than one sublevel within the same level, the electrons in the highest *l* sublevel are lost first.

The first rule means that the transition metals lose the outermost s electrons before they lose any d electrons, so the order in which the electrons are removed is not simply the reverse of the filling order. This is due to the fact that the energies of the 4s and 3d orbitals in an atom are very similar, and the changes in the environment of the valence electrons that result when a metal atom becomes an ion are sufficient to reverse the order of their energy. Thus, *most* transition elements readily form a +2 ion by losing their ns^2 electrons. The second rule applies to the heavy elements in the p block that lose the np electrons before the ns electrons. Tl, $6s^2 6p^1$, forms a +1 ion by losing its 6p electron first and a +3

* Monatomic ions are ions that consist of only one atom. For example, O^{2-} is a monatomic ion but O_2^{2-} and NO_3^{1-} are polyatomic ions.

† Isoelectronic means having the same electron configuration. Two species with the same number of electrons are isoelectronic.

ion by also losing its two 6s electrons. Tl does not form a +2 ion because that would require the loss of the 6s electrons prior to the loss of the 6p electron.

The charge on cations of Group 1A and Group 2A metals equals their group number. The elements of Groups 3A and 3B form +3 ions, but In and Tl also form +1 ions by emptying their valence p sublevel. Most transition metals form +2 ions, but several form +3 ions as well, and a few form +1 ions. Successive ionization energies* get very large because the effective nuclear charge experienced by the remaining electrons gets high, so monatomic cations with charges greater than +3 do not form. Similarly, adding electrons to an atom gets progressively more difficult as each electron reduces Z_{eff} and the electronegativity of the atom. Consequently, monatomic anions do not attain charges more negative than -3. Thus, carbon, a small Group 4A element, does not form isolated ions because a charge of +4 or -4 would be too great. However, the heavier Group 4A elements, Sn and Pb, do form +2 ions by losing only their p valence electrons.

Example 4.3

What is the charge on a zinc ion? What is its electron configuration? Is it expected to form more than one ion?

The 3d shell of zinc is full, so the only electrons that can be lost are the 4s. Consequently, zinc forms only the Zn^{2+} ion, which has an electron configuration of $[\text{Ar}] 3\text{d}^{10}$.

4.3 RELATIVE SIZES OF IONS

Like the size of an atom (Section 3.3), the size of an ion is determined by the n quantum number of the outermost electron and by the effective nuclear charge experienced by the outermost electrons. Remember that Dalton's billiard ball model is not an ideal way to view atoms and ions because they are not hard spheres. When we refer to the size of an atom or an ion, we are referring to the size of an electron cloud that does not have a sharp boundary. Thus, the size of an atom or an ion depends upon its environment and tables often differ on the sizes. The *relative* sizes of some atoms and their ions are shown in Figure 4.2. Ionic radii will be discussed in more detail in Section 8.7.

Cations are smaller than their parent atoms (Figure 4.2). One of the factors dictating the size of an atom or an ion is the n quantum number of the outermost electrons. In cations of most main group metals, the n quantum number of the outermost electrons is

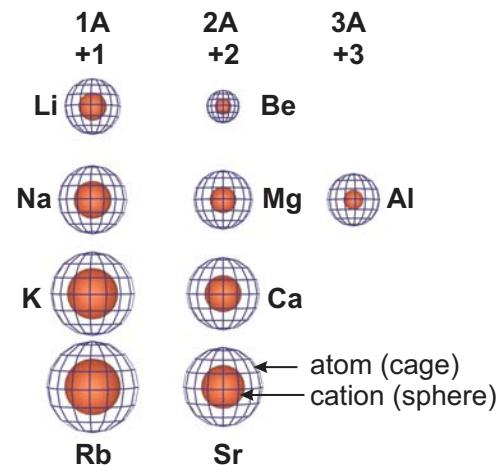
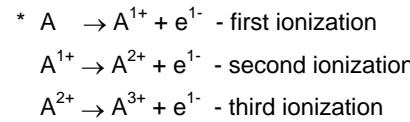


Figure 4.2 Relative sizes of metal atoms and their cations
The charge on each cation is given at the top of the column.

lowered by one because the outermost electrons of the atom are lost in forming the ion. This loss of the outermost shell makes the cation much smaller than the corresponding atom. In addition, the decrease in the number of electrons decreases the shielding experienced by the remaining electrons and increases Z_{eff} . The increased effective nuclear charge contracts the outer shell even further.

Anions are larger than their parent atoms (Figure 4.3). Anions have more electrons than protons; thus, the valence electrons are more effectively shielded from the positive charge of the nucleus, which decreases Z_{eff} . This decrease in effective nuclear charge causes the outer electron shell to expand. As the negative charge increases, the effective nuclear charge decreases and the size of the anion increases. Consequently, N^{3-} is larger than O^{2-} , which is larger than the F^{-} .

Example 4.4

Arrange the following in order of increasing size: S^{2-} , Ar , and Ca^{2+} .

Ar , S^{2-} and Ca^{2+} each have 18 electrons, so the screening is the same. Therefore, increasing the number of protons increases Z_{eff} and decreases the size.

Ca^{2+} (20 protons) < Ar (18 protons) < S^{2-} (16 protons).

Note that this order is different from that of atomic size. Calcium atoms are the largest because they have the highest n quantum number and the smallest effective nuclear charge. Sulfur is larger than argon because its effective nuclear charge is less. Thus, the order of atomic sizes is $\text{Ar} < \text{S} < \text{Ca}$.

4.4 OXIDATION STATES

The **oxidation state** (or **oxidation number**) of an atom is the charge it would have if its bonds were ionic. In ionic compounds, the oxidation state of an ion is the charge on the ion. For example, the oxidation states of sodium and chlorine in NaCl are +1 and -1, respectively. However, oxidation states are also used to account for the electrons in compounds that are not ionic (compounds with no metals). In these cases, the bonds are assumed to be ionic by *assigning* all bonding electrons to the more electronegative atom (atom with lower energy orbitals). Compare Figures 4.1 and 4.4a. In both, the electron is transferred from the high-energy orbital into the low-energy orbital to produce ions. The difference is that the orbital energy of hydrogen is much lower than that of sodium, so the electron does not actually transfer in HCl ; we simply assume that it does to determine the oxidation states. If the transfer took place, the hydrogen atom would become a +1 ion, so

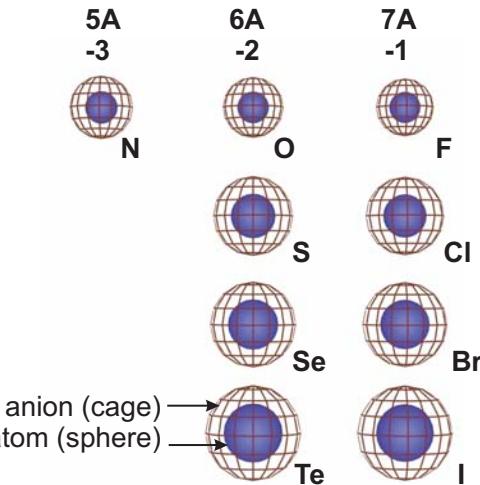


Figure 4.3 Relative sizes of nonmetal atoms and their anions
The charge on the anion is given at the top of each column.

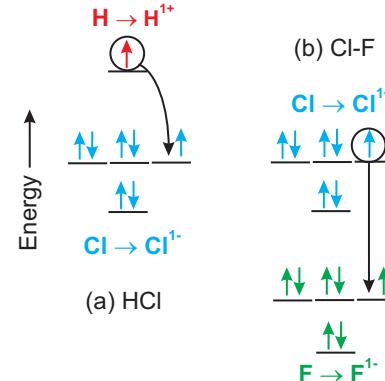


Figure 4.4 Oxidation states in H-Cl and Cl-F

(a) The valence orbitals of Cl are lower than the electron in H, so the bonding electrons would be assigned to Cl in HCl . Loss of an electron by H produces the H^{1+} ion, or a +1 oxidation state. Gain of an electron by Cl produces the Cl^{1-} , or a -1 oxidation state.

(b) The valence electrons of Cl are higher than the valence orbitals on F, so the bonding electrons would be assigned to F in ClF . Loss of an electron from Cl produces the Cl^{1+} ion, or a +1 oxidation state. Gain of an electron to F produces the F^{1-} ion, or a -1 oxidation state.

its oxidation state in HCl is +1. Similarly, the more electronegative chlorine would accept the electron to become a -1 ion, so its oxidation state in HCl is -1. In ClF (Figure 4.4b), the chlorine orbitals are above those of the more electronegative fluorine, so an electron would have to transfer from chlorine to fluorine and produce Cl^{1+} and F^{1-} ions. Thus, the oxidation states of Cl and F in ClF are +1 and -1, respectively. It is important to recognize that neither HCl nor ClF is ionic and the atoms do not have +1 or -1 charges. However, oxidation states are a convenient way to count electrons.

Atoms are assumed to lose and gain electrons when determining oxidation states just as they do when they form ions. Thus, the more electronegative element fills its sublevels, while the less electronegative element empties its sublevels.

Example 4.5

Consider the valence energy level diagrams for A, B, and C shown in the margin.

a) What are the likely oxidation states of A and B when they bond?

B is more electronegative, so it would be assigned the bonding electrons. It needs three electrons to fill its valence shell, so it would attain a -3 oxidation state. A would lose its one valence electron to empty its valence shell and attain a +1 oxidation state.

b) What are the likely oxidation states of B and C when they bond?

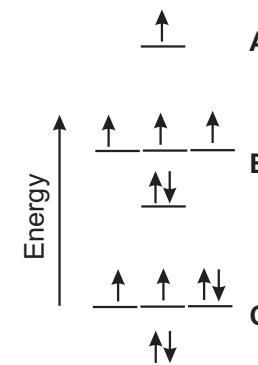
C is more electronegative than B, so B would either empty its p sublevel to become +3 or empty the entire valence shell to become +5. C would fill its valence shell by gaining two electrons to attain a -2 oxidation state.

We will use these oxidation states in Example 4.7 to determine the ratio in which the atoms must combine in their compounds.

Atoms fill or empty their valence sublevels, so the possible oxidation states of an atom can be predicted from its group number just as the charge of an ion can be predicted.

The oxidation states that can be realized by an element can range from minus the number of electrons required to fill its valence shell to plus the number of electrons that must be lost to empty its valence shell.

Chlorine is highly electronegative and is usually assigned the bonding electrons, but it is a Group 7A element, so it can only accept one electron before filling its valence shell. Therefore, Cl is usually found in the -1 oxidation state. However, both F and O are more electronegative than Cl, so the bonding electrons would be assigned to F and O, not Cl. In this situation, the chlorine atom would lose electrons to attain a positive oxidation state. It



Example 4.5

is a +1 in Cl-F and Cl₂O. The electrons in molecules and ions are usually paired, so chlorine typically loses an odd number of electrons to attain oxidation states of +1, +3, +5, and +7 as it does in the ions ClO⁻¹, ClO₂⁻¹, ClO₃⁻¹, and ClO₄⁻¹. The oxidation states of all of the elements of Group 7A range from -1 to +7. Similarly, the oxidation states of Group 6A elements can vary from -2 to +6 and those of Group 5A from -3 to +5.

Neither atom in a bond between identical elements is more electronegative, so the bonding electrons cannot be assigned to one element. Instead, half of the electrons in each bond are assigned to each atom in the bond. The result is that *the oxidation states of the atoms in an element are all zero*. Thus, chlorine has an oxidation state of zero in Cl₂.

The following guidelines are useful in predicting common oxidation states:

- The main group metals most often are in their highest oxidation state (group number). This is true because the valence electrons of main group metals are high in energy (metals have low ionization energies) and are readily transferred to nonmetals. The exceptions are the late metals: Sn, Tl, Pb, and Bi, which can lose only their p subshells or their entire valence shells.
- The most oxidation states formed by the transition metals are +2 and +3, but the following can be found in +1 oxidation states: Cu, Ag, Hg, and Au. Higher oxidation states can be achieved when the metal is surrounded by oxygen. For example, V₂O₅, CrO₄²⁻, and MnO₄⁻¹.
- Metals are *rarely* assigned negative oxidation states. This is expected because their unfilled orbital energies are quite high, which makes it unlikely that they will bond with an atom with a higher energy electron.

Many atoms have the same oxidation state in almost all of their compounds. Thus, to determine the oxidation state of an atom in a molecule or ion, you must first assign oxidation states to those atoms that tend to attain the same oxidation state in all of their compounds. *Use the following rules to determine common oxidation states. Apply them in the order given; that is, a rule at the top of the list takes precedence over any rule below it.*

Rule 1 The oxidation state of each atom in an elemental substance is zero.

Rule 2 Fluorine is -1.

Rule 3 Group 1A metals are +1, Group 2A metals are +2, and Groups 3A (except Tl*) and 3B are +3 in their compounds.

Rule 4 Hydrogen is +1.

Rule 5 Oxygen is -2.

Rule 6 Halogens are -1 except when bound to a more electronegative halogen.

* Tl can also form a +1 ion by emptying only its 6p sublevel, while the other Group 3 elements empty their entire valence shell.

Rule 1 restates our earlier conclusion that the electrons in a bond between identical atoms must be shared and cannot be assigned to one element. Some examples are Li, F₂ and P₄. **Rule 2** states that the most electronegative element (F) is always assigned the

bonding electrons. The metals listed in **Rule 3** all have low ionization energies and give up all of their outermost electrons. **Rule 4** results because the valence orbital of hydrogen is higher than most nonmetals (Figure 4.5), so its electron is assigned to nonmetals to produce the +1 oxidation state. However, its valence orbital is much lower than those of the metals in Rule 3, so the bonding electrons in metal-hydrogen bonds are assigned to hydrogen to give it a -1 oxidation state. A hydrogen atom in the -1 oxidation state is called a *hydride* ion, and CaH_2 is calcium hydride. **Rule 5** uses the fact that oxygen is the second most electronegative element, so it is assumed to gain two electrons to fill its 2p sublevel. Exceptions *can* occur in compounds with the atoms listed in Rules 1 - 4 because fluorine is more electronegative and is assigned the negative oxidation state in OF_2 , and oxygen can form both oxides and peroxides (O_2^{2-}) with the metals in Rule 3 and with hydrogen. For example, H_2O_2 is hydrogen peroxide and CaO_2 is calcium peroxide. The oxidation state of oxygen in a peroxide is -1. **Rule 6** includes the highly electronegative halogens. They are assigned the bonding electrons unless they are bound to a more electronegative element: F (Rule 1), O (Rule 5), or another more electronegative halogen. Some examples of iodine in an oxidation state other than -1 are IO_4^{1-} and IF_3 , where it is +7 and +3, respectively.

Oxidation states are used to count electrons, so *the sum of the oxidation states of all atoms must be zero in a molecule, but it must equal the charge on an ion*. The oxidation state of Ag is zero, but that of Ag^{1+} is +1.

Example 4.6

Determine the oxidation state of the underlined atom.

FeCl_3 : The sum of the oxidation states must be zero, and chlorine is a -1 ion (Rule 6), so $0 = y + (3 \text{ Cl})(-1 \text{ for each Cl})$ or $y = +3$. The oxidation state of iron is +3 in FeCl_3 .

NH_3 : Ammonia is a neutral molecule, and each hydrogen atom is +1 from Rule 4. Thus, $0 = y + (3 \text{ H})(+1 \text{ for each H})$ or $y = -3$. The oxidation state of N in NH_3 * is -3.

$\text{Cr}_2\text{O}_7^{2-}$: The dichromate ion carries a -2 charge, and oxygen must be a -2 by Rule 5 because Cr does not appear in a prior rule. Thus, $-2 = (2 \text{ Cr})(y \text{ for each Cr}) + (7 \text{ O})(-2 \text{ for each oxygen})$ or $2y = 12$, so each chromium is +6 in the dichromate ion.

MgO_2 : Group 2 metals (Rule 3) have priority over oxygen (Rule 5). Thus, the Mg is +2, which makes oxygen -1 and the compound a peroxide (O_2^{2-}), not an oxide.

$\text{C}_8\text{H}_{16}\text{O}_8$: H is +1 (Rule 4) and O is -2 (Rule 5), so $8y + 16(1) + 8(-2) = 0$ or $8y = 0$. The oxidation state of carbon is zero. Note that elements are not the only substances with atoms in zero oxidation states.

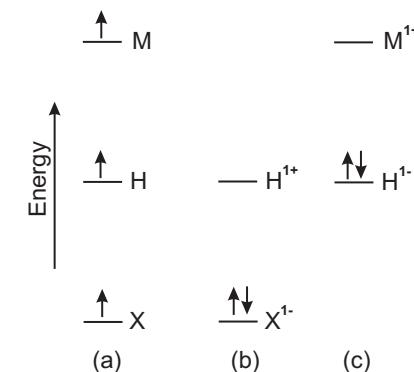


Figure 4.5 Oxidation states of hydrogen

- The valence orbital of H lies between those of most metals (M) and most nonmetals (X)
- The electrons would be assigned to the nonmetal in the HX bond because the valence orbitals of X are lower. Thus, H would have to give up an electron to become +1 as in Rule 4.
- The electrons would be assigned to the H in the MH bond because the valence orbitals of H are lower. Thus, H would gain an electron to become -1 as required by Rule 3.

* Note that NH_3 is an example of a formula in which the element with the positive oxidation state is not written first. Hydrogen is written first in a formula to show that it is acidic. The hydrogen in NH_3 is not acidic, so it is not written first. This is explained in more detail in Chapter 12.

We can also predict the formula of a binary inorganic compound by using likely oxidation states and the fact that compounds are electrically neutral; *i.e.*, the sum of the oxidation states of all atoms must be zero. There are only two elements in a binary compound, so one must have a positive oxidation state (OX_{pos}) and the other a negative oxidation state (OX_{neg}). To determine the formula of the compound, we need to know the ratio of the atoms with positive oxidation states (N_{pos}) to the number with negative oxidation states (N_{neg}). If the sum of all oxidation states is zero, we can write

$$N_{\text{pos}}\text{OX}_{\text{pos}} = -N_{\text{neg}}\text{OX}_{\text{neg}}$$

Eq. 4.1

Equation 4.1 states that the total positive charge (ions or oxidation states) must equal the total negative charge. Use the following steps to predict the formula:

- Step 1** Assign likely oxidation states to each of the elements. Typically, the Group number is used for OX_{pos} and (Group Number – 8) is used for OX_{neg} .
- Step 2** Find the lowest common multiple (LCM)* of OX_{pos} and OX_{neg} . This is the total positive or negative charge.
- Step 3** Determine how many atoms of each are required to deliver the charge determined in Step 2 (LCM). $N_{\text{pos}} = \text{LCM}/\text{OX}_{\text{pos}}$ and $N_{\text{neg}} = -\text{LCM}/\text{OX}_{\text{neg}}$.

* The lowest common multiple (LCM) of two integers is the smallest integer for which they are both factors. For example, the LCM of 4 and 6 is 12 because both 4 and 6 are factors of 12. Both 4 and 6 are also factors of 24, but 24 is not the LCM because it is not the smallest integer for which they are both factors.

Example 4.7

a) What is the formula of the compound between A and B in Example 4.5?

The oxidation states of A and B are +1 and -3, so LCM = 3.

$$N_{\text{pos}} = 3/1 = 3 \text{ A atoms and } N_{\text{neg}} = -(3/-3) = 1 \text{ B atom}$$

Three A atoms are required for every B atom, so the formula is A_3B . Note the A is written first in the formula because it is less electronegative than B.

b) What is the formula of the compound between B and C in Example 4.5?

If B is +5 and C is -2, then LCM = 10

$$N_{\text{pos}} = 10/5 = 2 \text{ B atoms and } N_{\text{neg}} = -(10/-2) = 5 \text{ C atoms}$$

Two B atoms are required for every five C atoms, so the formula is B_2C_5 .

If B is +3, then LCM = 6 and the compound is B_2C_3 .

A possible set of elements with the relative energies given in Example 4.5 would be A = H, B = N, and C = O, in which case the compounds would be NH_3 and N_2O_5 or N_2O_3 .

Example 4.8

Predict formulas for the binary compounds (compounds containing only two different types of atoms) formed between the following elements.

Oxygen and calcium: Ca is a Group 2A metal and forms a +2 ion, and the most common oxidation state of oxygen is -2 (Rule 5). LCM = 2, so LCM/OX = 1 for each ion. The formula is CaO.

Chlorine and cobalt: The chloride ion has a -1 charge (Rule 6). Co is a transition metal and forms both +2 and +3 ions. If cobalt is +2, two chloride ions are required and the formula is CoCl₂. If cobalt is +3, three -1 charges are needed, so the compound is CoCl₃.

Sulfur and aluminum: Al is +3 (Rule 3), and S is a 6A nonmetal, so its anion is -2. The LCM of 3 and 2 is 6, so N_{pos} = 6/3 = 2 cations and N_{neg} = -6/-2 = 3 anions. The compound is Al₂S₃. Two +3 ions deliver +6 charge and three -2 ions deliver -6 charge.

Oxygen and carbon: O is -2 from Rule 5. C is a 4A nonmetal that must be assigned the positive oxidation state, which we assume is +4, its group number. The N_{pos} = 4/4 = 1 and N_{neg} = -4/-2 = 2. The formula is CO₂.

4.5 POLYATOMIC IONS

A number of ionic compounds are composed of **polyatomic ions**, which are charged groups of covalently bound atoms. While the polyatomic ion forms ionic bonds with oppositely charged ions, *the atoms within a polyatomic ion are nonmetals held together by covalent bonds*. Many of the polyatomic ions are **oxoanions**; *i.e.*, they are negative ions that contain oxygen atoms covalently bound to another element. In the common polyatomic ions listed in Table 4.1, the only cations are ammonium and hydronium, and the only anions that are not oxoanions are hydroxide and cyanide.

Recall that ionic compounds can be identified as those that contain metals because metals represent almost all of the common monatomic cations. However, ions can also be polyatomic. Ammonium is by far the most common polyatomic cation in compounds. Thus, NH₄Cl, NH₄NO₃, and (NH₄)₂SO₄ are also ionic compounds. We conclude that

Ionic compounds are those that contain either a metal or a polyatomic cation such as ammonium.

Table 4.1 Some common polyatomic ions

Cations

NH ₄ ¹⁺	ammonium ion	H ₃ O ¹⁺	hydronium ion*
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Anions

C ₂ H ₃ O ₂ ¹⁻	acetate ion	OH ¹⁻	hydroxide ion
CO ₃ ²⁻	carbonate ion	NO ₃ ¹⁻	nitrate ion
ClO ₄ ¹⁻	perchlorate ion	NO ₂ ¹⁻	nitrite ion
ClO ₃ ¹⁻	chlorate ion	MnO ₄ ¹⁻	permanganate ion
ClO ₂ ¹⁻	chlorite ion	O ₂ ²⁻	peroxide ion
ClO ¹⁻	hypochlorite ion	PO ₄ ³⁻	phosphate ion
CrO ₄ ²⁻	chromate ion	SO ₄ ²⁻	sulfate ion
Cr ₂ O ₇ ²⁻	dichromate ion	SO ₃ ²⁻	sulfite ion
CN ¹⁻	cyanide ion		

* The hydronium ion is often used to represent the association of the proton with water (H₂O + H¹⁺ = H₃O¹⁺), but H¹⁺ is also used to represent the proton in water.

4.6 NAMING IONIC COMPOUNDS

The name of a binary ionic compound is simply the name of the cation (name of the metal atom) followed by the name of the anion (name of nonmetal with ending changed to *-ide*). If the metal has the same oxidation state in all of its compounds, the oxidation state is not indicated. The metals for which the oxidation state is usually omitted are the metals of Groups 1A and 2A, Al, Sc, Zn, Ag, and Cd. The remaining metals have more than one possible oxidation state, and so the oxidation state of the metal is indicated with a Roman numeral in parentheses after the name of the metal. Note that there is no space between the name of the metal and the Roman numeral in parenthesis.

Example 4.9

Name the following binary ionic compounds.



Al is aluminum, which is always +3, so the oxidation state is not required. Br represents the bromide ion. The name of the compound is *aluminum bromide*.



The cation is Zn²⁺, but zinc is always +2, so the oxidation state is not indicated in the name. The compound is *zinc chloride*.



Silver is always Ag¹⁺, and the name is simply *silver oxide*.



Iron is commonly found in the +2 and +3 oxidation states. Thus, there is more than one iron chloride. To distinguish between the two iron chlorides, we indicate that in this compound the iron is in the +2 oxidation state. The name is *iron(II) chloride*.



Copper is usually found as a +2 ion; but, as in this compound, it can also form compounds in the +1 oxidation state. To distinguish this compound from the more common CuCl₂, we name it *copper(I) chloride*.



Lead forms compounds in both the +2 and +4 oxidation states. Thus, this compound is named *lead(IV) oxide*.



Cl is -1 (Rule 6), so Hg must be +1. Hg also forms +2 ions, so the compound is *mercury(I) chloride*.

NAMING OXOANIONS*

In those oxoanions ending in *-ate*, the central atom is in its highest oxidation state. For example, nitrogen (a 5A nonmetal) is in a +5 oxidation state in the nitrate ion (NO_3^{1-}). Oxoanions ending in *-ite* have one less oxygen atom than those ending in *-ate*. Removing an oxygen *atom* from an oxoanion reduces the oxidation state of the central atom by two, but it does not affect the charge on the ion. Thus, the nitrite ion (NO_2^{1-}), which has one less oxygen atom than does the nitrate ion, retains the same charge as the nitrate ion, but the oxidation state of the nitrogen atom is reduced from +5 to +3.

The oxoanions of the Group 7A elements are an exception because, unlike the others, they each form four oxoanions. Consequently, both prefixes and suffixes must be used (see Table 4.2). In the perchlorate ion (ClO_4^{1-}), the chlorine is in its highest oxidation state (+7). The chlorate ion (ClO_3^{1-}) has one less oxygen, so the oxidation state of Cl is two less or +5. The chlorite ion (ClO_2^{1-}) has one less oxygen than chlorate, which lowers the oxidation state of Cl to +3. Finally, the hypochlorite ion (ClO^{1-}) has one less oxygen than chlorite, and the oxidation state of the Cl is reduced to +1. Similarly, perbromate is BrO_4^{1-} , bromate is BrO_3^{1-} , etc. Note, however, that fluorine is the most electronegative element, so it never has a positive oxidation state. Consequently, fluorine forms no oxoanions.

Oxoanions with charges of -2 or -3 can be protonated (a proton, H^{1+} , can be added) and still retain a negative charge. The resulting ion is named by placing “hydrogen” (or “dihydrogen” for two hydrogens) in front of the anion name. Thus, addition of H^{1+} to a phosphate ion, PO_4^{3-} , results in the hydrogen phosphate ion, HPO_4^{2-} , while the addition of two H^{1+} ions results in the dihydrogen phosphate ion, $\text{H}_2\text{PO}_4^{1-}$. It should be noted that the prefix “bi” is sometimes used instead of “hydrogen”. Thus, HCO_3^{1-} is the hydrogen carbonate ion or the bicarbonate ion, and HSO_4^{1-} is both the hydrogen sulfate ion and the bisulfate ion. The use of “bi” is an older method, but it is still quite common. The common examples of protonated oxoanions are given in Table 4.3.

No changes or additions are made to polyatomic ion names in their compounds. Some examples: NH_4Cl is ammonium chloride; Na_2CO_3 is sodium carbonate; NaHCO_3 is sodium hydrogen carbonate, $\text{Co}(\text{ClO}_4)_3$ is cobalt(III) perchlorate, and $(\text{NH}_4)_3\text{PO}_4$ is ammonium phosphate.

* Recall that oxoanions are those polyatomic anions that consist of a central atom surrounded by oxygen atoms.

Table 4.2 Prefixes and suffixes of the oxoanions formed by the 7A nonmetals.

Prefix	Suffix	Oxidation state of halogen	Formula of ion
Per-	-ate	+7	XO_4^{1-}
	-ate	+5	XO_3^{1-}
	-ite	+3	XO_2^{1-}
Hypo-	-ite	+1	XO^{1-}

Table 4.3 Some common protonated oxoanions

HCO_3^{1-}	hydrogen carbonate or bicarbonate ion
HPO_4^{2-}	hydrogen phosphate ion
$\text{H}_2\text{PO}_4^{1-}$	dihydrogen phosphate ion
HSO_4^{1-}	hydrogen sulfate ion or bisulfate ion
HSO_3^{1-}	hydrogen sulfite ion or bisulfite ion

Example 4.10

- a) Predict the formulas of selenate ion, hydrogen selenate ion, selenite ion, and hydrogen selenite ion.

Selenium is a 6A nonmetal, so an ending of -ate tells us that the selenium atom is in its highest oxidation state, +6. Oxygen is -2. Three oxygens would make the compound neutral, so a fourth oxygen is needed to make an anion. One selenium atom, at +6, combined with four oxygens, at -2 each, results in a -2 ion. Thus, selenate ion is SeO_4^{2-} , which is to be expected because sulfate ion is SO_4^{2-} , and sulfur and selenium are in the same family. Addition of an H^{1+} to selenate yields the hydrogen selenate ion, HSeO_4^{1-} .

Removal of an oxygen atom results in SeO_3^{2-} , the selenite ion, and adding an H^{1+} results in the hydrogen selenite ion, HSeO_3^{1-} .

- b) Predict the formulas of the chromate and dichromate ions.

Chromium is a 6B metal and is in the +6 oxidation state in the chromate ion. A minimum of four oxygen atoms, at -2 each, is required to produce the anion. Thus, the chromate ion is CrO_4^{2-} . Note the similarity of the chromate and sulfate ions. In each case, the central atom is a Group 6 element; one is a 6B while the other is a 6A.

The *di-* prefix in dichromate indicates that there are two chromium atoms in this ion, while the -ate suffix indicates that each is in a +6 oxidation state. A minimum of seven oxygen atoms is required to produce the anion. The charge on the anion is $2(+6) + 7(-2) = -2$. The formula of the dichromate ion is $\text{Cr}_2\text{O}_7^{2-}$.

4.7 STRUCTURE OF IONIC COMPOUNDS

Monatomic anions and cations are spherical charges that pack around one another in their compounds. The points of contact can be anywhere along the surface of the spheres. In other words, *ionic bonds are not directional*. In addition, several spheres of one charge can pack around one sphere of opposite charge, so there are no units that are identifiable as molecules. That is, *ionic compounds are not molecular*.

For example, consider the structure of a crystal of NaCl shown in Figure 4.6. Note that there is no unique NaCl pair that can be identified as an NaCl molecule. Instead, each Cl^{1-} ion is surrounded by six Na^{1+} ions and each Na^{1+} ion is surrounded by six Cl^{1-} ions. Consequently, a single crystal of table salt consists of an enormous number of sodium and chloride ions, which are all bound together in a solid network. Thus, NaCl is a compound, not a molecule. Molecular substances involve only nonmetals and are the topic of Chapters 5 and 6. We revisit solid networks in Chapter 8.

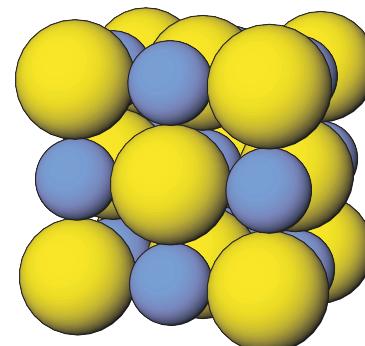


Figure 4.6 NaCl structure

NaCl is a network of alternating Na^{1+} (blue) and Cl^{1-} ions (yellow) with no clearly discernable NaCl molecules. Thus, NaCl forms an extended solid and is not molecular.

4.8 CHAPTER SUMMARY AND OBJECTIVES

The bonding electrons in ionic bonds reside totally on one of the atoms in the bond. This occurs when there is a large difference between the electronegativities of the bound atoms, which usually occurs when one atom is a metal and the other a nonmetal. The electrons added to the nonmetal give it a negative charge, while the reduced number of electrons on the metal gives it a positive charge. The ionic bond results from the electrostatic attraction of the opposite charges. Main group metals usually empty their valence shells to form cations with charges equal to their group numbers. Most transition metals lose their outermost s electrons to form +2 ions. Sn and Pb form only +2 ions, while Tl forms both +1 and +3 ions. The name of the cation is the same as that of the metal. Nonmetals fill their valence shell, so the charge on a nonmetal anion equals its group number minus 8. Anions are named by changing the end of the name of the nonmetal to *-ide*.

The oxidation state of an atom is the charge the atom would have if the bonds were ionic. Oxidation states are used for electron counting in both ionic and non-ionic compounds. Some common elements have the same oxidation state in almost all of their compounds. Using that fact and a series of priorities, we can assign oxidation states to atoms in molecules or ions. The chemical formulas for binary molecules and ions can be predicted by using the common oxidation states of the atoms and the fact that the oxidation states must sum to the charge on the species.

Polyatomic ions are ions that contain more than one atom. Polyatomic ions are very common, and most are oxoanions. The name of an ionic substance is simply the name of the cation followed by the name of the anion. Ionic compounds are solids at room temperature and exist as an extended network of ions, not as individual molecules.

After studying the material of this chapter, you should be able to:

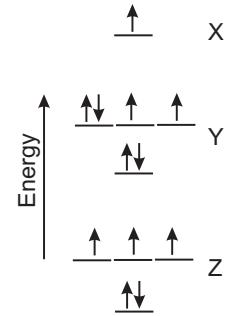
1. describe what happens when a metal atom reacts with a nonmetal atom (Section 4.1);
2. identify ionic compounds (Section 4.1);
3. determine the electron configurations of monatomic anions and cations (Section 4.2);
4. predict the relative sizes of atoms and their ions (Section 4.3);
5. determine the oxidation states of the atoms in an ion or molecule (Section 4.4);
6. use oxidation states to predict formulas of compounds (Section 4.4);
7. write the formulas of common polyatomic ions (Section 4.5);
8. predict the formula of an oxoanion from its name (Section 4.6);
9. name ionic compounds (Section 4.6); and
10. explain why ionic compounds are not molecular (Section 4.7).

4.9 EXERCISES

1. Define the term “isoelectronic.”
2. Which of the following compounds are ionic?
 - a) SiCl_4
 - b) ScCl_3
 - c) NCl_3
 - d) NH_4Cl
3. Which of the following compounds are ionic?
 - a) KCN
 - b) HNO_2
 - c) CoPO_4
 - d) NH_4NO_2
4. Metals and nonmetals tend to achieve noble gas configurations. In each case, explain how they do it?
5. What are the charges on the ions formed by the main group elements?
6. How many ions are in the formula of a compound composed of a 2A metal and a 7A nonmetal? Give two examples of compounds with this type of formula.
7. Oxygen can have a positive oxidation state when bound to only one element. What is the element? Use orbital energies to explain.
8. Use orbital energies to explain why hydrogen is -1 when bound to metals and +1 when bound to nonmetals.
9. Which element in each pair would have the positive oxidation state.
 - a) N & O
 - b) Cl & P
 - c) S & Sn
 - d) K & N
10. Which element in each pair would have the positive oxidation state.
 - a) N & H
 - b) C & O
 - c) S & Ca
 - d) F & O
11. Write electron configurations for the following ions.
 - a) Ca^{2+}
 - b) Ga^{3+}
 - c) Co^{3+}
 - d) I^{1-}
12. Write electron configurations for the following ions.
 - a) Te^{2-}
 - b) P^{3-}
 - c) Pb^{2+}
 - d) In^{1+}
13. Explain the following observations.
 - a) K^{1+} is larger than Na^{1+} .
 - b) Na is larger than Cl, but Na^{1+} is much smaller than Cl^{1-} .
 - c) Lead forms two oxides, PbO and PbO_2 .

14. Determine the oxidation state of the underlined atom.
 - a) KMnO_4
 - b) $\underline{\text{C}}_{12}\text{H}_{22}\text{O}_{11}$
 - c) CoPO_4
 - d) $\text{Na}_2\underline{\text{O}}_2$
15. Determine the oxidation state of the underlined atom.
 - a) $\underline{\text{C}}_{60}$
 - b) LiAlH_4
 - c) $\underline{\text{O}}\text{F}_2$
 - d) CaSiO_3
16. Name the following compounds:
 - a) CaCl_2
 - b) $\text{Fe}(\text{NO}_3)_2$
 - c) K_2CO_3
 - d) CoCl_3
17. Name the following compounds:
 - a) $\text{Zn}_3(\text{PO}_4)_2$
 - b) Ag_2S
 - c) Cr_2O_3
 - d) NH_4Cl
18. Name the following ionic compounds using the “hydrogen” prefix for the anion:
 - a) KHSO_4
 - b) NaH_2PO_4
 - c) Li_2HPO_4
 - d) $\text{Co}(\text{HSO}_3)_2$
19. What two names can be used for $\text{Ca}(\text{HCO}_3)_2$?
20. Predict the formulas of the arsenate and arsenite ions.
21. Predict the formulas of the vanadate and titanate ions.

Use the energy diagram for the valence orbitals of atoms X, Y, and Z shown to the right in Exercises 22, 23, and 24.



22. Consider the compound formed between X and Y.
 - a) What is the formula of the ionic compound formed between these two elements?
 - b) What is the oxidation state of X in the compound?
 - c) What is the oxidation state of Y in the compound?
23. Consider the compound formed between Y and Z.
 - a) What are the maximum and minimum oxidation states of Y?
 - b) What are the maximum and minimum oxidation states of Z?
 - c) What is the formula of the compound that is most likely formed between atoms Y and Z in their maximum and minimum oxidation states?
24. Elements X, Y, and Z are all main group elements. In which groups are they located? (See Exercises 22 and 23.)

25. Write formulas for the following compounds:
- a) gallium(III) oxide b) strontium bromide
c) zinc acetate d) manganese(II) sulfide
26. Write formulas for the following compounds.
- a) strontium phosphide b) potassium dichromate
c) platinum(IV) oxide d) aluminum nitrate
27. Write formulas for the following compounds:
- a) sodium bicarbonate b) iron(II) hydrogensulfate
c) calcium dihydrogenphosphate d) magnesium hydrogensulfite
28. What is the mass of 0.057 mol of magnesium chlorate?
29. How many moles of iron(III) oxide are present in a 5.00 g sample?
30. How many moles of oxygen atoms are present in 0.20 mol aluminum dichromate?
31. A sample of calcium nitrate contains 0.025 mol of oxygen atoms. What is the mass of the sample?
32. How many moles of bicarbonate ions are present in 12.0 g of aluminum bicarbonate?
33. How many moles of protons are required to convert all of the phosphate ions in 25.0 g of magnesium phosphate into dihydrogen phosphate ions?
34. How many moles of electrons would be required to convert 10.0 g of phosphorus atoms into phosphide ions?
35. How many moles of electrons must be removed to convert 7.5 g Zn to zinc ions?

Chapter 5

The Covalent Bond

5.0	<i>Introduction</i>	5.6	<i>Determining Lewis Structures</i>
5.1	<i>The Covalent Bond</i>	5.7	<i>Resonance</i>
5.2	<i>Bond Polarity</i>	5.8	<i>Formal Charge and Oxidation State</i>
5.3	<i>Naming Binary Covalent Compounds</i>	5.9	<i>Practice with Lewis Structures</i>
5.4	<i>Lewis Symbols of the Elements</i>	5.10	<i>Chapter Summary and Objectives</i>
5.5	<i>Lewis Structures of Diatomic Molecules</i>	5.11	<i>Exercises</i>

5.0 INTRODUCTION

We concluded Chapter 4 with the observation that *ionic substances* are extended networks of large numbers of ions and not individual molecules. For example, in a crystal of NaCl, six chloride ions are bound to each sodium ion, but no one chloride ion can be clearly identified with any one sodium ion. This is because the charge on the ions is spherical, which makes the ionic bond non-directional. However, in compounds that are composed only of nonmetals, the bond between the atoms is directional. For example, in ICl, each iodine atom is bound to a clearly identifiable chlorine atom, so there are distinct molecules of ICl, and ICl is said to be a *molecular substance*. Bonds that are directional are called **covalent bonds**. Whereas ionic bonds usually form between metals and nonmetals, covalent bonds are formed between nonmetals. We discuss the nature of the covalent bond in this chapter, and then, in Chapter 6, we look at the impact that directional bonds have on the structures of molecules and consider two theories for the covalent bond.

THE OBJECTIVES OF CHAPTER 5 ARE TO:

- discuss the theory of the covalent bond;
- distinguish between the ionic bond and the covalent bond;
- describe how covalent compounds are named;
- define Lewis structures and show how to generate them;
- define bond polarity;
- describe resonance and its effects;
- define formal charge and explain how to determine it; and
- distinguish between formal charge and oxidation state.

5.1 THE COVALENT BOND

In Chapters 2 and 3, we discussed the energy of interaction between a nucleus and its electrons, which reduces their potential energy and is responsible for the existence of atoms. However, valence electrons can reduce their energy even farther by interacting with more than one nucleus. Consider Figure 5.1, which shows the energy of interaction between two hydrogen atoms as a function of their separation, r .

- At a separation of r_1 , the two hydrogen atoms are too far apart to interact; i.e., they have zero energy of interaction, and the electrons are in spherical 1s orbitals.
- At a distance of r_2 , each electron is attracted by the nucleus of the other atom as well as its own. There is also repulsion between the nuclei, but it is much less because the nuclei are still relatively far apart. The greater attractive force between the oppositely charged particles lowers the energy of the system. The electron density begins to concentrate in the region between the nuclei, distorting the orbitals from their spherical shape.
- At r_3 , the atoms are weakly bound together, and the two orbitals overlap one another.
- At r_4 , the energy of the system has reached a minimum as the electron/nuclear attraction just balances the internuclear repulsion. The bonding electrons are in an orbital that concentrates the electron density in the region between the two nuclei. The negative charge of the two electrons holds the positively charged nuclei together in an H-H covalent bond.
- At r_5 , the repulsion between the nuclei is the dominating force, so the energy rises sharply.

The separation between the nuclei at the minimum energy is called the **bond length**. The bond length of the H-H bond is 0.74 Å (74 pm)*, which is quite short, while the I-I bond length, which is nearly 2.7 Å, is a very long bond. The difference in the two bond lengths is due to the difference in size of the bound atoms (Figure 3.3). Smaller nuclei can get closer to other atoms than can larger nuclei.

The amount by which the energy of the two atoms is reduced by forming the bond is known as the **bond energy**. Most bond energies lie between 100 and 1000 kJ/mol, so the H-H bond energy (436 kJ/mol) lies in the middle of this range. The I-I bond energy, which is 151 kJ/mol, is a relatively weak bond.

5.2 BOND POLARITY

The electronegativity (χ) of an atom (Table 5.1) measures its ability to attract the bonding electrons. Atoms with high electronegativities have unfilled, low-energy orbitals and strong affinities for bonding electrons. In H_2 the bound atoms have identical electronegativities, so the bonding electrons are shared equally. However, if the electronegativities of the bound atoms differ, the bonding electrons are not shared equally

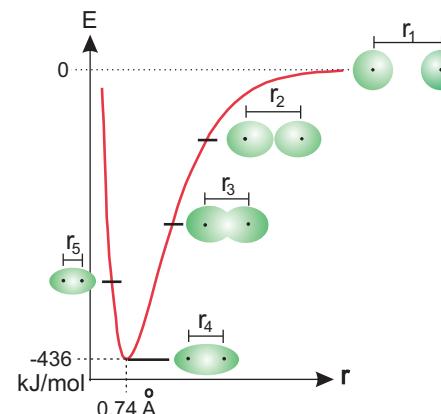


Figure 5.1 Interaction of two H atoms

Energy of interaction between two H atoms as a function of r , the distance between the nuclei, which are represented by the small dots

* Å is the Angstrom. $1\text{\AA} = 10^{-10}\text{ m}$. The Angstrom is a common unit for bond lengths because most bond lengths fall between 1 and 3 Å. The picometer (pm) and nanometer are the common SI units for bond lengths. $1\text{ pm} = 10^{-12}\text{ m}$ and $1\text{ nm} = 10^{-9}\text{ m}$, and most bond lengths lie between 100 and 300 pm or 0.1 to 0.3 nm.

Table 5.1 Electronegativities of the Main Group elements.

H						
2.2						
Li	Be	B	C	N	O	F
1.0	1.6	2.0	2.6	3.0	3.4	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.3	1.6	1.9	2.2	2.6	3.2
K	Ca	Ga	Ge	As	Se	Br
0.9	1.0	1.8	2.0	2.2	2.6	3.2
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.8	2.0	2.1	2.1	2.7
Cs	Ba	Tl	Pb	Bi	Po	At
0.8	0.9	2.0	2.3	2.0	2.0	2.2

as the more electronegative atom becomes electron rich and the less electronegative atom becomes electron poor. The result is that negative charge is produced on the more electronegative atom and positive charge on the less electronegative atom. The charge that is produced in a covalent bond is only a part of what it would be if the bond were ionic, so it is said to be a *partial charge*, which is represented with a δ (delta). Thus, a covalent bond involving atoms of different electronegativities has two electrical poles (δ^- and δ^+) and is said to have a **bond dipole**. The bond dipole is represented by a vector pointing from the center of positive charge toward the center of negative charge with a line drawn through the positive end to make a '+' as shown in Figure 5.2. The strength of a bond dipole (the polarity of the bond) increases as the electronegativity difference ($\Delta\chi$) between the bound atoms increases. Consider the four molecules in Figure 5.3.

Figure 5.3a: The two iodine atoms in I_2 have identical electronegativities, so $\Delta\chi = 0$ and $\delta = 0$. The atoms attract the bonding electrons equally and form a purely covalent bond. There is no charge separation in purely covalent bonds (no red and blue regions in the figure).

Figure 5.3b: Iodine ($\chi = 2.7$) is more electronegative than hydrogen ($\chi = 2.2$), so the bonding electrons in an H-I bond are pulled away from the hydrogen and toward the iodine atom. As a result, the iodine atom is electron rich and has a partial negative charge, while the less electronegative hydrogen atom develops a partial positive charge. H-I has a bond dipole, but the bond is not very polar (as indicated by the very pale shading) because $\Delta\chi$ is only 0.5. The bond dipole in HI points from H to I.

Figure 5.3c: $\Delta\chi = 1.3$ for an I-F bond, so it is more polar than an H-I bond (as indicated by the darker shading). Fluorine is the more electronegative atom in this bond, so the bond dipole points toward fluorine.

Figure 5.3d: $\Delta\chi = 1.8$ for an H-F bond, so the H-F bond is more polar than an I-F bond (darker shading). The bond dipole points from H to F.

The bond between two atoms is purely covalent if their electronegativities are identical, but it becomes increasingly polar as the difference in their electronegativities increases. At a sufficiently large difference, the bond is so polar that it is considered to be an ionic bond. The nature of the bond is sometimes given in terms of its **percent ionic character**. The more polar a bond is, the higher is its percent ionic character. An F-F bond ($\Delta\chi = 0$) is purely covalent and has no ionic character (0% ionic), while a RbF bond ($\Delta\chi = 3.2$) is 90% ionic, which means that the charge (δ) on the rubidium is +0.9.

As shown in Figure 5.4, the change from covalent to ionic is gradual with no distinct line between the two bond types. In the following discussion, we will assume that a bond is covalent if it is less than 5% ionic, that a bond is polar covalent if it is between 5 and

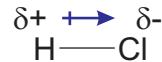


Figure 5.2 Bond dipole in HCl

The bond dipole is shown as the blue arrow. Cl is more electronegative than H, so the H-Cl bond dipole points from H to Cl. A line perpendicular to the arrow is placed at the positive end to produce a '+' in the arrow.

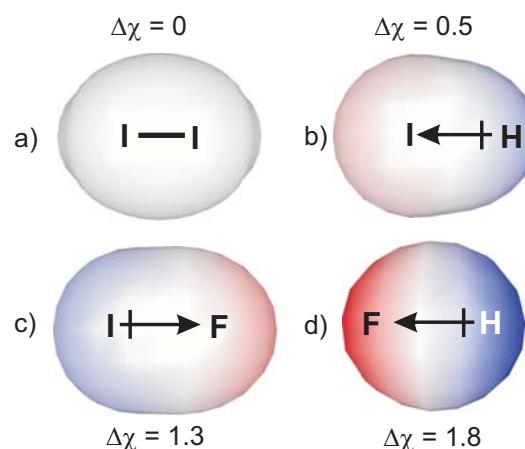


Figure 5.3 Charge distribution in some covalent bonds

Red is used to show regions that carry negative charge, while blue is used for regions that carry positive charge. The dipole arrow is used to show direction only.

50% ionic, and that a bond is ionic if it is over 50% ionic. Thus, the C-H bond ($\Delta\chi = 0.4$) is less than 5% ionic and is considered to be a covalent bond, while the HCl bond ($\Delta\chi = 1.0$) is slightly less than 20% ionic, so it is considered to be a polar covalent bond. The KBr bond ($\Delta\chi = 2.3$) is ~75% ionic, so it is considered to be ionic. No bond is 100% ionic because every atom exerts some pull on the bonding electrons; *i.e.*, no atom has zero electronegativity. Hence, the bonding electron density near a metal in an ionic bond may be very low, but it is not zero.

The electronegativities of the nonmetals are not that dissimilar, so bonds between nonmetals are usually covalent or polar covalent. However, this is a broad generalization and care should be made in its use. For example, $\Delta\chi = 1.8$ for an H-F bond, which makes the bond between these two nonmetals ~55% ionic. Large values of $\Delta\chi$ occur most frequently in bonds between metals (low χ) and nonmetals (high χ), so these bonds are *usually* considered to be ionic, but care must also be taken with this rule as well. Metals, such as Ag, Hg, and Pb, that lie on the right side of the periodic table, have high electronegativities ($\chi = 1.9$ for Ag and 2.3 for Pb), so their bonds to nonmetals are not very ionic. In fact, the Ag-Cl and Pb-Cl bonds ($\Delta\chi = 1.1$ and 0.7) are only ~30% and ~15% ionic, respectively!* Although there are exceptions, we will frequently make use of the generalization that *nonmetal-nonmetal bonds are covalent, while metal-nonmetal bonds are ionic*.

Example 5.1

Determine the more polar bond in each pair and the direction of the bond dipole.

C-F or Si-F bond

Fluorine is more electronegative than either C or Si; thus, the bond dipole points toward the fluorine atom in both bonds. The electronegativity difference in each bond is $\Delta\chi = \chi(F) - \chi(Si \text{ or } C)$. Because carbon is more electronegative than silicon, $\Delta\chi$ is greater for the Si-F bond, which makes it the more polar bond.

C-H or O-H bond

$\chi(H) = 2.1$, which makes it less electronegative than most of the other nonmetals; thus, the bond dipole will point away from the hydrogen atom. Oxygen is more electronegative than carbon, which means that the electronegativity difference, $\Delta\chi = \chi(O \text{ or } C) - \chi(H)$, is greater for the O-H bond. The O-H bond is the more polar bond. It should be noted that $\Delta\chi = 0.4$ for a C-H bond. Such a low value for $\Delta\chi$ indicates that the C-H bond is almost completely covalent (it has less than 5% ionic character).

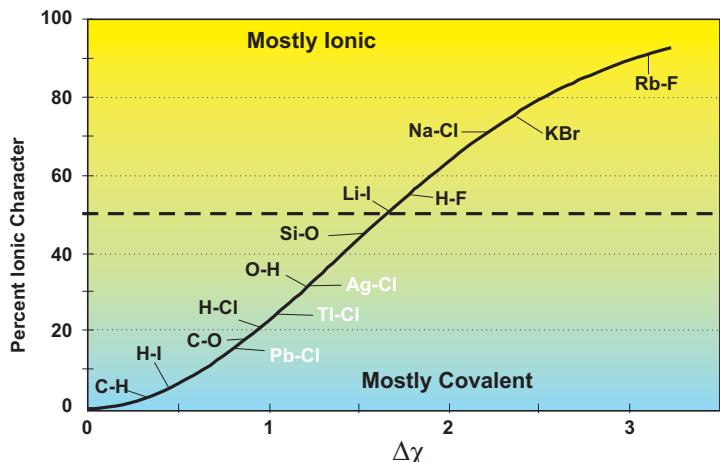


Figure 5.4 Percent ionic character in a bond versus the electronegativity difference between the bound atoms

Bond types change continuously from covalent (blue) to ionic (yellow). Bonds that are over 50% ionic are called ionic. Note that bonds labeled in white are considered polar covalent, but they are between a metal and a nonmetal.

* The fact that these atoms have such high electronegativities and form covalent bonds with nonmetals is an important feature that will be used in Chapters 10 and 12 to explain some of their chemistry.

5.3 NAMING BINARY COVALENT COMPOUNDS

Binary compounds are compounds that consist of only two elements; they are named by giving the name of the less electronegative atom followed by the name of the more electronegative atom with its ending changed to *-ide*. Greek prefixes (Table 5.2) are used to indicate the number of each type of atom in the molecule except that the prefix “mono” is not used to denote a single atom if it is referring to the first element in the compound. Thus, CO is carbon monoxide[†], not monocarbon monoxide. Hydrogen always has a +1 oxidation state when it is bound to nonmetals, so the formula of its binary compounds is not ambiguous. Therefore, prefixes are frequently omitted. For example, H₂S is commonly called hydrogen sulfide rather than dihydrogen sulfide. Finally, many binary covalent molecules have common names, such as water (H₂O), ammonia (NH₃), nitric oxide (NO), and nitrous oxide (N₂O), which is frequently referred to as laughing gas.

By convention, *the less electronegative element is written first in the formula* (carbon dioxide is written CO₂, not O₂C because O is more electronegative than C). Exceptions do occur if one of the elements is hydrogen because many hydrogen containing compounds are acids, and, by convention, hydrogens at the beginning of the formula are considered to be acidic hydrogens. Hydrogen sulfide is written H₂S because it is acidic, but ammonia is written NH₃ because it is not acidic.

Example 5.2

a) Name the following compounds:

H₂Se: Two H atoms would ordinarily require a prefix of “di”, and the name would be dihydrogen selenide. However, there is only one compound formed between H and Se, so it is frequently called hydrogen selenide.

N₂O₃: Two N atoms and three O atoms, so the name is dinitrogen trioxide.

SnCl₄: It is tempting to name this compound tin tetrachloride, and it is sometimes called that. However, tin is a metal, so the compound should be named using the rules given in Chapter 4. The accepted name is tin(IV) chloride.

ClF₃: Three fluorine atoms, so this is chlorine trifluoride.

b) What is the formula of disulfur decafluoride?

The prefix di means two and the prefix deca is ten, so the compound is S₂F₁₀.

Table 5.2 Prefixes used to indicate the number of atoms of each element present in the formula of covalent compounds

Number	Prefix	Example	
1	mono	CO	carbon monoxide
2	di	CO ₂	carbon dioxide
3	tri	SO ₃	sulfur trioxide
4	tetra	CCl ₄	carbon tetrachloride
5	penta	PF ₅	phosphorus pentafluoride
6	hexa	SF ₆	sulfur hexafluoride
7	hepta	Cl ₂ O ₇	dichlorine hept(a)oxide [†]
8	octa	*	
9	nona	*	
10	deca	*	

* These prefixes are common in naming both organic and inorganic compounds, but there are few examples of binary compounds of the type considered here.

† The final vowel in the prefix is usually omitted when the first letter of the element begins with a vowel. Thus, CO is carbon monoxide, not carbon monooxide, and Cl₂O₇ is a heptoxide rather than a heptaoxide.

5.4 LEWIS SYMBOLS OF THE ELEMENTS

The structure and bonding in a covalent molecule can be determined from its **Lewis structures**, which is a representation of the molecule that shows the distribution of the valence electrons of its constituent atoms. Thus, drawing Lewis structures is an important skill in chemistry, and one we will use frequently. However, before we learn how to draw Lewis structures of groups of bonded atoms, we must first consider the Lewis symbols of the atoms themselves. As shown in Figure 5.5, the Lewis symbol of an atom shows the valence electrons spread into four different orbitals while obeying Hund's rule. You should note that this picture is not consistent with the atomic electron configurations presented in Chapter 2. For example, a carbon atom has a valence electron configuration of $2s^22p^2$, with four valence electrons in three orbitals and only two unpaired electrons, while the Lewis symbol shows the four valence electrons as unpaired in four different orbitals. The reason for this difference is that *Lewis symbols represent an atom that is about to bond, not an isolated atom*, so the orbitals have already adopted the positions required for bonding. The number of valence electrons for a main group element is simply the element's group number, so the electron distributions given in the Lewis symbols are the same for all atoms in a group.

In ionic compounds, nonmetals *gain electrons from a metal* to attain filled valence shells. In covalent compounds, nonmetals *share electrons with other nonmetals* to attain filled valence shells. A closed valence shell for a nonmetal consists of eight electrons (filled s and p sublevels), which is called an **octet** of valence electrons. Thus, nonmetals strive to obtain an octet of valence electrons when they bond. The tendency of nonmetals to obtain eight valence electrons is known as the **octet rule**. In Chapter 4, we used the octet rule to predict that the charge on an anion was its Group Number - 8. We now use it to determine the number of electrons that an atom must share in its covalent bonds.

Hydrogen is an important exception to the octet rule. This is because hydrogen's valence electrons are in the $n = 1$ shell, which can accommodate only two electrons. Thus, *hydrogen requires only a duet of electrons in its covalent compounds*, which means that only one bond is ever drawn to a hydrogen atom.*

1A	2A	3A	4A	5A	6A	7A	8A
H·							He:
Li·	·Be·	·B·	·C·	··N·	··O·	··F·	··Ne·
Na·	·Mg·	·Al·	·Si·	··P·	··S·	··Cl·	··Ar·

Figure 5.5 Lewis symbols for the elements of the first three periods

* There are exceptions to this rule when hydrogen atoms are 'bridging' atoms. For example, two BH_3 molecules are bridged by two hydrogen atoms to form B_2H_6 . The two bridging H atoms are actually bonded to both boron atoms. However, we will not consider molecules of this type further in this text.

5.5 LEWIS STRUCTURES OF DIATOMIC MOLECULES

Lewis structures of molecules are obtained by giving each atom (except hydrogen) an octet of valence electrons. Consider the covalent bond in Cl_2 , shown in Figure 5.6. The separated chlorine atoms each have 7 valence electrons, but they each achieve an octet by sharing their unpaired electrons. The bonding pair is shared equally by the two atoms because their electronegativities are identical; consequently the bond is nonpolar.

Each chlorine atom in Figure 5.6 has three pairs of electrons that are not involved in bonding and are called **nonbonding electrons** or **lone pairs**. Thus, the Cl_2 molecule contains six lone pairs (three pairs on each chlorine atom) and one bonding pair.

The number of electrons that must be shared in a molecule is the difference between the number of electrons required (ER) to give each atom an octet (or duet for H) with no sharing and the number of electrons available in the molecule, which is the number of valence electrons (VE). The number of shared pairs (SP) is one-half the number of shared electrons, so we write: $\text{SP} = \frac{1}{2}[\text{ER} - \text{VE}]$. For example, the number of electrons required without sharing in Cl_2 is: $\text{ER} = (2 \text{ atoms})(8 \text{ electrons needed per atom}) = 16$, and the number of valence electrons available is: $\text{VE} = (2 \text{ atoms})(7 \text{ valence electrons each}) = 14$. The number of shared pairs of electrons in Cl_2 is: $\text{SP} = \frac{1}{2}[16 - 14] = 1$.

Now, let's consider the Lewis structures of H_2 , O_2 and N_2 .

For H_2 (Figure 5.7a),

$$\text{ER} = (2 \text{ atoms})(2 \text{ e}^{\text{-}} \text{ needed/atom}) = 4 \text{ e}^{\text{-}} \text{ required}$$

$$\text{VE} = (2 \text{ atoms})(1 \text{ e}^{\text{-}}/\text{atom}) = 2 \text{ valence e}^{\text{-}} \text{ available}$$

$$\text{SP} = \frac{1}{2}(4 - 2) = 1 \text{ pair must be shared}$$

For O_2 (Figure 5.7b),

$$\text{ER} = (2 \text{ atoms})(8 \text{ e}^{\text{-}} \text{ needed/atom}) = 16 \text{ e}^{\text{-}} \text{ required}$$

$$\text{VE} = (2 \text{ atoms})(6 \text{ e}^{\text{-}}/\text{atom}) = 12 \text{ valence e}^{\text{-}} \text{ available}$$

$$\text{SP} = \frac{1}{2}(16 - 12) = 2 \text{ pairs must be shared}$$

For N_2 (Figure 5.7c),

$$\text{ER} = (2 \text{ atoms})(8 \text{ e}^{\text{-}} \text{ needed/atom}) = 16 \text{ e}^{\text{-}} \text{ required}$$

$$\text{VE} = (2 \text{ atoms})(5 \text{ e}^{\text{-}}/\text{atom}) = 10 \text{ valence e}^{\text{-}} \text{ available}$$

$$\text{SP} = \frac{1}{2}(16 - 10) = 3 \text{ pairs must be shared}$$

An electron pair can be represented as two dots or one line. In this text, we use the more common convention of representing bonding pairs as lines and lone pairs as dots. Thus, *each line in a bond represents two electrons*. Note that the number of electrons

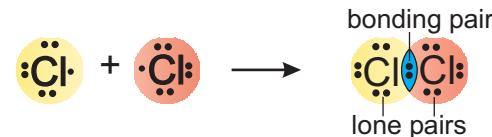


Figure 5.6 Lewis structure of Cl_2

The two Cl atom in Cl_2 must share two electrons (one pair) to achieve octets. One electron from each Cl is used to form the bonding pair. The bonding pair is highlighted by the blue area, while the red and yellow circles highlight the valence electrons on each atom. The colored regions are shown for emphasis only and are not used in subsequent Lewis structures.



Figures 5.7a Lewis structure of H_2

H_2 contains one shared pair but no lone pairs.



Figure 5.7b Lewis structure of O_2

O_2 contains two shared pairs and four lone pairs.



Figure 5.7c Lewis structure of N_2

N_2 contains three shared pairs and two lone pairs.

shown in each Lewis structure must equal the sum of the valence electrons of the atoms in the molecule.

An important feature of a bond is its **bond order**, which is the number of shared pairs it contains. The chlorine-chlorine bond is said to be a **single bond** or to have a bond order of one because it contains a single pair of shared electrons. The bond in O₂ contains two shared pairs of electrons, which gives it a bond order of two; it is a **double bond**. The three shared pairs of electrons in N₂ form a **triple bond**, or a bond with a bond order of three. As shown in Table 5.3, *the bond strength of a specific bond increases and its bond length decreases as its bond order increases*. However, the bond length also depends on the bound atoms (Section 5.1), so this generalization cannot be applied to bonds of different types. Thus, we can predict that a C-C bond is longer than a C≡C bond, but we cannot compare an H-H bond with a C≡C bond. Indeed, the H-H bond (0.74 Å) is shorter than the C≡C bond (1.20 Å) even though the bond order of the H-H bond is lower because the bound atoms are much smaller.

Example 5.3

Draw the Lewis structure for carbon monoxide, determine the carbon-oxygen bond order, and describe the bond dipole.

Carbon monoxide is CO, so

1. ER = (2 atoms)(8 electrons/atom) = 16 electrons.
2. VE = 4 from carbon + 6 from oxygen = 10 valence electrons, or five pairs.
Our Lewis structure must show five pairs of electrons.
3. SP = $\frac{1}{2}(16 - 10) = 3$ pairs must be shared.
4. The three shared pairs give each atom six electrons, so each needs one lone pair to obtain an octet. See Lewis structure in the margin.

The C-O bond contains three shared pairs, so it is a triple bond; *i.e.*, the bond order is 3.

Oxygen is more electronegative than carbon, so the bond dipole would point from the carbon to the oxygen.

Table 5.3 Average bond energies and bond lengths of bonds involving C, N, and O

Bond	Bond Energy (kJ/mol)	Bond Length (Å)	Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-O	358	1.43	N-O	201	1.44
C=O	799	1.23	N=O	607	1.20
C≡O	1072	1.13	O-O	204	1.48
C-C	347	1.54	O=O	498	1.21
C=C	612	1.33	N-N	163	1.47
C≡C	820	1.20	N=N	418	1.24
C-N	305	1.47	N≡N	941	1.10
C=N	615	1.27			
C≡N	891	1.15			



Example 5.3

5.6 DETERMINING LEWIS STRUCTURES

The same prescription used to determine the number of shared pairs in diatomic molecules can be used for polyatomic molecules. In order to determine the Lewis structure of any molecule obeying the octet rule, simply use the following prescription:

- Determine the number of electrons required (ER) to give each isolated non-hydrogen atom eight electrons and each hydrogen two electrons. ER is eight times the number of non-hydrogen atoms (N_A) plus two times the number of hydrogen atoms (N_H).

$$ER = 8N_A + 2N_H$$

- Determine the number of valence electrons in the molecule (VE), which is the number of electrons that must be shown in the final structure.
- The difference, ER - VE, divided by 2 is the number of shared pairs (SP).
$$SP = \frac{1}{2}(ER - VE)$$
- Draw the molecule with the bonded atoms connected by single bonds. Then satisfy the number of shared pairs required (SP) by adding double or triple bonds as necessary. Finally, add lone pairs of electrons to complete each atom's octet, but remember that hydrogen atoms have only two electrons.

The following should also be considered when constructing a Lewis structure:

- The first atom in the formula is the least electronegative and is generally the central atom.
- Hydrogen atoms have only one bond.
- Multiple bonds should not be drawn to terminal halogen atoms.* More than one single bond can be drawn to a halogen when it is the central atom, as in the perchlorate ion (ClO_4^{1-}).

* The halogens are the elements of Group 7A (F, Cl, Br, and I).

Example 5.4

Draw the Lewis structure for carbon dioxide, CO_2

- ER = 3 atoms x 8 electrons/atom = 24 electrons.
- VE = 4 from carbon + 6 from each oxygen = $4 + (2)(6) = 16$ valence electrons. Our Lewis structure must show eight pairs of electrons.
- SP = $\frac{1}{2}(24 - 16) = 4$ pairs must be shared.
- The four shared pairs can be distributed as two double bonds (Figure 5.8A) or as a single and a triple bond (Figures 5.8B). In Section 5.8, we explain why structure A better represents the bonding in CO_2 .



Figure 5.8 Two possible Lewis structures of CO_2

5.7 RESONANCE

Resonance structures are Lewis structures that differ only in the placement of electrons.

The two structures of CO_2 shown in Figure 5.8 are two resonance structures. The most common form of resonance results when multiple bonds can be placed in more than one position. When the resonance structures are clearly different, it is usually the case that only one of the structures is important in the description of the bonding. Thus, only one of the two resonance structures shown for CO_2 in Figure 5.8 is expected to be important.

Example 5.5

How many resonance forms can be drawn for SO_2 ?

Use the method presented in Section 5.6 to determine the Lewis structure:

1. ER = 3 atoms x 8 electrons/atom = 24 electrons.
2. VE = 6 from sulfur + 6 from each oxygen = 6 + (2)(6) = 18 valence electrons. The Lewis structure must contain nine pairs of electrons.
3. SP = $\frac{1}{2} (24 - 18) = 3$ pairs must be shared.
4. The three shared pairs must be distributed as one double bond and one single bond, but the double bond can be placed between the sulfur and either oxygen.

Thus, SO_2 exists in two resonance forms, as shown in Figure 5.9.

When the different resonance forms are equivalent, each form contributes equally to the bonding. The two resonance structures of SO_2 shown in Figure 5.9 are equivalent, so the bonding is the average of both forms. Consequently, one of the bonding pairs is shared between the two equivalent bonds, and neither bond is a single or double bond. The two sulfur-oxygen bonds in sulfur dioxide are of equal length, both being shorter than a S-O single bond but longer than a S=O double bond. The bond order of each of the bonds affected by the resonance is equal to the number of bonding pairs involved in those bonds divided by the number of bonding regions in which the bonds can be found. In SO_2 , there are three bonding pairs spread over two sulfur-oxygen bonding regions, so the sulfur-oxygen bond order in SO_2 is $(3 \text{ bonding pairs})/(2 \text{ bonding regions}) = 1.5$. Resonance in SO_2 results because one of the bonding pairs is spread over both bonding regions rather than localized in one. Note that curved arrows are used to show a mechanism that converts between the two resonance forms. Curved arrows from a lone pair to a bond indicate that the lone pair becomes a bonding pair, while a curved arrow from a bond to an atom indicates that the bond becomes a lone pair.

5.8 FORMAL CHARGE AND OXIDATION STATE

Bonding can result in an uneven distribution of the bonding electrons to produce electrically charged regions within a molecule. Chemists use these regions of charge to explain both chemical and physical properties of the molecules, so assigning charge to the atoms in a molecule is an important task in chemistry. Charge is assigned to the atoms by *assigning* each of the valence electrons in a molecule to one of the atoms. The nonbonding electrons are readily assigned to their atoms, but in order to assign the bonding electrons,

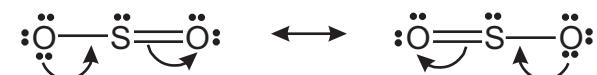


Figure 5.9 Two resonance forms of SO_2

Note that resonance is indicated by a line with arrows at both ends, and that curved arrows are used to show the movement of electron pairs. A curved arrow from a lone pair to a bond indicates that the lone pair becomes a bond, and a curved arrow from a bond to an atom indicates that the bonding pair becomes a lone pair on that atom.

the type of bond, ionic or covalent, must first be established. If the bonds are assumed to be covalent, the resulting charge on the atom is called its **formal charge**, but if they are assumed to be ionic, the charge is the atom's **oxidation state**. Thus, oxidation states better describe ionic substances, while formal charge is a better description in covalent substances. However, as the bonds in a covalent substance become more polar, the charge distribution becomes more like the oxidation states. The **assigned charge** on an atom in a molecule is equal to the number of valence electrons in the free (neutral) atom minus the number of valence electrons assigned to the atom in the molecule. The number of valence electrons in the free atom (VE) is given by the atom's group number. The number of electrons assigned to the atom in the molecule is the number of nonbonding electrons (NB) shown in the Lewis structure plus those bonding electrons (BE) that are assigned to it. In the following, we show that the only difference between the formal charge and oxidation state of an atom is how BE is determined.

FORMAL CHARGE

To determine the **formal charge** (FC) on an atom, we assume that all of the bonds are purely covalent. In a covalent bond, the bonding electrons are shared equally, so each atom is assigned all of its nonbonding electrons (NB) but only *half* of its bonding electrons ($\frac{1}{2}$ BE). As a result, the formal charge of atom A (FC_A) is determined to be

$$FC_A = VE - (NB + \frac{1}{2} BE) \quad \text{Eq. 5.1}$$

The sum of the formal charges must equal the charge on the species (zero for a molecule). For example, the sum of the formal charges on the nitrogen and three oxygen atoms in NO_3^{1-} must equal -1, the charge on the ion.

Consider the nitrogen atom in ammonia shown in Figure 5.10. A free nitrogen atom has five valence electrons ($VE = 5$), but the nitrogen atom in NH_3 is surrounded by six bonding electrons and two nonbonding electrons. The N-H bonding electrons are assumed to be shared equally between N and H when determining formal charge, so only one-half of the bonding electrons are assigned to the nitrogen. The formal charge on the nitrogen is determined with Equation 5.1 to be $FC_N = 5 - [2 + \frac{1}{2}(6)] = 0$. For the H atoms, NB = 0 and BE = 2, so $FC_H = 1 - [0 + \frac{1}{2}(2)] = 0$. We conclude that there is no non-zero formal charge in ammonia, and the sum of the formal charges is zero, which it must be for a molecule.

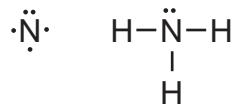


Figure 5.10 Lewis formulas of a nitrogen atom and the ammonia molecule

Example 5.6

Determine the formal charges on the atoms in SO_2 .

The Lewis structure of SO_2 : $\ddot{\text{O}}-\ddot{\text{S}}=\ddot{\text{O}}$

1. The oxygen atom that is shown with the double bond has four nonbonding electrons plus one-half of the four bonding electrons. Thus, the Lewis structure puts a total of six valence electrons around the oxygen. The number of valence electrons in a free oxygen atom is also six, so this oxygen atom has no formal charge.
2. The oxygen atom that is shown with a single bond has six nonbonding electrons and one-half of the two bonding electrons, for a total of seven valence electrons. This is one more electron than the free atom, so this oxygen carries a -1 formal charge.
3. The sulfur atom contains two nonbonding electrons and one-half of six bonding electrons, for a total of five valence electrons. A free sulfur atom has six valence electrons. Thus, the number of valence electrons around a sulfur atom in SO_2 is one less than around a free atom, so sulfur carries a +1 formal charge.

Nonzero formal charges should always be indicated in a Lewis structure by showing the formal charge with a circle around it. The Lewis structures of the two resonance forms of SO_2 are shown in Figure 5.11.

When more than one Lewis structure can be drawn for a molecule, formal charge can be used to help determine the preferred structure because energy is required to separate positive and negative charge (Coulomb's law). Consequently, a Lewis structure that shows no formal charge is energetically favored over one that does. In addition, electrons are more likely to reside on electronegative atoms. We conclude the following:

The Lewis structure that is preferred is the one in which the formal charges of all atoms are closest to zero. If non-zero formal charge must be assigned, negative formal charge should reside on the more electronegative atoms.

An atom has zero formal charge in a molecule if the number of bonds in which it is involved is equal to the number of unpaired electrons in its Lewis symbol (Figure 5.5). Table 5.4 summarizes this fact for the atoms encountered most frequently. Because structures with zero formal charge are preferred, the numbers of bonds shown in Table 5.3 are the ones most frequently drawn for these atoms. However, there are many cases in which the formal charges are not zero,* and the number of bonds to the atom is different from the number shown in the table.



Figure 5.11 Formal charge in SO_2

Lewis structures of sulfur dioxide that show all non-zero formal charge. Recall that the line with an arrow at each end is used to indicate resonance.

Table 5.4 The number of bonds to an atom that results in zero formal charge.

Atom	Number of bonds
C	4
N	3
O	2
F, Cl, Br, I	1

* Carbon has zero formal charge in all of its compounds, so **four bonds are always drawn to carbon atoms in their compounds!** Carbon is the basis of organic chemistry, and the number of compounds that contain carbon is infinite, so this is a very important rule that will aid us in drawing many Lewis structures.

Example 5.7

- a) Which of the two resonance forms of CO_2 shown in Example 5.4 is preferred? Refer to Figure 5.12 for the Lewis structures of the two resonance forms.

Structure A: Each oxygen has four nonbonding electrons and one-half of the four bonding electrons, for a total of six valence electrons. Thus, both oxygen atoms have zero formal charge. Alternatively, each oxygen has zero formal charge because each is involved in two bonds. The carbon has one-half of the eight bonding electrons for a total of four valence electrons, which is the same as the free atom. Consequently, the carbon atom also has a zero formal charge. Alternatively, each carbon has zero formal charge because each is involved in four bonds.

Structure B: Neither oxygen has two bonds, so they each have nonzero formal charge. The triple bonded oxygen has two nonbonding electrons and one-half of six bonding electrons, for a total of five valence electrons, one less than the free atom. Thus, this oxygen carries a +1 formal charge. The single bonded oxygen contains six nonbonding and one-half of two bonding electrons, for a total of seven valence electrons, one more than the free atom. It, therefore, carries a -1 formal charge. The carbon has one-half of eight bonding electrons and therefore a zero formal charge.

Structure A is preferred because it has no charge separation.

- b) The Lewis structure of FCHO requires four shared pairs. Use formal charge to decide which of the structures in the margin is preferred.

Structure A: $\text{FC}_\text{F} = 7-6-1 = 0$; $\text{FC}_\text{O} = 6-4-2 = 0$; $\text{FC}_\text{C} = 4-0-4 = 0$

Structure B: $\text{FC}_\text{F} = 7-4-2 = +1$; $\text{FC}_\text{O} = 6-6-1 = -1$; $\text{FC}_\text{C} = 4-0-4 = 0$

Structure C: $\text{FC}_\text{F} = 7-4-2 = +1$; $\text{FC}_\text{O} = 6-4-2 = 0$; $\text{FC}_\text{C} = 4-2-3 = -1$

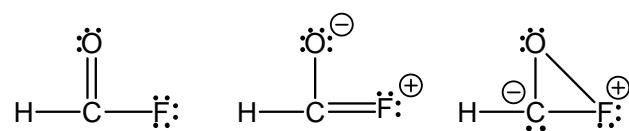
Structures B and C both place two bonds to F, which puts positive formal charge on the most electronegative atom. There is only a single shared pair to F in Structure A, so it has no formal charge. Structure A is the preferred structure because it contains no formal charge – only one bond to a terminal halogen and four bonds to carbon.

Example 5.7 demonstrates that *placing more than one bonding pair to a halogen should be avoided* because it places positive formal on these electronegative atoms. Placing positive formal charge on a halogen is unavoidable in compounds or ions in which it is the central atom. However, the other atoms are highly electronegative in these cases, so the positive formal charge is more reasonable. For example, the formal charge on Cl in ClO_4^{1-} is +3. Recall from Chapter 4, that the oxidation state of Cl in ClO_4^{1-} is +7, so a formal charge of +3 is still much less than the charge the chlorine atom would have if the bonds were ionic.



Figure 5.12

Structure A is the preferred resonance form of CO_2 because there is no charge separation. The non-zero formal charges on the oxygen atoms in structure B make it less favorable.



Example 5.7b

OXIDATION STATE

The **oxidation state** or **oxidation number** of atom A (OX_A) was defined in Section 4.4 as the charge the atom would have if all bonds were *ionic*; that is, if all of the bonding electrons were assigned to the more electronegative atom in each bond.

$$\text{OX}_A = \text{VE} - (\text{NB} + \sum_j a_j \text{BE}) \quad \text{Eq. 5.2}$$

The sum is over all bonds in which that atom is involved. $a_j = 1$ if the atom is the more electronegative atom in the j^{th} bond, and $a_j = 0$ if the atom is the less electronegative atom in the bond. In cases where the two bound atoms are identical, the bonding electrons are assigned to each atom equally (*i.e.*, $a_j = \frac{1}{2}$).

Using the method presented in Section 4.4 to determine oxidation states leads to the average oxidation state of each atom type in a compound, not to the oxidation state of each individual atom. This is the reason that fractional oxidation states are sometimes encountered. For example, the oxidation state of iron in Fe_3O_4 as determined by the methods of Chapter 4 is $\frac{8}{3}$, which is the average of the three iron atoms: two at +3 and one at +2. Although, the method outlined in Chapter 4 is the more common, the method that uses Lewis structures is instructive and is presented here.

Consider the oxidation states of the atoms in ammonia. Nitrogen is more electronegative than hydrogen, so $a = 1$ for N and $a = 0$ for H and all six bonding electrons are assigned to the nitrogen. The oxidation states are determined as follows:

$$\text{OX}_N = 5 - (2 + 6) = -3 \quad \text{OX}_H = 1 - 0 = +1$$

Note that these values are the same as determined in Chapter 4.

Example 5.8

- a) Determine the oxidation state of carbon in acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) using the rules given in Section 4.4.

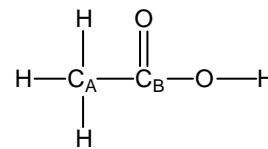
The oxidation states of H and O are +1 and -2, respectively. The sum of the oxidation states of the atoms in a molecule must sum to zero, so we write $2x + 4(1) + 2(-2) = 0$, where x is the oxidation state of the carbon atom. Solving for x , we determine the oxidation state of carbon to be 0.

- b) Use electron counting and the Lewis Structure of acetic acid shown in the margin to determine the oxidation states of the individual carbon atoms.

C_A is assigned all of the C-H bonding electrons ($a = 1$ because C is more electronegative) and one of the two C-C bonding electrons ($a = \frac{1}{2}$ because the atoms are identical). BE = 7 for C_A . C_B is assigned one electron from the C-C bond but none from the C=O or C-O bonds because O is more electronegative. BE = 1 for C_B . Neither atom has any nonbonding electrons, so we can write the following:

Atom	VE	NB	BE	Oxidation State (OX)
C_A	4	0	7	$4 - [0 + 7] = -3$
C_B	4	0	1	$4 - [0 + 1] = +3$

One atom is -3 , while one is $+3$. The average of both carbon atoms is 0, the result obtained in Part a.



Example 5.8b Acetic acid, $C_2H_4O_2$

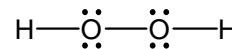
Example 5.9

What are the oxidation states of the atoms in H_2O_2 (hydrogen peroxide)?

The Lewis structure of hydrogen peroxide is shown in the margin.

Oxygen is more electronegative than hydrogen, so the O-H bonding electrons are assigned to the oxygen atom. The oxidation state of each hydrogen atom is $OX_H = 1 - [0 + (0 \times 2)] = +1$. The two oxygen atoms have identical electronegativities, so the O-O bonding electrons are shared equally between the two oxygen atoms, but the O-H bonding electrons are assigned to the oxygen. The oxidation state of each oxygen atom is then determined to be -1 . The oxidation state of oxygen is -1 in peroxides.

$$OX_O = 6 VE - [4 NB + (1)(2 BE_{O-H}) + (\frac{1}{2})(2 BE_{O-O})] = -1.$$



Example 5.9 Lewis structure of hydrogen peroxide

5.9 PRACTICE WITH LEWIS STRUCTURES

We conclude this chapter with several examples of drawing Lewis structures and determining formal charge and oxidation numbers.

Example 5.10

Draw the Lewis structure of SO_3 , indicate all nonzero formal charges, and determine the oxidation state of each atom.

1. ER = (4 atoms)(8 electrons/atom) = 32 electrons.
2. VE = (1)(6) from sulfur + (3)(6) from oxygen = 24 valence electrons or 12 pairs.
3. SP = $\frac{1}{2}(32 - 24)$ = 4 pairs must be shared in the three sulfur-oxygen bonds.

The Lewis structure of SO_3 shows 24 electrons in four shared pairs and eight lone pairs. The three sulfur-oxygen bonds share the double bond because the three resonance structures are identical. The actual structure is a combination of all three structures shown in the margin, and the S-O bond order is $\frac{4}{3}$ (four shared pairs in three S-O bonds). Note that Lewis structures always include all equivalent resonance forms. The nonzero formal charges are acceptable here because (1) no Lewis structure can be drawn for SO_3 that has all zero formal charges, and (2) the negative formal charge resides on the more electronegative oxygen atoms.

The formal charges on the atoms are

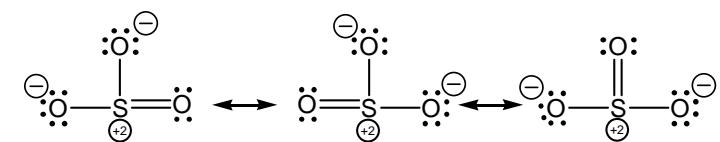
$$\begin{aligned} \text{FC}_S &= 6 \text{ VE} - [0 \text{ NB} + \frac{1}{2}(8 \text{ BE})] = +2 \\ \text{FC}_O &= 6 \text{ VE} - [4 \text{ NB} + \frac{1}{2}(4 \text{ BE})] = 0 \quad (\text{double bonded O}) \\ \text{FC}_O &= 6 \text{ VE} - [6 \text{ NB} + \frac{1}{2}(2 \text{ BE})] = -1 \quad (\text{each single bonded O}) \end{aligned}$$

The sum of the formal charges is $+2 + 0 + 2(-1) = 0$, as it must be for a molecule.

Oxygen is more electronegative than sulfur, so the oxidation states are:

$$\begin{aligned} \text{OX}_S &= 6 \text{ VE} - [0 \text{ NB} + (0)(8 \text{ BE})] = +6 \\ \text{OX}_O &= 6 \text{ VE} - [4 \text{ NB} + (1)(4 \text{ BE})] = -2 \quad (\text{double bonded O}) \\ \text{OX}_O &= 6 \text{ VE} - [6 \text{ NB} + (1)(2 \text{ BE})] = -2 \quad (\text{each single bonded O}) \end{aligned}$$

Note that the sum of the oxidation states is $+6 + (-2) + 2(-2) = 0$.



Example 5.10 Resonance structures of SO_3

Example 5.11

Draw the Lewis structure of SO_3^{2-} , indicate all nonzero formal charges, and determine the oxidation state of each atom.

1. ER = $4 \times 8 = 32$ electrons
2. VE = (1)(6) from S + (3)(6) from O + 2 for the -2 charge = 26 valence electrons
3. SP = $\frac{1}{2}(32 - 26) = 3$ pairs must be shared.

All three SO bonds are single bonds because there are only three shared pairs to bond three oxygens to the sulfur. The three shared pairs give the sulfur six electrons, so it needs 1 lone pair to complete its octet. Each oxygen must have three lone pairs to obtain an octet. Note that 26 electrons are shown in the structure in the margin.

The formal charges are determined as follows:

$$FC_S = 6 \text{ VE} - [2 \text{ NB} + \frac{1}{2}(6 \text{ BE})] = +1 \text{ and } FC_O = 6 \text{ VE} - [6 \text{ NB} + \frac{1}{2}(2 \text{ BE})] = -1.$$

Note the sum of the formal charges is $+1 + 3(-1) = -2$, the charge on the ion. The negative charge on the ion is distributed equally among the three oxygen atoms.

Oxygen is more electronegative than sulfur, so the oxidation states are:

$$OX_S = 6 \text{ VE} - [2 \text{ NB} + (0)(6 \text{ BE})] = +4 \text{ and } OX_O = 6 \text{ VE} - [6 \text{ NB} + (1)(2 \text{ BE})] = -2.$$

Because oxygen is very electronegative, the bonding electrons are almost always assigned to it, which gives it a -2 oxidation state in most of its compounds. The sum of the oxidation states is $+4 + [3 \times (-2)] = -2$, the charge on the ion.

Example 5.12

Draw the Lewis structure of C_2H_4 , indicate all nonzero formal charges, and determine the oxidation state of each atom.

$$ER = (2)(8) \text{ for C} + (4)(2) \text{ for H} = 24 \text{ electrons.}$$

$$VE = (2)(4) \text{ from C} + (4)(1) \text{ from H} = 12 \text{ valence electrons, or 6 pairs.}$$

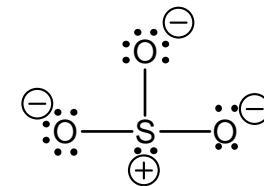
$$SP = \frac{1}{2}(24 - 12) = 6 \text{ pairs must be shared. There are no lone pairs.}$$

Each H atom can have only one shared pair, so the four C-H bonds require four shared pairs, which leaves two shared pairs for the C-C bond. All atoms have zero formal charge. The Lewis structure is shown in the margin.

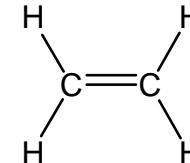
Carbon is more electronegative than hydrogen, but the two carbons have the same electronegativities, so the C=C bonding electrons are divided equally between the carbons when determining the oxidation states. Therefore,

$$OX_C = 4 \text{ VE} - [0 \text{ NB} + 4 \text{ BE}_{C-H} + \frac{1}{2}(4 \text{ BE}_{C=C})] = -2$$

$$OX_H = 1 \text{ VE} - 0(2 \text{ BE}) = +1.$$



Example 5.11 Lewis structure of SO_3^{2-} that shows all non-zero formal



Example 5.12 Lewis structure of C_2H_4

Example 5.13

Draw the Lewis structure of acetone (C_3H_6O), indicate all nonzero formal charges, and determine the oxidation state of each atom. The oxygen atom is attached to the central carbon atom, and there are no O-H bonds.

$$ER = 3(8) \text{ for C} + 1(8) \text{ for O} + 6(2) \text{ for H} = 44 \text{ electrons}$$

$$VE = 3(4) \text{ from C} + 1(6) \text{ from O} + 6(1) \text{ from H} = 24 \text{ valence electrons}$$

$$SP = \frac{1}{2}(44 - 24) = 10 \text{ pairs must be shared.}$$

The skeleton formed by the carbon and oxygen atoms that is consistent with the given information, which is shown in the margin figure labeled Example 5.13a, contains three shared pairs. The skeleton with the six C-H bonds will require another six pairs, for a total of nine pairs. Ten shared pairs are required, so there must be a double bond, which cannot be drawn to a hydrogen atom. Therefore, there is either a C=C or C=O double bond. We use the fact that carbon always has four bonds to decide where the double bond must be. If the double bond is a C=C bond, then one of the terminal atoms can have only two C-H bonds (1 C=C + 2 C-H = 4 bonds), and the central carbon will have four bonds (1 C-C + 1 C-O + 1 C=C). Only three C-H bonds can be drawn to the other carbon atom, so the sixth H would have to be bound to O, which is a violation of the given information. We conclude that the double bond must be a C=O bond to arrive at the structure shown as the margin figure labeled Example 5.13b.

The oxidation states are determined by again dividing the C-C bonding electrons between the carbon atoms and assigning the C-H bonding electrons to the more electronegative carbon atom. The C=O bonding electrons are assigned to the oxygen. Therefore, the oxidation states of the carbon atoms can be determined to be

$$OX_C = 4 VE - [0 NB + 6BE_{C-H} + \frac{1}{2}(2 BE_{C-C})] = -3 \quad (\text{terminal carbons})$$

$$OX_C = 4 VE - [0 NB + \frac{1}{2}(4 BE_{C-C}) + 0(4 BE_{C=O})] = +2 \quad (\text{central carbon})$$

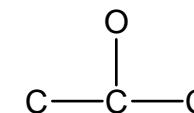
Thus, the three carbon atoms have an average oxidation state of $(-3 - 3 + 2)/3 = -4/3$. Using the method of Section 4.4, we would determine the oxidation state of carbon in C_3H_6O as $3OX_C + 6(+1) + 1(-2) = 0$, which also yields $-4/3$. Thus, the method in Section 4.4 determines the average oxidation state of each atom in a molecule, while the method presented in this chapter determines the oxidation state of each individual atom.

The oxygen is assigned all four bonding electrons, so its oxidation state is

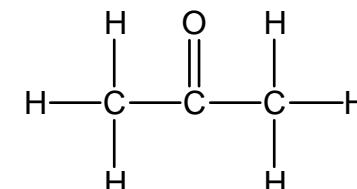
$$OX_O = 6 VE - [4 NB + 4 BE] = 6 - 8 = -2$$

No bonding electrons are assigned to the hydrogen, so its oxidation state is

$$OX_H = 1 VE - [0 NB + 0 BE] = +1$$



(a) Skeletal structure



(b) Lewis Structure

5.10 CHAPTER SUMMARY AND OBJECTIVES

Covalent bonds result when bonding electrons are shared. The energy of the bound atoms is less than that of the separated atoms because the bonding electrons experience the positive charge of both nuclei. The energy required to break the bond is called the bond energy. When the electronegativities of the atoms are different, the bonding electrons are not shared equally to produce a bond dipole. The polarity of a bond increases as the electronegativity difference between the two atoms increases. The less electronegative atom is written first in the formula and maintains its name, while the more electronegative element is written last, and its ending is changed to *-ide*. The number of each atom present in the formula is given by a prefix.

Lewis structures show the valence electrons in a compound as dots if they are in lone pairs or lines if they are bonding pairs. The number of shared pairs is determined as $SP = \frac{1}{2}(VE - ER)$. The number of shared pairs in a bond is called the bond order. Resonance structures are Lewis structures that differ only in the placement of the electron pairs.

Electron counting can be done with formal charge or oxidation state. Bonding electrons are assigned equally to the bound atoms in the formal charge, but they are assigned to the more electronegative element in the oxidation state. Thus, formal charge is a better description of charge distribution in purely covalent compounds, while oxidation state gives a better picture in very polar or ionic compounds.

After studying the material presented in this chapter, you should be able to:

1. describe the covalent bond (Section 5.1);
2. predict relative bond polarities (Section 5.2);
3. distinguish between an ionic and a covalent bond (Section 5.2);
4. name binary compounds formed from nonmetals (Section 5.3);
5. identify bonded and nonbonded electrons (Section 5.5);
6. determine the number of valence electrons in a molecule (Sections 5.4 and 5.5);
7. draw Lewis structures (Section 5.6);
8. determine bond orders of all bonds in a Lewis structure (Sections 5.5 and 5.6);
9. identify and draw different resonance forms (Section 5.7);
10. distinguish between a formal charge and an oxidation state (Section 5.8);
11. assign formal charges and oxidation states to the atoms in compounds (Section 5.8);
and
12. identify important resonance forms based on formal charges (Section 5.8).

5.11 EXERCISES

1. What two opposing forces dictate the bond length? (Why do bonds form, and what keeps the bonds from getting any shorter?)
2. Why is a Br-Br bond longer than a F-F bond?
3. List the following bonds in order of increasing length: H-Cl, H-Br, H-O.
4. Use the electronegativities to describe the following bonds as purely covalent, mostly covalent, polar covalent, or ionic.

a) C-H	b) Si-O	c) Sn-Cl	d) Rb-Cl
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5. Use the electronegativities to describe the following bonds as purely covalent, mostly covalent, polar covalent, or ionic.

a) P-Cl	b) K-O	c) N-H	d) In-Br
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6. Name the following compounds:

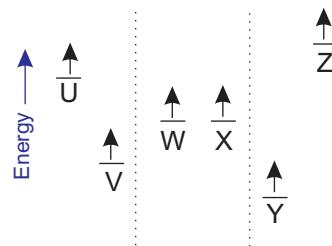
a) XeF ₆	b) N ₂ O ₃	c) BCl ₃	d) NH ₃
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7. Name the following compounds:

a) S ₂ Cl ₂	b) CCl ₄	c) PCl ₅	d) HCl
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8. Name the following compounds:

a) Hg ₂ Cl ₂	b) CS ₂	c) NO	d) CsCl
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9. Write formulas for each of the following compounds:

a) dinitrogen tetroxide	b) nitrogen monoxide	c) dinitrogen pentoxide
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10. Write formulas for each of the following compounds:

a) oxygen difluoride	b) phosphorus trichloride	c) chlorine trifluoride
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11. Use the orbital diagrams for the orbitals involved in the U-V, W-X, and Y-Z bond shown below to determine if the bond is polar. If so, indicate the direction of the bond dipole with an arrow. Rank the bonds in order of increasing polarity.



12. Use an arrow to indicate the bond dipole direction in each of the following bonds:

a) C-F	b) C-Si	c) Cl-F	d) Cl-I
---------------	----------------	----------------	----------------
13. Use an arrow to indicate the bond dipole direction in each of the following bonds:

a) S-O	b) C-H	c) O-H	d) C-O
---------------	---------------	---------------	---------------
14. Use only the position of the atoms on the periodic table to list the following bonds in order of decreasing polarity:

a) O-F, C-F, Ga-F	b) H-O, H-S, H-Cl	c) S-O, Cl-O, P-O
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15. Use only the position of the atoms on the periodic table to list the following bonds in order of decreasing polarity:

a) S-O, Se-O, As-O	b) F-F, H-F, N-F	c) P-Cl, Sb-Cl, Sn-Cl
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16. For each of the species listed below, indicate the number of electrons required to give each atom an octet or duet (ER), the number of valence electrons (VE), and the number of shared pairs (SP) in the Lewis structure.

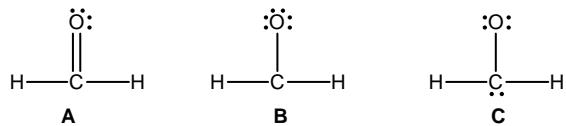
a) C ₆ H ₆	b) C ₃ O ₂	c) NH ₂ ⁻¹⁻	d) PH ₄ ¹⁺
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17. For each of the species listed below, indicate the number of electrons required to give each atom an octet or duet (ER), the number of valence electrons (VE), and the number of shared pairs (SP) in the Lewis structure.

a) N ₂ O ₄	b) CH ₄ O	c) HBrO ₂	d) S ₂ O ₈ ²⁻
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18. Draw Lewis structures for each of the following molecules, and indicate all nonzero formal charges. Note that O₃ is not triangular, and the skeleton of S₂N₂ is N-S-S-N.

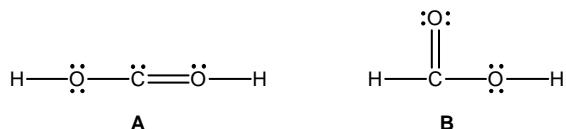
a) PF ₃	b) O ₃	c) S ₂ N ₂	d) N ₂ H ₂
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19. Organic compounds are those based on carbon. Because of the way carbon atoms can bond to one another, there are literally an infinite number of organic compounds. Drawing Lewis structures of organic compounds is very important, and the procedure is simplified because there are always four bonds drawn to a carbon atom (a double bond counts as two bonds and triple bond as three). Draw Lewis structures for each of the following organic compounds and indicate all nonzero formal charges.

a) C ₂ H ₂	b) C ₃ H ₄	c) C ₃ H ₆	d) COF ₂
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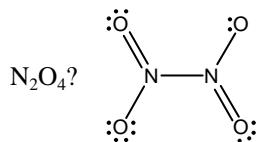
20. Draw Lewis structures for each of the following ions and indicate all nonzero formal charges.
- CO_3^{2-}
 - NH_4^{1+}
 - CHO_2^{1-}
 - ClO_2^{1-}
21. Draw Lewis structures for each of the following ions and indicate all nonzero formal charges.
- NO_3^{1-}
 - NO^{1+}
 - N_3^{1-}
 - NO_2^{1-}
22. For which molecules in Exercises 18 and 19 are more than one resonance form important?
23. For which ions in Exercises 20 and 21 are more than one resonance form important?
24. Indicate all nonzero formal charge on the resonance structures of formaldehyde shown below and rank the structures in order of importance in describing the bonding. Explain your reasoning.



25. Which of the Lewis structures of formic acid shown below is preferred? Justify your answer.

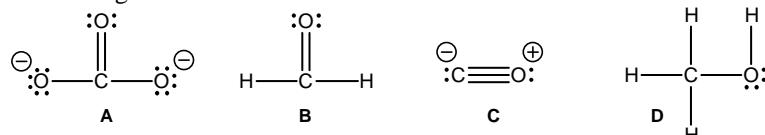


26. The hypochlorite ion, ClO^{1-} , is the active ingredient in bleach. Draw its Lewis structure and determine the formal charges and oxidation states of both atoms. Hypochlorous acid is made by adding H^{1+} to the hypochlorite ion. Based on the formal charges, does hypochlorous acid have an H-Cl bond or an H-O bond?
27. What are the formal charges and oxidation states of the nitrogen atoms in N_2O_4 ?



28. Draw three resonance structures for the hyponitrite ion, $\text{N}_2\text{O}_2^{2-}$ (one N-N bond and two N-O bonds) and show all nonzero formal charges. Which structure is the preferred structure? Justify your answer.

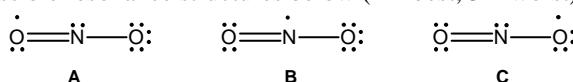
29. List the following in order of increasing carbon-oxygen bond lengths and bond energies:



30. List the following in order of increasing nitrogen-oxygen bond lengths and bond energies: NO_3^{1-} , NO^{1+} , NOCl , NO_2^{1-}

31. List the following in order of increasing nitrogen-nitrogen bond lengths and bond energies: N_2H_2 , N_2 , N_2H_4 .

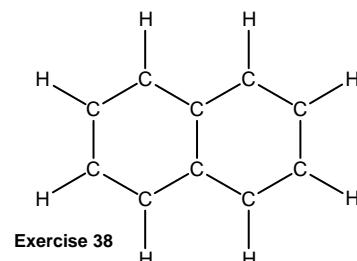
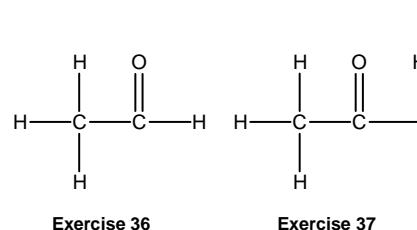
32. NO_2 has an odd number of electrons. Using only formal charge, rate the three possible resonance structures below (1 = best, 3 = worst).



The lone electron on two NO_2 molecules combines to form N_2O_4 with the Lewis structure shown in Exercise 27. Based on this fact where is the lone electron on NO_2 ? The difference is due to the fact that the oxygen atom is so electronegative that it takes the electrons it needs to fill its valence shell.

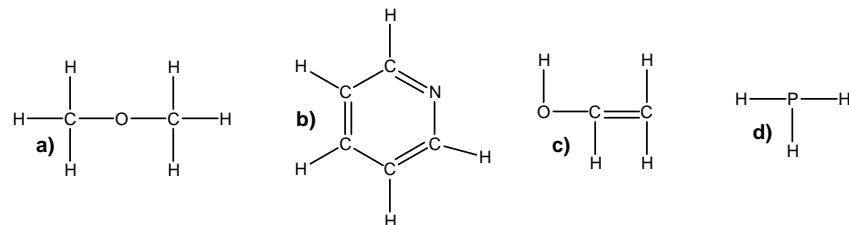
33. Draw two structures for BF_3 , one that obeys the octet rule and one in which boron is electron deficient. Based on formal charge considerations, which structure is preferred?
34. Exercises 32 and 33 are examples of exceptions to the octet rule. What atom is the most common exception to the octet rule?
35. Draw Lewis structures that show all nonzero formal charge for the three resonance forms of the cyanate ion (NCO^{1-}) and the fulminate ion (CNO^{1-}). In each case, determine the resonance structure that is most important in describing the bonding in the ion. The cyanate ion is a stable ion, but the fulminate ion is used in explosives. Suggest a reason for this dramatic difference in stability.

Use the following Lewis structures for Exercises 36–38.



- 36.** In compounds with more than one atom of the same type, the oxidation state of those atoms derived from the procedure presented in Section 4.4 leads to the average oxidation state of the atom, not the oxidation states of the individual atoms. For example, consider the molecule $\text{C}_2\text{H}_4\text{O}$.
- Use the method of Section 4.4 to determine the oxidation state of the carbon.
 - Use the Lewis structure of the compound shown in the margin and the method presented in Section 5.8 to determine the oxidation state of each carbon atom in $\text{C}_2\text{H}_4\text{O}$. Does either carbon have the oxidation state derived in part a?
- 37.** Apply the discussion given in Exercise 36 to acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ (See above for the Lewis structure.)
- Use the method of Section 4.4 to determine the oxidation state of the carbon.
 - Use the Lewis structure of acetic acid shown to the right and the method presented in Section 5.8 to determine the oxidation state of each carbon atom in $\text{HC}_2\text{H}_3\text{O}_2$. Does either carbon have the oxidation state derived in part a?
- 38.** Add double bonds to the Lewis structure of naphthalene (C_{10}H_8 , see top of page for the Lewis structure), the active ingredient in mothballs, so that each carbon atom has an octet. How many resonance structures can be drawn for naphthalene? Estimate the lengths of the carbon-carbon bonds.
Hint: refer to Table 5.3 and the discussion in Section 5.7.

- 39.** Lone pairs are often left out of molecular drawings, but, as we shall see in Chapter 6, they are important in determining the shape of the molecule. Indicate any missing lone pairs in the following. (Assume that all atoms except H obey the octet rule.)



Chapter 6

Molecular Structure & Bonding

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|---|--|
| <i>6.0 Introduction</i> | <i>6.4 Valence Bond Theory and Hybridization</i> |
| <i>6.1 Molecular Shapes</i> | <i>6.5 Molecular Orbital Theory and Delocalized Bond</i> |
| <i>6.2 Central Atoms with Expanded Valence Shells</i> | <i>6.6 Chapter Summary and Objectives</i> |
| <i>6.3 Larger Molecules</i> | <i>6.7 Exercises</i> |
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6.0 INTRODUCTION

A molecule is characterized by its three-dimensional structure, which is the arrangement of its nuclei. The positions of the nuclei are determined by the lengths of the bonds between them and the angles at which those bonds intersect. A molecular structure plays a key role in determining both the physical and chemical properties of the molecule. The positions, strengths, and polarities of the bonds influence a molecule's reactivity. Size and shape are primary factors in governing the cellular processes in which biomolecules, like proteins and DNA, participate. The structure of a molecule dictates whether it is a solid, liquid, or gas at a given set of conditions.

In this chapter, we apply increasingly sophisticated models to the study of structure and bonding. We first use the valence-shell electron-pair repulsion model (electrostatic arguments) to describe the arrangements of electron groups around an atom. Then we explain how and why bonds are formed with valence bond theory. We conclude the chapter with a brief introduction into molecular orbital theory to explain shortcomings in the valence bond theory and to introduce the electronic structure of molecules.

THE OBJECTIVES OF CHAPTER 6 ARE TO:

- explain the VSEPR (valence-shell electron-pair repulsion) model and demonstrate how to use it to predict the geometry of the electron regions around a central atom;
- show how to extend the VSEPR model to larger molecules;
- describe valence bond theory;
- distinguish between sigma and pi bonding;
- define hybridization and show how it is used;
- use molecular orbital theory to explain delocalized bonding; and
- infer the structure and bonding in a molecule from its Lewis structure.

6.1 MOLECULAR SHAPES

Just as a two-dimensional blueprint provides information about a three-dimensional building, the Lewis structure of a molecule provides information about the three-dimensional structure of a molecule. The transition from a two- to a three-dimensional structure is accomplished with the valence-shell electron-pair repulsion (VSEPR) model. VSEPR is based on the premise that the regions of negative charge around an atom adopt positions that minimize the repulsions between them.

Our discussion uses the general terms ‘electron groups’ and ‘electron regions’ rather than ‘electron pairs’ in describing the results of VSEPR. An electron group or region can be a lone pair*, a single bond, a double bond, or a triple bond. A lone pair and a single bond each consist of a single electron pair and constitute a single electron region. A double bond consists of two electron pairs, but both pairs lie in the region between the two bound nuclei, so they cannot move away from one another. Consequently, the two electron pairs in a double bond represent a single electron region that minimizes its interactions with other electron regions. Similarly, the three electron pairs of a triple bond represent a single electron region because the three pairs cannot move apart.

Atoms obeying the octet rule can have only two, three, or four electron groups, and Figure 6.1 shows the orientations of the groups as predicted by VSEPR. Two electron groups are oriented such that the angle between them is 180° (Figure 6.1a). Three electron groups reside in a plane with an angle of 120° between them (Figure 6.1b). Four electron groups disperse themselves in the directions shown in Figure 6.1c. The angle between any two groups in the four-electron group arrangement is 109° .

The angles between the groups shown in Figure 6.1 assume that the electron groups are all the same. When the electron groups surrounding a central atom are not identical, the interactions between the groups are not identical, and the angles deviate somewhat from those given in the figure. The relative strengths of the interactions are

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

The **bond angles**, which are the angles formed by the intersection of the bonds, are an important characteristic of molecular shape, and the above considerations help us to predict them. The bond angles are generally reduced from the values given in Figure 6.1 by the presence of lone pairs because the interaction between lone pairs and bonding pairs is stronger than between bonding pairs. As a result, the bonding pairs move away from the lone pairs by moving closer to one another. The deviation from the angles shown in Figure

* In molecules with an odd number of valence electrons, a single electron rather than a lone pair may occupy an electron region.

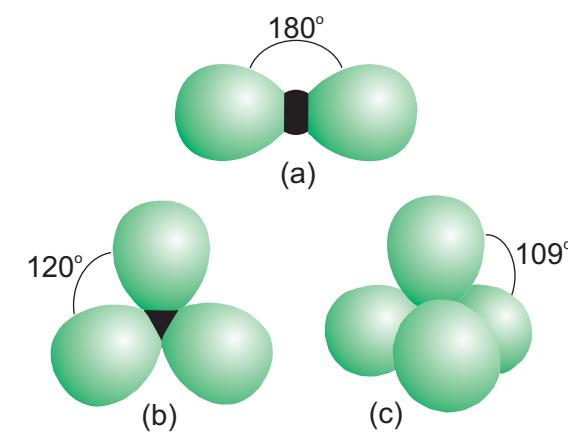


Figure 6.1 Distributions of electron groups that minimize electron-electron repulsions

6.1 increases with the number of lone pairs. We will indicate that the bond angle deviates from the predicted value with a ' \sim ' in front of the angle.

The shapes shown in Figure 6.1 show the orientations that can be adopted by the electron groups surrounding a central atom that obeys the octet rule. However, we typically determine the positions of only the atoms, not the lone pairs. Thus, a **molecular shape** describes the shape adopted by only the atoms. The lone pairs help establish what that shape is, but the name of the shape applies only to that taken by the atoms. We now consider the shapes of some generic molecules. The analysis we will follow has three steps:

1. Determine the number of electron groups around the central atom.
2. Determine which of the electron distributions shown in Figure 6.1 applies.
3. Name the molecular shape adopted by the atoms.

We limit the discussion to molecules with two, three or four atoms (X) attached to one central atom (A), which may have one or more lone pairs (E). The possibilities for molecules in which A obeys the octet rule are discussed below and summarized in Table 6.1.

AX_2 : The A atom is surrounded by two electron groups that orient as shown in Figure 6.1a. Three atoms bound by these two electron groups lie in a straight line, so AX_2 molecules are linear (Figure 6.2a) with an X-A-X bond angle of 180° .

AX_2E : The A atom is surrounded by three electron regions, two bonding and one lone pair. The regions orient as shown in Figure 6.1b, but the angles deviate from 120° because the lone pair-bonding pair interaction is stronger than the bonding pair-bonding pair interaction, which closes the bond angle slightly. We conclude that molecules of this type are bent with bond angles of $\sim 120^\circ$.

AX_2E_2 : A has four electron groups, two bonding and two lone pairs. The regions orient as shown in Figure 6.1c, but the angles deviate from the 109° because the two lone pairs force the bond angle to close from the predicted value. The shape of the molecule is bent with bond angles of $\sim 109^\circ$ (Figure 6.2c). Water is an AX_2E_2 molecule, and the H-O-H bond angle is actually 104° . However, we will refer to the angle as simply $\sim 109^\circ$.

AX_3 : There are three identical bonding electron groups around A that orient as shown in Figure 6.1b. All four atoms lie in the same plane, so the molecule is said to be planar or trigonal planar to show that the three X atoms form a triangle (Figure 6.3a). The bond angles are 120° , which is not approximate because the three groups are identical.

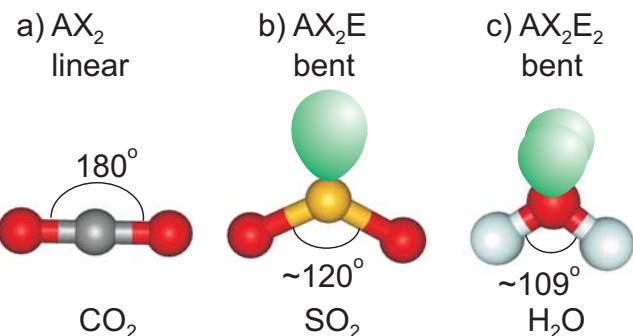


Figure 6.2 Shapes of molecules with three atoms
Green lobes represent lone pairs.

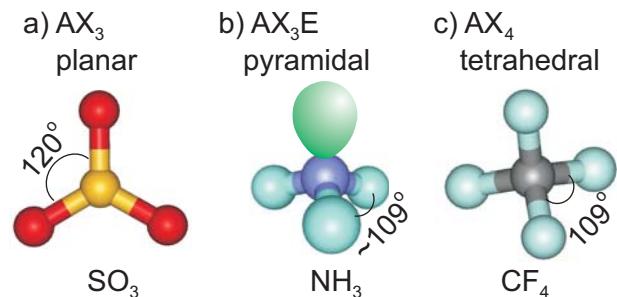


Figure 6.3 Shapes of molecules with four and five atoms
Green lobes represent lone pairs.

Table 6.1 Shapes of simple molecules

Molecule	Shape	Bond Angle
AX_2	linear	180°
AX_2E	bent	$\sim 120^\circ$
AX_2E_2	bent	$\sim 109^\circ$
AX_3	planar	120°
AX_3E	pyramidal	$\sim 109^\circ$
AX_4	tetrahedral	109°

AX_3E : A has four electron regions, which orient as shown in Figure 6.1c. Unlike AX_3 , the central atom is not in the plane of the three X atoms, so the four atoms form a pyramid and the molecule is said to be pyramidal or trigonal pyramidal to indicate that the base of the pyramid has three corners (Figure 6.3b). The bond angles are $\sim 109^\circ$ because the four regions are not identical. NH_3 is an AX_3E molecule, and the H-N-H bond angle is 107° , which is greater than the H-O-H bond angle in water because the single lone pair in NH_3 does not close the angle as much as the two lone pairs in H_2O .

AX_4 : A has four identical bonding regions, which orient as shown in Figure 6.1c. The four X atoms are at the corners of a tetrahedron and the molecule is described as tetrahedral with 109° bond angles (Figure 6.3c).

MOLECULAR REPRESENTATIONS

In Chapter 5, we represented molecules as their Lewis structures, and we will continue to do so throughout this text. However, we will also use three other representations: line-wedge-dash, ball-and-stick, and space-filling. In a **line-wedge-dash** representation, such as the one shown in Figure 6.4, lines represent bonds between two atoms that lie in the plane of the paper, solid wedges are used to show bonds to atoms that lie in front of the plane of the paper, and dashed wedges indicate bonds to atoms that lie behind the plane of the paper. In a **ball-and-stick** model, atoms are represented as spheres and bonds as cylinders. Ball and stick models are the best representation to use when discussing molecular structure because the bond angles are easy to see. A **space-filling** model, which shows atoms as spheres and bonds as the penetration of two spheres into one another, gives the truest picture of the molecule. The relative diameters of the spheres represent the relative sizes of the atoms. Lone pairs were shown in the ball-and-stick models in Figure 6.3 to emphasize their role in determining structure, but lone pairs are not normally included in either the ball-and-stick or space-filling representations. The various ways in which we will represent ammonia, an AX_3E molecule, are shown in Figure 6.5.

Example 6.1

Use the Lewis structures of CO_2 , SO_2 , and H_2O determined in Chapter 5 to predict their shapes and to estimate their bond angles.

CO_2 : The Lewis structure of CO_2 is $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$

There are no lone pairs on C (an AX_2 molecule), so the three atoms lie on a line, and the shape is described as linear (bond angle = 180°). The ball-and-stick and space-filling models of CO_2 are presented in the margin.

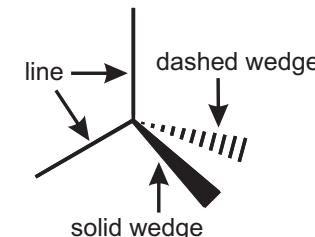


Figure 6.4 Line-wedge-dash representation

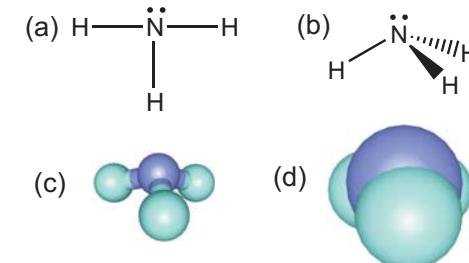


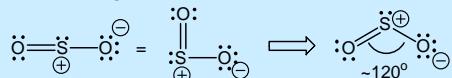
Figure 6.5 Representations of ammonia (NH_3)

(a) Lewis structure (b) Line-wedge-dash drawing
 (c) Ball-and-stick (d) Space-filling model
 Note that the ball-and-stick and space filling models do not show the lone pairs.

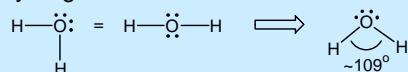


Ball-and-stick and space-filling models of CO_2

SO₂: There is a lone pair on the S (an AX₂E molecule), so the molecule is bent with a bond angle of ~120°. The Lewis structure is shown below and the ball-and-stick and space-filling representations are shown in the margin.



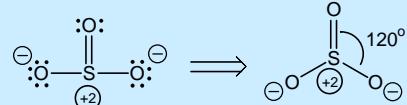
H₂O: There are two lone pairs on the oxygen atom, so H₂O is an AX₂E₂ molecule. The four electron regions adopt the arrangement shown in Figure 6.1c, which results in a bent shape and a bond angle of ~109° (Figure 6.2c and margin). Note that drawing water with the four regions in the plane of the paper makes it appear that the two hydrogen atoms can either be next to one another or opposite one another. In fact, all four positions are equivalent, so the structure is the same no matter which two positions are occupied by the hydrogen atoms.



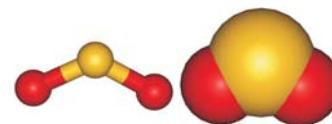
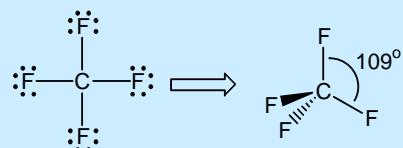
Example 6.2

Predict the shapes of SO₃ and CF₄ and estimate their bond angles.

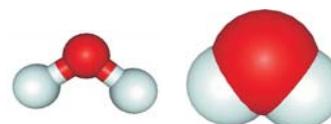
SO₃: The Lewis structure (Example 5.10) indicates that SO₃ is an AX₃ molecule. The three electron regions, which are identical due to resonance, adopt the arrangement shown in Figure 6.1b and in the margin. The molecular shape is trigonal planar (Figure 6.3a), and the three identical O-S-O bond angles are 120°.



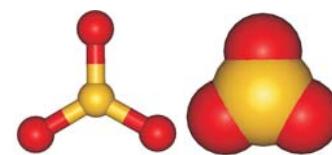
CF₄: The four shared pairs adopt the arrangement shown in Figure 6.1c. All of the regions are occupied by atoms, so the molecular geometry is tetrahedral (Figure 6.3c and margin). The actual bond angles are the predicted values (109°) because all of the regions around the carbon are the same.



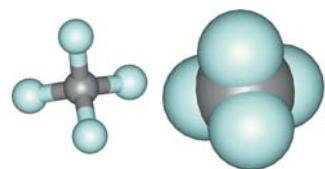
Ball-and-stick and space-filling models of SO₂



Ball-and-stick and space-filling models of H₂O



Ball-and-stick and space-filling models of SO₃

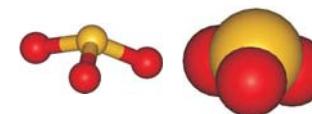
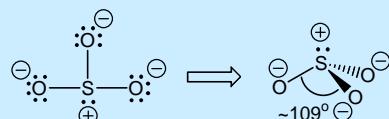


Ball-and-stick and space-filling models of CF₄

Example 6.3

What is the shape of the sulfite ion, SO_3^{2-} ?

The Lewis structure shows four electron regions around the sulfur atom (three S-O bonds and one lone pair). As a result, the sulfur atom becomes the apex of a trigonal pyramid. The sulfite ion is trigonal pyramidal, and the O-S-O bond angle is $\sim 109^\circ$.



Ball-and-stick and space-filling models of SO_3^{2-}

6.2 CENTRAL ATOMS WITH EXPANDED VALENCE SHELLS

The octet rule applies rigidly only to C, N, O and F, and even nitrogen violates it occasionally because it has an odd number of electrons in some of its molecules (*e.g.*, NO). This may seem quite restrictive until you realize that C is the basis of organic chemistry, and the number of compounds that can be made using only C, N, H and O is limitless. Atoms after the second period often have more than eight valence electrons. An atom with more than an octet of valence electrons is said to have an **expanded valence shell**. While our discussion of atoms with expanded valence shells is postponed to Chapter 14, Inorganic Chemistry, we show the two most common structures adopted by such molecules in Figure 6.6. Five groups around a central atom adopt a **trigonal bipyramidal** structure (Figure 6.6a), which contains two distinctly different types of positions: two positions are **axial** (blue spheres) and three are **equatorial** (green spheres). Interactions with other groups are less in the equatorial positions, so lone pairs are always in the equatorial plane. Six groups assume an **octahedral** structure (Figure 6.6b). All six positions of an octahedron are identical, so lone pairs can be placed in any one. However, two lone pairs are always situated opposite to one another. The number of lone pairs around a central atom (LP) can be determined from its group number and its oxidation state as follows:

$$\text{LP} = \frac{1}{2}[\text{Group Number} - \text{Oxidation State}]$$

Eq. 6.1

Atoms with expanded valence shells can be identified because the predicted number of shared pairs is always too small to accommodate all of the bonds. For example, if we were to attempt to draw the Lewis structure of SF_4 , we would determine the following:

$$\text{ER} = 5(8) = 40 \text{ electrons}; \text{VE} = 6 + 4(7) = 34 \text{ electrons}; \text{SP} = \frac{1}{2}(40 - 34) = 3 \text{ shared pairs}$$

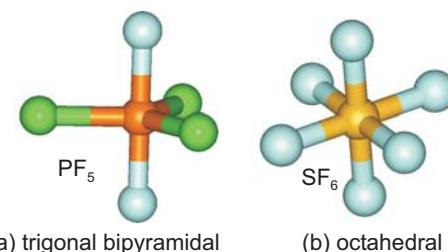
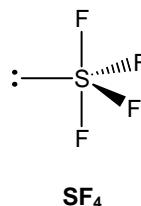


Figure 6.6 Molecules with five and six electron groups

- a) The green spheres occupy equatorial positions, while the blue spheres are in the axial positions. Lone pairs occupy equatorial positions.
- b) All of the positions of an octahedron are identical.

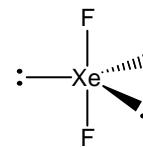
SF_4 requires a minimum of 4 shared pairs for the four S-F bonds, so the three shared pairs determined above cannot be correct and the octet rule cannot be obeyed. The group number of sulfur is 6 and its oxidation state in SF_4 is +4, so the number of lone pairs around the sulfur atom is $\text{LP} = \frac{1}{2}(6-4) = 1$ lone pair. Thus, there are five electron groups around the sulfur: four S-F bonds and one lone pair. As shown in the margin, the five groups adopt the trigonal bipyramidal structure with the lone pair in the equatorial plane.



Example 6.4

a) What is the shape of XeF_2 ?

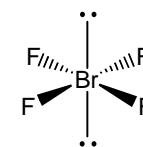
$\text{SP} = \frac{1}{2}(24-22) = 1$, which is insufficient for two Xe-F bonds, so Xe uses an expanded valence shell. The group number for Xe is 8 and its oxidation state in XeF_2 is +2, so there are $\frac{1}{2}(8-2) = 3$ lone pairs around the xenon atom in XeF_2 . Two Xe-F bonds and three lone pairs adopt a trigonal bipyramidal structure with the lone pairs in the equatorial plane to make XeF_2 a linear molecule as shown in the margin.



b) Describe the shape of the BrF_4^{1-} ion.

$\text{SP} = \frac{1}{2}(40-36) = 2$, which is insufficient for four Br-F bonds, so Br has an expanded valence shell. Bromine is a 7A nonmetal and its oxidation state in BrF_4^{1-} is 3, so it must have $\frac{1}{2}(7-3) = 2$ lone pairs. The six electron groups adopt an octahedral geometry with the lone pairs situated opposite to one another. As shown in the margin, the four bromine atoms are at the corners of a square with the bromine in the center. All five atoms are coplanar, so the BrF_4^{1-} ion is said to be square planar.

Example 6.4a XeF_2



Example 6.4b BrF_4^{1-}

6.3 LARGER MOLECULES

Molecules are three-dimensional, and their bonds are seldom at right angles, but a Lewis structure is typically a two-dimensional representation in which bond angles are drawn at 180° or 90° . The structure of a molecule is inferred by applying what we have learned about the shapes of molecules with a single central atom to *each* atom in a larger molecule: count the electron groups around an atom and then determine the geometry at that position. Most molecules twist and bend and are not rigid structures, so we cannot look at a Lewis structure of a large, flexible molecule and know its overall structure, but we can envision the possibilities. In this section, we consider a few simple cases.

Acetic acid is $\text{HC}_2\text{H}_3\text{O}_2$ and has the Lewis structure shown in Figure 6.7a. The bond angles can be determined by applying VSEPR to each of the atoms. There are four electron regions around the carbon at position 1, so it has a tetrahedral geometry with bond

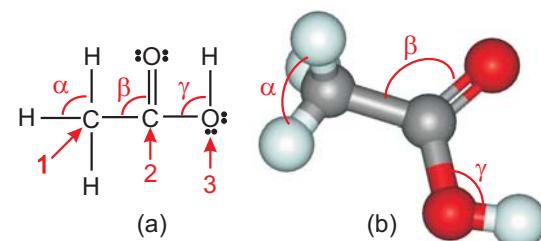


Figure 6.7 Lewis structure (a) and ball-and-stick model (b) of acetic acid

angles (α) of $\sim 109^\circ$. Thus, the carbon atom is in the center of a tetrahedron with the three H's and another C at the apices. The carbon atom at position 2 is surrounded by three electron regions, so it lies in the center of a trigonal planar arrangement with $\beta \sim 120^\circ$. The oxygen atom at position 3 has four electron regions (two bonds and two lone pairs), so $\gamma \sim 109^\circ$. The resulting three-dimensional representation of acetic acid is shown as a ball-and-stick model in Figure 6.7b. The COOH group is called a carboxylic acid group, which is what makes acetic acid acidic.

Benzene has the formula C_6H_6 and is a six-membered ring (the six carbon atoms bond so as to form a hexagon). The Lewis structures of its two resonance forms are shown in Figure 6.8a. Each carbon has three regions, so each is trigonal planar and all bond angles are 120° . In addition, the double bonds require that the molecule is planar. As a result of resonance, all of the carbon atoms are identical as are all six of the bonds between them. The bond lengths between carbon atoms (1.4 \AA) lie between those of a single C-C bond (1.5 \AA) and those of a C=C double bond (1.3 \AA), which is consistent with a bond order of 1.5. Thus, the three double bonds are shared equally between the six bonding regions in the ring. Indeed, the double bonds are frequently represented as a circle rather than three lines (Figure 6.8b) to emphasize the equivalence of the carbon-carbon bonds. We will revisit this important bonding characteristic of benzene in our discussion of molecular orbital theory at the end of the chapter.

The Lewis structure of aspirin, $C_9H_8O_4$, is shown in Figure 6.9a. Note that lone pairs are not drawn in this figure, but carbon and oxygen both obey the octet rule. Thus, the two oxygen atoms numbered 3 and 4 each have four electron regions because each must have two lone pairs in addition to the regions shown. The structure of aspirin combines the structural features described for acetic acid and benzene. The C at position 1 is part of a benzene ring, and the three regions are 120° apart. As in benzene, the bonds between the carbon atoms in the ring have the same lengths due to resonance. The C and O at positions 2 and 3 are part of a carboxylic acid group (COOH) and have the same geometry as the C and O atoms at positions 2 and 3 in the structure of acetic acid. The carboxylic acid group makes aspirin acidic, which is why it can upset your stomach. The O at position 4 has four electron regions, so it is tetrahedral with $\sim 109^\circ$ bond angles. The C at position 5 is in the center of a plane with $\sim 120^\circ$ separating the three electron groups. The carbon atom at position 6 is in the center of a tetrahedron with $\sim 109^\circ$ separating its four electron groups. The ball-and-stick model in Figure 6.9b summarizes these conclusions.

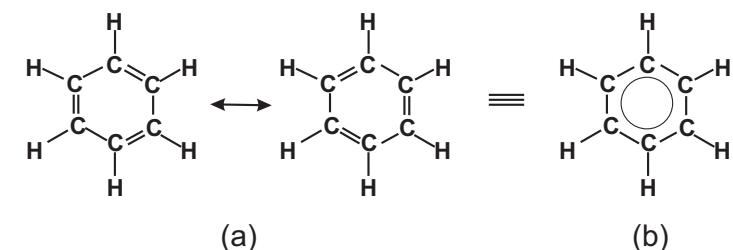


Figure 6.8 Lewis structure of benzene

(a) Two resonance forms of benzene and (b) the structure frequently used to show that all of the bonds between carbon atoms are identical. The circle shows the double bonds are shared between all C-C bonding regions.

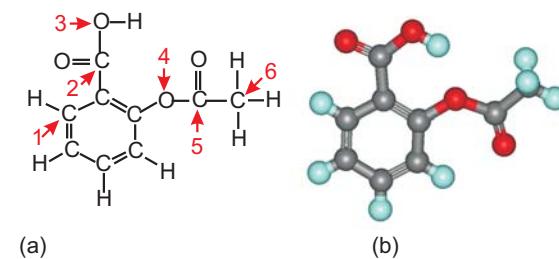


Figure 6.9 Lewis structure (a) and ball-and-stick (b) representations of aspirin

6.4 VALENCE BOND THEORY AND HYBRIDIZATION

In **valence bond theory**, each bond results from the overlap of two atomic orbitals on two adjacent atoms. The bonding electrons in such bonds are localized in the region between the two atoms. A single bond is composed of two bonding electrons, so the total number of electrons in the two overlapping atomic orbitals used to produce a bond cannot exceed two. In most cases, each bonding orbital contains one electron and the two electrons pair when the orbitals overlap. However, both electrons can reside in one of the atomic orbitals (a lone pair), but in this case, the other orbital must be empty. A bond in which a lone pair is converted into a covalent bond is called a **coordinate covalent bond**. Coordinate covalent bonds are produced in Lewis acid-base reactions, which are discussed in Chapter 12. We limit our discussion here to cases where each overlapping orbital has one electron.

SIMPLE OVERLAP MODEL

The H-H bond discussed in Section 5.1 is produced when the distance between the two H atoms is so small that their 1s orbitals overlap (the overlap region is highlighted in yellow in Figure 6.10a). The valence electron configuration of a fluorine atom is $2s^22p^5$, so an unpaired electron resides in one of the 2p orbitals, and the F-F bond results from the overlap of two p orbitals as shown in Figure 6.10b. In these two examples, the bonding atoms were the same, so the overlapping orbitals were the same type (both s or both p orbitals). However, the overlapping orbitals do not have to be the same type. The H-F bond is the result of overlap between the 1s orbital of H and the 2p orbital of F (Figure 6.10c). The lone pairs on fluorine would then reside in its s and remaining p orbitals.

The line between the two atoms in a bond is called the **internuclear axis**, and bonds in which the bonding electron density falls on the internuclear axis are called **sigma (σ) bonds**. The bonds in Figure 6.10 are σ bonds. The σ bond in F_2 (Figure 6.10b) results from the end-on overlap of two p orbitals, but p orbitals can also overlap in a side-on fashion as shown in Figure 6.11. In Figure 6.11a, the two orbitals are not interacting. In Figure 6.11b, the p orbitals begin to overlap (yellow region) and to distort into the bonding orbital shown in Figure 6.11c. Note that the overlap lies above and below the internuclear axis, but not on it, so the bond is not a σ bond. Bonds that place bonding electron density above and below, but not on, the internuclear axis are called **pi (π) bonds**. The internuclear axis lies in the nodal plane of a π bond. We conclude that σ bonds result from end-on overlap and place electron density on the internuclear axis, while π bonds are produced from side-on overlap and contain a nodal plane through the internuclear axis.

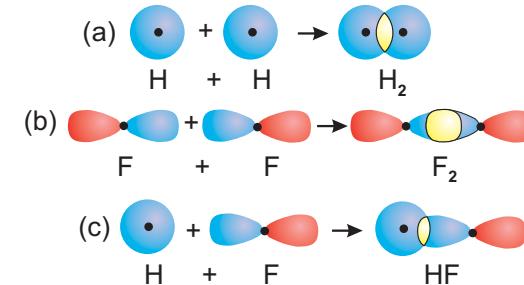


Figure 6.10 Overlap of atomic orbitals

When atoms get close enough to bond, their atomic orbitals overlap. The overlap region is shown in yellow.

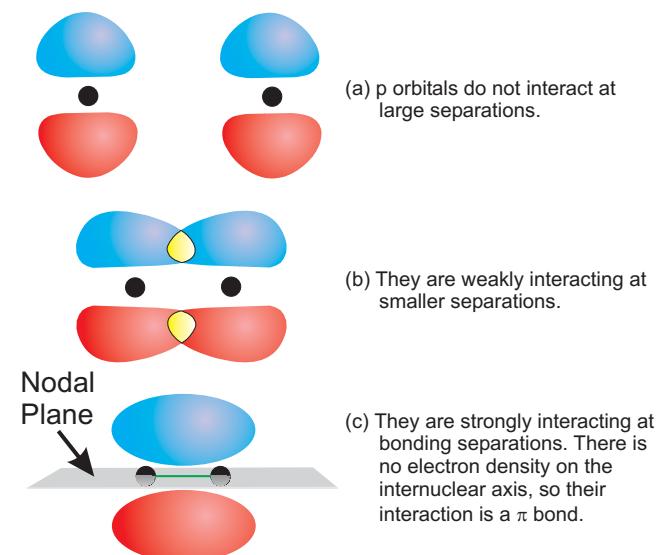


Figure 6.11 π bond formation

The internuclear axis is shown as the green line in Figure c. There is electron density above and below it, but none resides on it.

O_2 is a diatomic molecule that contains both σ and π bonds. The valence electron configuration of an oxygen atom is $2s^22p^4$, so there are paired electrons in the $2s$ and one of the $2p$ orbitals. The unpaired electrons in an oxygen atom lie in the other two p orbitals. In Figure 6.12, the unpaired electrons are assumed to be in the p_z and p_y orbitals. As the atoms approach along the z -axis, the p_z orbitals of the two oxygen atoms overlap in an end-on fashion (orange line) to produce a σ bond, while the p_y orbitals overlap side-on (both violet lines) to produce a π bond. Thus, the $O=O$ double bond consists of one σ and one π bond. All bonds contain one and only one sigma bond. Double bonds contain one σ and one π bond. Triple bonds contain one σ and two π bonds. The bond order of a bond is simply the sum of the number of σ and π bonds that it contains.

ORBITAL MIXING AND HYBRIDIZATION

The simple overlap of atomic orbitals used for diatomic molecules cannot be used for larger ones. Consider the molecule formed between a carbon atom and hydrogen atoms. Carbon has a valence electron configuration of $2s^22p^2$, so it has two unpaired electrons in its p orbitals. If carbon used only atomic orbitals with one electron, its compound with hydrogen would be CH_2 , and the H-C-H bond angle would be 90° (the angle between two p orbitals). However, the simplest compound involving carbon and hydrogen is CH_4 , which has 109° bond angles. In order to account for molecular geometries in the valence bond model, we must use a different set of orbitals on the central atom. These new orbitals are produced by *mixing* the atomic orbitals, but before discussing these new orbitals, we need to examine the process of mixing.

Recall from Chapter 2 that atomic orbitals describe algebraic functions that are solutions to an atom's wave equation. Mixing orbitals is the mathematical combination of these functions by addition and/or subtraction. Consider the two combinations of the functions P and Q shown in Figure 6.13. Regions where the functions are positive are shaded in blue, while negative regions are shown in red. This is consistent with our use of these colors to describe the sign of orbital functions. In Figure 6.13a, the two functions are added to produce function $R = P + Q$. R is amplified on the ends because both P and Q have the same phase (sign) there, but it is reduced dramatically in the center because the phases of P and Q are opposite there. We conclude the following:

Adding regions of the same phase (blue + blue) is **constructive** and produces a region of increased amplitude, while adding regions of opposite phase (blue + red) is **destructive** and produces a region of decreased or even annihilated amplitude.

To obtain the difference $S = P - Q$ in Figure 6.13b, the phase of Q is reversed (its sign is

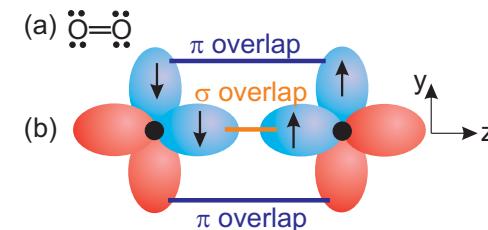


Figure 6.12 Bonding in O_2

(a) Lewis structure of O_2 . (b) Head-on overlap of the two p_z orbitals produces a σ -bond, while side-on overlap of the two p_y orbitals produces a π -bond.

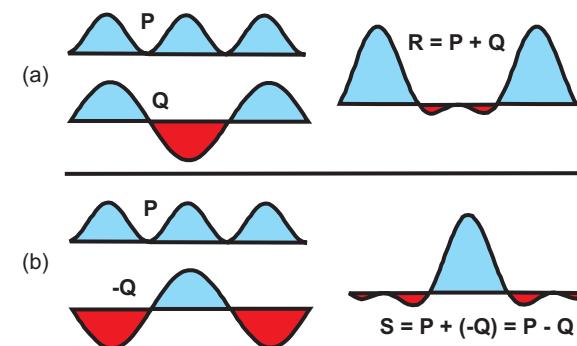


Figure 6.13 Mixing two functions

Regions where P and Q have the same phase add constructively, while regions of different phase add destructively.

(a) $P + Q = R$: Both P and Q have the same phase on the two ends but opposite phases in the center. Thus, R has enhanced wings and an annihilated center.

(b) $P - Q = S$: The phase of Q is reversed to produce $-Q$, which is then added to P . The wings have opposite phase and add destructively, while the centers have the same phase and add constructively.

changed) to produce $-Q$ and then the two waves are added to produce S . The ends of P and $-Q$ have different phases, so they add destructively to nearly annihilate one another, while the regions in the middle have the same phase and add constructively to produce an amplified region in S .

Mixing atomic orbitals is done in a manner very similar to that described above: adding two atomic orbitals in a region where they have the same phase is constructive, while adding them in a region where they have opposite phase is destructive and often results in annihilation. In addition we will use the following rule when mixing orbitals:

The number of orbitals produced must equal the number of atomic orbitals that are mixed.

Thus, mixing two atomic orbitals A and B must produce two new orbitals. One new orbital is obtained by adding the two atomic orbitals, $A + B$. The second orbital is produced when one atomic orbital is subtracted from the other atomic orbital, $A - B$. To subtract orbital B , we change its phase to produce $-B$ and then add $-B$ to orbital A .

The orbitals that adopt the geometries for two, three, and four electron groups predicted by VSEPR (Figure 6.1) can all be constructed from combinations of the atom's s and p orbitals. These combinations are called **hybrid orbitals**, and the process by which they are formed is called **hybridization**. Hybrid orbitals are constructed to have the geometry of the electron groups, so we conclude that

Hybrid orbitals are occupied by lone pairs and σ bonds. The p orbitals that are not used in the construction of the hybrid orbitals are used to form π bonds.

The orbitals constructed from the addition and subtraction of one s and one p orbital are called *sp hybrid orbitals*. The sp hybrid orbitals are formed from $s + p$ and $s - p$. In Figure 6.14a, the s and p orbitals are added to produce $s + p$, one sp hybrid orbital. Both atomic orbitals are positive (blue) to the right, but they have opposite phases to the left. Thus, they add constructively to the right to produce a large lobe, but they add destructively to the left to produce a small negative lobe. The other hybrid is produced by taking the difference between the atomic orbitals (Figure 6.14b). To obtain $s - p$, we change the phase of the p orbital and then add it to the s orbital. Now, the regions to the left have the same phase and add constructively and those on the right add destructively. The two sp hybrid orbitals are centered on the same atom, so they would look like Figure 6.14c. However, the small negative lobes are not used in bonding and are usually omitted. Thus, the two sp hybrid orbitals are normally represented as in Figure 6.14d. Note that forming the two sp hybrid orbitals required the use of only one p orbital, so an sp hybridized atom would have two p orbitals available to form π bonds.

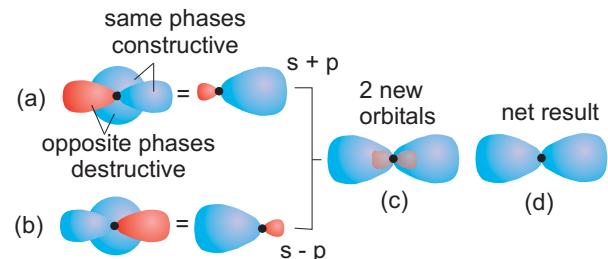


Figure 6.14 Mixing s and p orbitals

- The blue regions combine constructively to produce a large region to the right, but the blue and red regions combine destructively to produce a small red region to the left.
- The phase of the p orbital is reversed, so this combination produces $s - p$.
- The two new orbitals are shown centered on the same atom.
- The common representation of the two orbitals that does not show the smaller lobes.

Combining more than two orbitals involves more than two combinations, which are done in a similar manner, but their construction is beyond the scope of our discussion. Thus, only the results are summarized here.

1. Two sp hybrid orbitals are produced by combining one s and one p orbital as shown in Figure 6.14. They are oriented 180° from one another as shown in Figure 6.15a. Only one p orbital is used in their construction, so two p orbitals are available to form π bonds. Thus, sp hybridized atoms form two π bonds (one triple bond or two double bonds) and have bond angles of 180°. Note that sp hybrid orbitals lie along the axis of the p orbital used to construct them, so if the σ bonds are directed along the z-axis, then the s and the p_z orbitals would be used to make the hybrid orbitals, and the p_x and p_y orbitals would be used to form π bonds.
2. Three sp^2 (spoken “sp two”) hybrid orbitals are produced by combining one s and two p orbitals (Figure 6.15b). The three hybrid orbitals lie in the plane defined by the two p orbitals used to construct them and are oriented 120° from one another. Two p orbitals are used in the hybridization, so only one p orbital remains to form a π bond. Thus, sp^2 hybridized atoms have one double bond and 120° bond angles. If the hybrid orbitals lie in the xy plane, then the p_x and p_y orbitals must be used to construct them, which leaves the p_z orbital available for π bonding.
3. Four sp^3 (spoken “sp three”) hybrid orbitals are produced by combining the s and all three p orbitals (Figure 6.15c). There are no p orbitals available to form π bonds, so sp^3 hybridized atoms form only single bonds and have bond angles of 109°.

The hybridization of an atom can be determined from the number of electron groups around it because the number of hybrid orbitals must equal the number of electron groups. For example, an atom with four electron groups requires four hybrid orbitals, so the atom must be sp^3 hybridized. In addition, atoms that are sp or sp^2 hybridized have unused p orbitals that are used to form π bonds, so the hybridization of an atom describes both the structure and bonding around the atom (Table 6.2). An atom that is sp^2 hybridized has three electron groups, 120° bond angles, and is involved in one π bond, while an sp hybridized atom has two electron groups, 180° bond angles, and two π bonds.

We conclude our discussion of valence bond theory by using it to explain why the planes of the two CH₂ groups of allene (Figure 6.16) are perpendicular. We start by determining the hybridization of each carbon atom. The central atom is surrounded by two electron groups and is involved in two π bonds, so it is sp hybridized. If the bonding axis is the z-axis, then the p_z orbital must be used to construct the hybrid orbitals, which leaves the p_x and p_y orbitals available to form the two π bonds. Each of the terminal carbon atoms (C_A and C_B) is surrounded by three electron groups and is involved in one π bond, so each

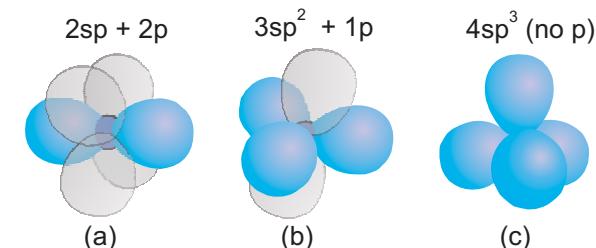


Figure 6.15 Hybrid orbitals and unused p orbitals

The orientation of hybrid (blue) and unused p (grey) orbitals

Table 6.2 Hybridization and arrangement of electron groups around central atoms obeying the octet rule

number of groups	hybridization	bond angle	π bonds
2	sp	180°	2
3	sp^2	120°	1
4	sp^3	109°	0

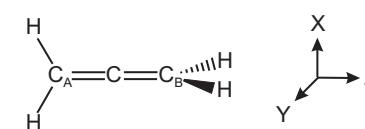


Figure 6.16 Coordinate system used in allene, C₃H₄

is sp^2 hybridized. The sp^2 hybrid orbitals of C_A lie in the xz plane because that is the plane defined by the C-H bonds, so the s, p_x and p_z orbitals are used to construct them. This leaves the p_y orbital available to form a π bond with the central carbon. If the central carbon uses its p_y orbital to π bond to C_A , then it must use its p_x orbital to π bond with C_B . If C_B uses its p_x orbital to form a π bond, then it must use its s, p_y , and p_z orbitals to form the sp^2 hybrid orbitals, which lie in the yz plane and are perpendicular to the sp^2 plane of C_A . Thus, the two CH_2 groups must be perpendicular if the central atom is to π bond to both terminal carbon atoms because each π bond requires a different p orbital. Figure 6.17 shows the bonding geometry in allene.

We now apply VSEPR and valence bond theory to the Lewis structures of several molecules and ions. The procedure gives us a very powerful tool to be used in the understanding molecular properties. With Lewis structures we can:

- determine shapes of molecules and ions, and
- understand the bonding in terms of orbitals, hybridization, and bond type (σ or π).

Example 6.5

Describe the bonding at the labeled positions in the aspirin molecule, shown in the margin. Note that the lone pairs have been omitted, but C and O obey the octet rule.

Position 1. The C is in a benzene ring. It has three electron regions and is sp^2 hybridized. The three sp^2 hybrid orbitals are used for two C-C σ bonds and one C-H σ bond. The p orbital is involved in π bonding.

Position 2. The C is in an acid group (COOH). It is sp^2 hybridized. It has a C-C σ bond, two C-O σ bonds, and a C-O π bond.

Positions 3 & 4. Both O atoms are sp^3 hybridized. Only four electrons are shown around each in the figure, but oxygen obeys the octet rule, so there must be two lone pairs as well. Two orbitals are used for σ bonds and two contain lone pairs.

Position 5. There are three electron groups around this C, so it is sp^2 hybridized. The three sp^2 orbitals are involved in σ bonds, and the remaining p orbital is used in the π bond to the oxygen atom.

Position 6. The C has four electron regions and is sp^3 hybridized. Three of the hybrids are used in C-H σ bonds and one is used in a C-C σ bond.

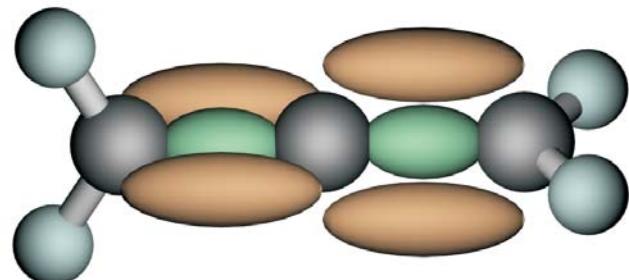
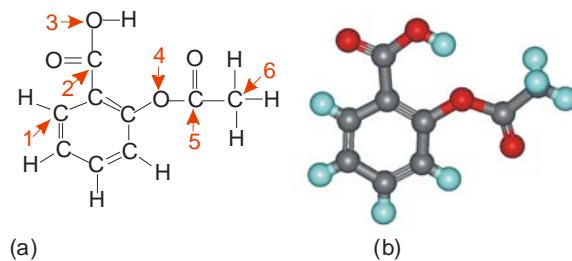


Figure 6.17 Bonding in allene

Green identifies electron density in the two C-C σ bonds, while brown represents electron density in the two C-C π bonds. Note that the planes of the two π bonds are perpendicular (π_x and π_y) as are the planes of the two CH_2 groups.



Example 6.5 Aspirin

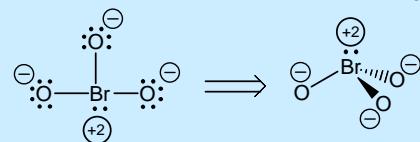
(a) Lewis structure (b) ball-and-stick structure

Example 6.6

Describe the bonding in and the structure of the following ions:

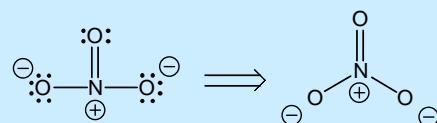
a) **Bromate ion, BrO_3^{1-}**

The Lewis structure of the bromate ion shows four electron regions around the bromine atom, so it is sp^3 hybridized. The three O atoms form the base of this trigonal pyramidal ion. All BrO_3^{1-} bonds are single bonds and, therefore, σ bonds. The O-Br-O bond angles are $\sim 109^\circ$. The negative charge of the ion is distributed equally over all of the oxygen atoms. The ball-and-stick and space-filling models are shown in the margin.



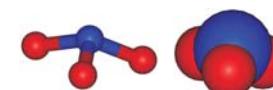
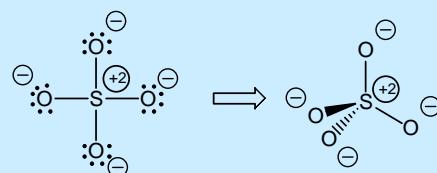
b) **Nitrate ion, NO_3^{1-}**

The Lewis structure of NO_3^{1-} has three electron groups around the nitrogen, so it is sp^2 hybridized and the ion is planar. The π bond is shared by all three N-O bonds, which are equivalent with bond orders of $\frac{4}{3}$ (four shared pairs spread equally over three bonding regions). The O-N-O bond angles are all 120° . Resonance places the negative formal charge equally on all of the oxygens. Positively charged species bond to one of the oxygens but not to the nitrogen. For example, addition of H^{1+} to NO_3^{1-} results in HNO_3 , nitric acid, which contains an O-H bond, not an N-H bond.

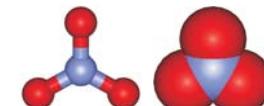


c) **Sulfate ion, SO_4^{2-}**

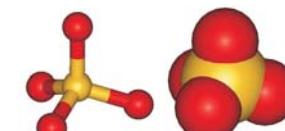
The Lewis structure of the sulfate ion indicates four electron regions around the sulfur atom, so the sulfur is sp^3 hybridized. The sulfate ion is tetrahedral. The S-O bonds are all single bonds (that is, σ bonds). The O-S-O bond angles are all 109° . The negative charge on the ion is distributed equally among the oxygens. Note that the sum of the formal charges is -2, the charge on the ion. When the sulfate ion bonds to H^{1+} ions to form covalent bonds, it does so through the oxygen atoms. Thus, sulfuric acid (H_2SO_4) has two O-H bonds.



BrO_3^{1-} ion



NO_3^{1-} ion

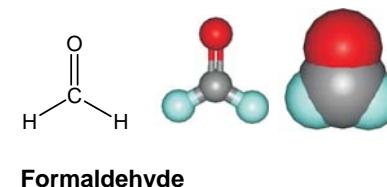


SO_4^{2-} ion

Example 6.7

Draw the Lewis structure of and discuss the bonding in formaldehyde, CH₂O.

VE = 4 + 2(1) + 6 = 12; ER = 2(8) + 2(2) = 20; SP = $\frac{1}{2}$ (20 - 12) = 4. Four shared pairs are required, but double bonds cannot be placed to H, so the C=O bond must be a double bond. There are no other acceptable resonance forms that obey the octet rule. The three electron regions around the carbon make it sp² hybridized. CH₂O is planar, with bond angles ~120°. The C-H bonds are σ bonds while the C=O double bond contains one σ bond and one π bond. All formal charges are zero. The Lewis, ball-and-stick, and space-filling representations of formaldehyde are given in the margin.



6.5 MOLECULAR ORBITAL THEORY AND DELOCALIZED BONDS

In **molecular orbital** (MO) theory, atomic orbitals *on different atoms* mix to produce bonds that can be localized between two atoms but are frequently delocalized over several. MO theory is more powerful in its predictive power, but it is also more difficult to use. Thus, chemists use both theories, choosing the one that is easier to use while still providing sufficient predictive power. In this section, we present a qualitative introduction to molecular orbital theory; one that introduces some important terms, presents a more satisfying picture of delocalization, and explains the electronic structure of molecules.

In MO theory, atomic orbitals (AOs) are combined to form molecular orbitals (MOs) using the same rules that were used for constructing hybrid orbitals:

1. Regions in which the phases of the atomic orbitals are the same add constructively to produce large lobes, but regions in which the phases are opposite add destructively and often annihilate.
2. The number of MOs produced must equal the number of AOs used in their construction.

The case of combining two s orbitals is considered below and in Figure 6.18.

- a) **Bonding interactions** result when the interacting lobes of the AOs have the same phase (Figure 6.18a). Bonding interactions are characterized by an accumulation of electron density between the nuclei, which lowers the energy of the molecular orbital relative to that of the interacting AOs.
- b) **Antibonding interactions** are produced when the interacting lobes of the AOs are of opposite phase (Figure 6.18b). They are characterized by an annihilation of electron density between the two atoms. We conclude that antibonding interactions contain nodal planes perpendicular to the bonding axis. Decreased electron density between the nuclei results in more interaction between the positive charges, which raises the energy of the molecular orbital relative to that of the interacting AOs. Antibonding MO's are designated with a σ^* . For example, the σ^* and π^* , (pronounced "sigma star" and "pi star") are the antibonding combinations that contain nodal planes perpendicular to the bonding axis.

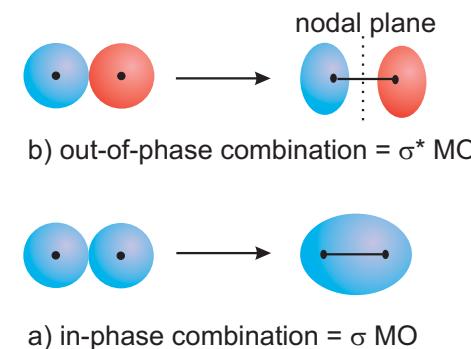


Figure 6.18 Combining s orbitals

The orbitals on the left are the AOs that combine to produce the MOs on the right. MOs can be represented in either way.

While the color of each AO in diagrams such as Figure 6.18 represents its phase in the combination, the *size of the sphere represents its relative contribution to the MO*. The fact that the two AOs are the same size in Figure 6.18 means that the two AOs contribute equally to the MO, which means that the electron density in the MO is distributed equally over both atoms. MOs can be represented by either the resulting combination as shown on the right of Figure 6.18 or as the combining orbitals as shown on the left of Figure 6.18. We will use the latter method, where spheres showing the sign and relative magnitude of the contributing AOs will be shown rather than the resulting MO.

As shown in Figure 6.18, σ and σ^* MOs are formed from the combination of two s orbitals on different atoms. However, σ interactions are also produced by the head-on combination of p orbitals. The combination of orbitals that mixes lobes of the same phase (Figure 6.19a) increases electron density on the bonding axis, so it is a σ bonding orbital. The combination in which lobes of opposite phase interact (Figure 6.19b) annihilates electron density between the two atoms to produce a nodal plane perpendicular to the bonding axis, so it is a σ^* antibonding orbital.

The side-on combination of two p orbitals (Figure 6.20) results in no electron density on the bonding axis, so both combinations are classified as π . The combination of orbitals of the same phase increases electron density between the bound atoms, so it is the π bonding orbital. The combination in which lobes of opposite phase interact produces a nodal plane perpendicular to the bonding axis, so it is an antibonding π^* orbital.

DIATOMIC MOLECULES

The two nuclei in a **homonuclear diatomic molecule** are nuclei of the *same* element, so the interacting atomic orbitals (AOs) are identical and contribute equally to the MO. Consequently, the electron density in each MO is symmetric and the bonds are nonpolar. Each MO is characterized by an energy level, and electrons occupy the molecular orbitals in the same manner that they do atomic orbitals; *i.e.*, they fill the molecular orbitals at lowest energy while obeying both Hund's rule and the Pauli Exclusion Principle.

The energies of the σ and σ^* orbitals relative to the s orbitals used to construct them are shown in an MO diagram. Three important characteristics of MO diagrams like those in Figure 6.21 are:

1. The energy of bonding interactions is lower than that of the atomic orbitals (ΔE).
2. The energy of antibonding orbitals is higher than that of the atomic orbitals (ΔE^*).
3. $\Delta E^* > \Delta E$.



Figure 6.19 σ bonds from end-on combinations of p orbitals

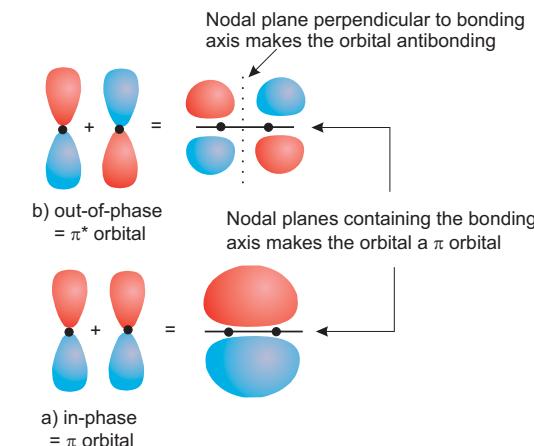


Figure 6.20 π bonds from side-on combinations of p orbitals

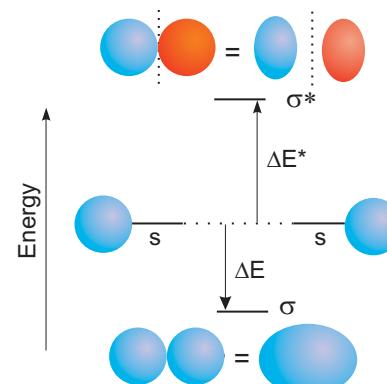


Figure 6.21 MO diagram for combining two s orbitals

Electrons occupying bonding orbitals lower the energy of the system and make the MO more bonding, while those occupying antibonding orbitals raise the energy and make the MO less bonding. Indeed the bond order (BO) is defined in terms of the difference between the number of bonding and antibonding electrons in the bond as follows:

$$BO = \frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$$

As an example of the use of a diagram like the one shown in Figure 6.21, we examine the differences predicted for the H₂ and He₂ molecules (Figure 6.22). Each H atom has one electron in its 1s orbital, so two electrons must be placed in the diagram for H₂. Both electrons occupy the σ bonding orbital, so the H-H bond order = $\frac{1}{2}(2 - 0) = 1$. Consequently, H₂ has a single bond and is a stable molecule. An He atom has two electrons in its 1s orbital, so four electrons would have to be placed into the diagram for He₂, which fills both the σ and σ^* orbitals. The He-He bond order would be $\frac{1}{2}(2 - 2) = 0$, which means that, consistent with observation, there is no He-He bond and He₂ is not a stable molecule.

In the valence bond description of O₂ described in Figure 6.14, all of the electrons are paired. However, O₂ molecules are paramagnetic (they are deflected in a magnetic field), which means that O₂ molecules contain unpaired electrons. This observation was a major dilemma for the valence bond model, and its explanation was a major victory for molecular orbital theory. We now present the MO description of O₂ to see how it explained the paramagnetism of O₂. We start by determining the order of the energy levels in Figure 6.23.

- The 2s orbitals interact to form the $\sigma(2s)$ and $\sigma^*(2s)$ orbitals. The 2s orbitals are the lowest energy valence orbitals in an oxygen atom, so the two MO's are the lowest energy MO's derived from the valence AO's.
- The 2p orbitals that are directed along the bonding axis interact in a head-on manner similar to that shown in Figure 6.19 to produce the $\sigma(2p)$ and $\sigma^*(2p)$ orbitals. Head-on interactions are usually stronger than side-on interactions, so the $\sigma(2p)$ is the lowest energy MO derived from the 2p interactions, while the $\sigma^*(2p)$ is the highest energy MO.
- The remaining 2p orbitals interact in a side-on fashion as shown in Figure 6.20 to produce a pair of $\pi(2p)$ and a pair of $\pi^*(2p)$ orbitals. Note that the members of each pair have the same energy because the two $\pi(2p)$ orbitals are identical except for their orientation relative to one another.

Each oxygen atom has six valence electrons ($2s^2 2p^4$), so a total of 12 electrons must be placed into the energy diagram. The electrons are placed in the same manner as they are into the orbitals of an atom, so the lowest energy orbitals are occupied first while obeying

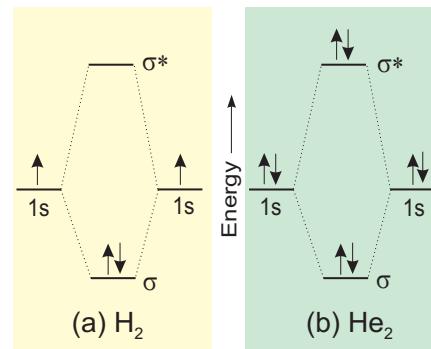


Figure 6.22 MO diagrams for H₂ and He₂

Note the dotted lines simply show which atomic orbitals are used to construct each molecular orbital.

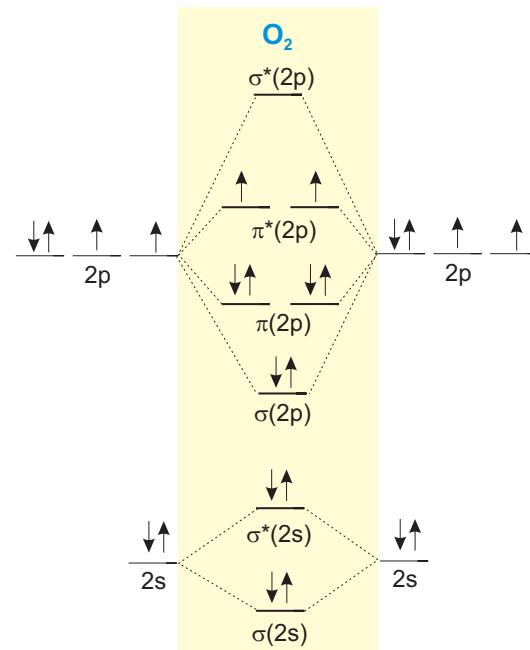


Figure 6.23 MO diagram for O₂

The MOs are in the yellow region, while the AOs used to construct them are shown on either side. The notation $\sigma(2s)$ is used to show that the σ molecular orbital is formed by mixing of the two 2s atomic orbitals as represented by the dotted lines.

the Pauli Exclusion Principle and Hund's rule. The result of adding 12 electrons in the diagram is shown in the figure. Many of the properties of a molecule are dictated by the nature of its **Highest Occupied Molecular Orbital** or **HOMO** and its **Lowest Unoccupied Molecular Orbital** or **LUMO**. Three important predictions can be made based on this diagram:

1. There are a total of eight bonding electrons and four antibonding electrons, so the O-O bond order is $\frac{1}{2}(8 - 4) = 2$, which is the same prediction made from valence bond theory.
2. Unpaired electrons in the π^* orbitals account for the paramagnetism of O₂. This prediction was a major success for MO theory.
3. The HOMO is the $\pi^*(2p)$ and the LUMO is the $\sigma^*(2p)$.

The two nuclei in **heteronuclear diatomic molecules** are nuclei of different elements, so the AOs that mix to form the bonding MO are at different energies. Whereas the two atoms of a homonuclear diatomic molecule make equal contributions to each MO in the molecule, the energy difference between the AOs in a heteronuclear diatomic molecule results in MOs that are not composed of equal amounts of the AOs. Instead, the AOs mix in the ratio that achieves the lowest energy possible for the bonding MO. The lowest energy MO is produced when the AO at lower energy contributes more to the MO than does the AO at higher energy. Consider the bonding between of atom X to atoms A, B, and C as described in Figure 6.24.

- Figure 6.24a: The energy of s_x (the s orbital atom X) is less than that of s_A by an amount ΔE_{XA} . s_x is the lower energy AO, so it contributes more to the bonding MO (σ_{XA}) than does s_A , which is shown by the relative sizes of the spheres describing the MO. The larger sphere on X means that there is more electron density on atom X in the bond, so the XA bond is polar with atom X carrying the negative charge.
- Figure 6.24b: s_B is lower in energy than s_x by an amount ΔE_{XB} . s_B is the lower energy orbital, so it contributes more to the bonding MO (σ_{XB}). The XB bond is polar with atom B carrying the negative charge.
- Figure 6.24c: s_C is lower in energy than s_x by an amount ΔE_{XC} . $\Delta E_{XC} > \Delta E_{XB}$, so s_C contributes even more to the XC bond than did s_B to the XB bond. The small sphere representing the contribution of s_x to the σ_{XC} MO indicates that only a small amount of the electron density in the bond resides on atom X. The result is that the XC bond is more polar than the XB bond.

Recall that electronegativity is a measure of how well an atom attracts the bonding electrons, but, as shown in the preceding paragraph, the electron density in a bond is greater around the atom with the lower energy orbital; *i.e.*, the atom with the lower energy orbital attracts the electrons more, so it is the more electronegative atom. This is why we

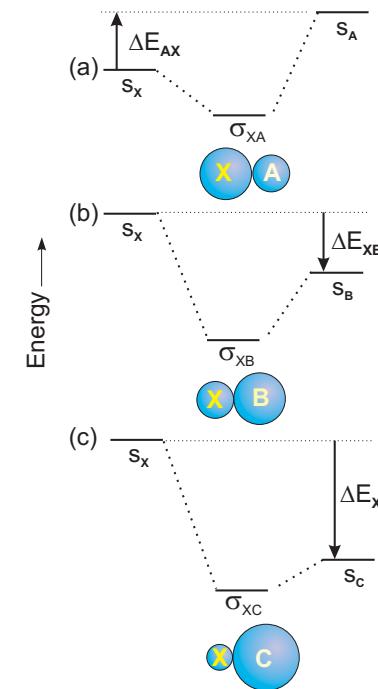


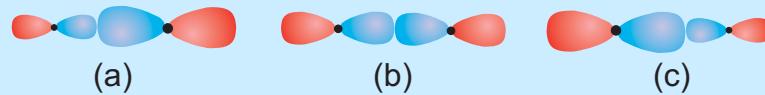
Figure 6.24 Mixing AOs of different energy

The relative sizes of the spheres represent the contributions of the AOs in each MO. The contribution of each AO in the bonding MO increases relative to that of X as the energy of the AO gets lower. (a) A is higher in energy than X, so the contribution of X (sphere size) to the bonding MO is greater. (b) B is lower in energy than X, so the contribution of B to the bonding MO is greater. (c) C is lowest in energy, so the contribution of s_C is the greatest.

used the energy of the unfilled orbitals to predict relative electronegativities in Chapter 3! Using the relative energies of atoms X, A, B, and C in Figure 6.24, we conclude that atom C is the most electronegative atom and atom A is the least electronegative. The bond dipole of the AX bond points toward atom X because X is more electronegative than A, but it points toward atom C in the XC bond because atom C is more electronegative than atom X.

Example 6.8

Indicate which representation best describes the interaction of p orbitals in each of the following O-X bonds. Assume the oxygen orbital is on the left in each case.



O-F bond

Oxygen is less electronegative than fluorine, so its p orbital is higher in energy and would contribute less to the MO. Figure (a) would be the best representation. Note that the size of the p orbital in the MO indicates the contribution to the MO, not the size of the atom. Oxygen is larger than F, but it contributes less to the MO, so its p orbital is shown smaller in the figure.

O-N bond

Oxygen is more electronegative than nitrogen, so its p orbital is at lower energy would contribute more to the MO. Figure (c) would be the best representation.

O-O bond

The atoms are identical, so their contributions would be identical as shown in Figure (b).

MOs FOR SIMPLE π SYSTEMS

So far, we have discussed the MO's formed by interacting only two atoms, but all of the atoms in a molecule can be involved in a single MO. Computers are used to determine the MO's of complicated molecules, so we limit our discussion to the π MO's of some simple molecules to show how MO theory deals with delocalized bonds. The discussion also points out the importance of symmetry in molecular systems.

The number and placement of the nodal planes is the key factor in generating the π MOs in the systems we will examine. In the following rules for creating MO's, we use N to denote the number of AOs used to construct the MOs.

Rules for constructing MOs.

1. The number of MO's equals the number of AO's used to construct them (N).
2. The energies of the MO's increase with the number of nodal planes they contain. The lowest energy MO contains no nodal planes, the next highest contains one nodal plane, the next has two nodal planes, and so on to the highest energy MO, which contains (N-1) nodal planes (one between each pair of atoms).
3. The nodal planes are placed symmetrically even if it means placing them on an atom. The atom that lies on the nodal plane has no electron density on it in that MO.
4. Recall that the phase of the AOs must change at a nodal plane, so nodal planes cannot be placed on adjacent atoms.

Bonding interactions increase the bonding character of an MO, while antibonding interactions decrease the bonding character. Thus, the bonding character of an MO spread over several atoms depends upon the *relative number of bonding and antibonding interactions*. Bonding interactions arise when the AO's of two adjacent atoms have the same phase, while antibonding interactions arise when the AO's have opposite phase, *i.e.*, when there is a nodal plane between the atoms. In addition, there is a third type of MO, the nonbonding MO, which is occupied by lone pairs. The following rules can be used to determine the bonding character of an MO:

- **Antibonding MOs** are produced when the number of bonding interactions < antibonding interactions. The energy of antibonding MOs is greater than the energy of the AO's used to construct them, so antibonding MOs lie at the highest energies.
- **Nonbonding MOs** are formed when the number of bonding and antibonding interactions is the same or there are no interactions between adjacent atoms. The energy of nonbonding MOs is close to that of the AO's used to construct them, so they lie above the bonding MOs and below antibonding MOs.
- **Bonding MOs** result when the number of bonding interactions > antibonding interactions. The energy of bonding MOs is lower than the energy of the AO's used to construct them, so they are at the lowest of the three types of MOs.

We now use MO theory to better understand the delocalized bonds first introduced in our discussion of the resonance structures of SO₂ in Chapter 5. The two resonance structures, which are shown at the top of Figure 6.25, differ in both the position of the π bond, which is shared between both S-O bonds, and the location of one of the lone pairs, which is shared by both oxygen atoms. We begin by determining the number of MO's that must be produced and the number of electrons that will occupy them. As is frequently the case, delocalization occurs only in the π system, which involves one p orbital from each atom (the one perpendicular to the molecular plane). If only three atomic orbitals are used

to construct the π molecular orbitals, then only three molecular orbitals are produced. The Lewis structures show that there are four electrons in the π system: two from the π bond and two from the lone pair that appears on both oxygen atoms. Using the Rules for MO construction of simple multi-atom systems, we obtain the three MO's shown in Figure 6.25. The lowest energy orbital contains no nodal planes perpendicular to the bonding axis, so both interactions between adjacent atoms are bonding. The number of bonding interactions (2) is greater than the number of antibonding interactions (0), so it is a bonding MO. The orbital is delocalized over all three atoms (both bonds), so it is a delocalized π bond. The next highest energy MO must contain one nodal plane that must be situated in the center of the molecule, which is on the central atom in this case. Placing a nodal plane on the central atom means that there is no electron density on the atom in this MO. The phases of the other orbitals must be opposite because they must change at the nodal plane. There are no interactions between adjacent atoms, so this is a non-bonding MO that is delocalized over both oxygen atoms. The highest energy MO has nodal planes between each pair of atoms, so both interactions are antibonding. The number of bonding interactions (0) is less than the number of antibonding interactions (2), so it is the π^* antibonding MO. Two electrons occupy the π bonding MO, and two the nonbonding (n) MO. The π^* antibonding orbital is unoccupied.

We now consider the example of the π system of butadiene (C_4H_6), which is a four-orbital system constructed from the four carbon p orbitals that are perpendicular to the plane of the molecule (we will refer to these as the p_z orbitals). There are four atomic orbitals, so four molecular orbitals must be produced. Each carbon p orbital contains one electron, so four electrons occupy the molecular orbitals. We again use the rules for MO construction to construct the four molecular orbitals shown in Figure 6.26. The lowest energy MO contains no nodal planes, and has three bonding interactions, so it is a π MO that is delocalized over all four atoms. The nodal plane in the next highest energy MO must be placed in the center of the molecule. The MO contains two bonding interactions and one antibonding interaction, so it is still a bonding π MO. The third highest MO contains two nodal planes that must be placed symmetrically. However, *phase changes must occur at nodal planes*, so they cannot be placed on adjacent atoms. Therefore, the two nodal planes must be placed between the atoms as shown. There are two antibonding interactions and one bonding interaction, so this is an antibonding π^* MO. The highest energy MO contains nodal planes between each pair of atoms, so it is an antibonding π^* MO. The four electrons are placed into the two lowest energy levels (π_1 and π_2) as shown,

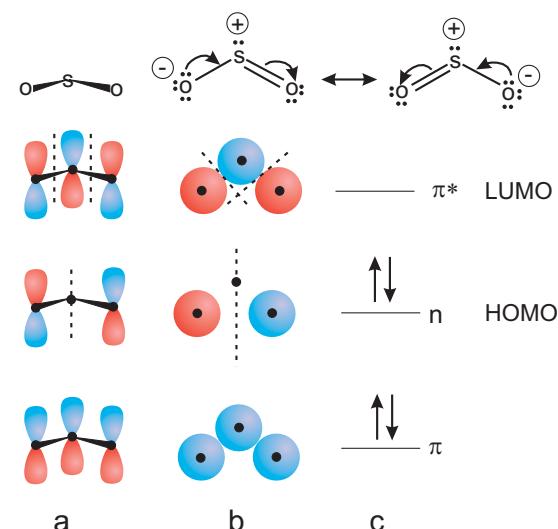


Figure 6.25 MO's for the π system of SO_2

(a) The p orbitals from the side of the molecule, so the 'figure 8' shape is apparent (b) The p orbitals viewed from the top of the molecule, so only the tops of the lobes are visible (c) The relative MO energies

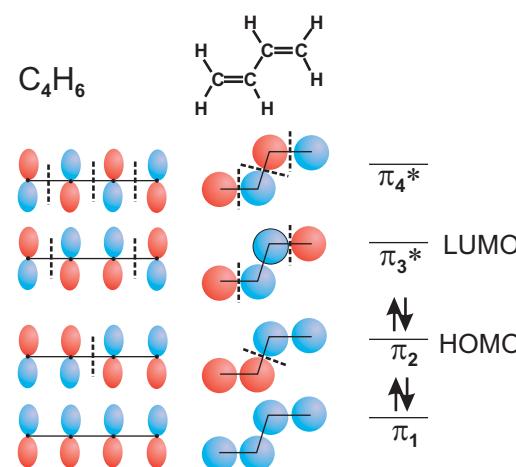


Figure 6.26 π MOs of C_4H_6

Atomic orbitals viewed from the side (left) and top (right)

so π_2 is the highest occupied MO (HOMO) and π_3 is the lowest unoccupied MO (LUMO). Note that both pairs of electrons reside in bonding orbitals, consistent with the Lewis structure that shows two double bonds. However, the orbitals are delocalized over all four carbon atoms, not localized between two atoms as shown in the Lewis structure.

As our last example, we examine the delocalized π system in benzene (C_6H_6) shown in Figure 6.27. Recall that the double bonds in benzene are sometimes represented by a circle (Figure 6.8b) due to resonance in the molecule. Although the construction of the MOs is beyond the scope of this text, an examination of them demonstrates the rules for construction and provides a better understanding of the bonding in this very important molecule. There are six carbon atoms and six p orbitals, so there are six π MOs. The lowest energy MO has no nodal planes and is a bonding orbital delocalized over all six atoms. The highest energy orbital has a nodal plane between each pair of atoms, but, due to the symmetry of benzene, this requires only three nodal planes. Thus, the four remaining MOs must contain either one or two nodal planes. In fact, two MOs have one nodal plane, and two MOs have two nodal planes. The π system has six electrons, so only the three bonding MOs are occupied, which gives rise to the three double bonds in the Lewis structure. The three MOs are delocalized over all six carbon atoms, so, consistent with representing the double bonds with a circle, the π electron density is spread over the entire molecule with no localized double bonds.

6.6 CHAPTER SUMMARY AND OBJECTIVES

According to the valence shell electron pair repulsion (VSEPR) model, the valence electron groups, or regions (lone pairs and σ bonds) adopt positions around the atom so as to minimize electron-electron repulsion. The geometries that minimize the interactions require bond angles of 109° for four groups, 120° for three groups, and 180° for two groups. Thus, the application of VSEPR theory to a Lewis structure provides an excellent way to determine the geometry of atoms around a central atom.

In valence bond theory, bonds are produced by the overlap of two orbitals on the bound atoms. The bond that results is called a σ bond if the internuclear axis is enveloped by the bonding electron density or a π bond if the axis lies in a nodal plane of the bond. All bonds contain one and only one σ bond, but multiple bonds also contain π bonds. The bond order of a bond is the sum of the σ and π bonds that it contains. Overlap of simple atomic orbitals does not account for the bond angles obtained from VSEPR, so the atomic

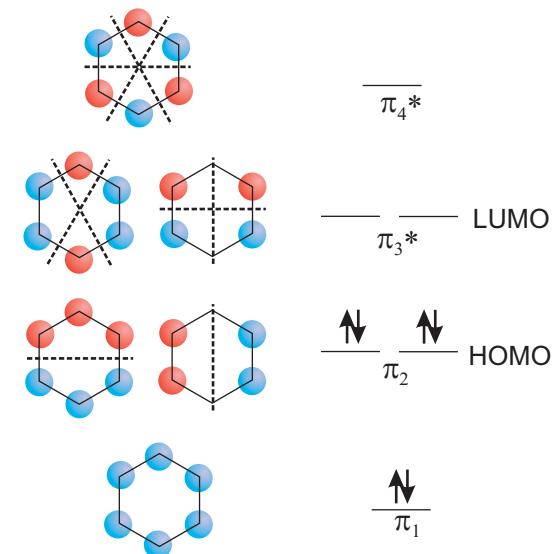


Figure 6.27 MOs for C_6H_6 viewed from the top

Hydrogen atoms have been omitted. Only the relative phases of the orbitals, not their relative contributions to the MOs, are shown.

orbitals must first be mixed in a process called hybridization. The resulting hybrid orbitals are used to form the σ bonds and hold the lone pairs. The hybridization of an atom is used to describe both the bonding and structure around the atom because hybrid orbitals have the geometries required by VSEPR. The orbitals that are not used to construct the hybrid orbitals are used to form π bonds.

In molecular orbital theory, electrons occupy molecular orbitals just as the electrons in an atom occupy atomic orbitals. The molecular orbitals are constructed by combining the atomic orbitals of different atoms. Unlike the bonds produced in valence bond theory, molecular orbitals can be delocalized over several atoms, which explains the observations that valence bond theory invokes resonance to explain.

After studying the material presented in this chapter, you should be able to:

1. predict molecular and ionic shapes based on VSEPR theory (Section 6.1);
2. determine whether an atom obeys the octet rule or uses an expanded octet (Section 6.2);
3. predict the shapes of molecules and ions with atoms using expanded octets (Section 6.2);
4. visualize the three-dimensional arrangement of atoms around a central atom in a complicated molecule (Section 6.3);
5. represent the overlap of two atomic orbitals qualitatively with a drawing (Section 6.4);
6. define and identify σ and π bonds (Sections 6.4 and 6.5);
7. draw the σ and π components of a multiple bond (Section 6.4);
8. determine an atom's hybridization, draw pictures of hybrid orbitals, and account for molecular shapes based on hybridization (Section 6.4);
9. construct molecular orbitals of simple systems and explain resonance in terms of molecular orbitals (Section 6.5);
10. determine whether an MO is bonding, antibonding, or nonbonding (Section 6.5); and
11. identify the HOMO and LUMO for a molecule given its MO diagram and the number of electrons that go in it (Section 6.5).

6.7 EXERCISES

1. Draw the Lewis structure of each of the following ions, showing all nonzero formal charges. Indicate whether each ion is linear or bent. If the ion is bent, what is the bond angle?
 - a) NO_2^{1-}
 - b) N_3^{1-}
 - c) ClO_2^{1-}

2. Draw the Lewis structure of each of the following molecules, showing all nonzero formal charges. Indicate whether each molecule is linear or bent. If the molecule is bent, what is the bond angle?
 - a) N_2O
 - b) HCN
 - c) OF_2

3. Draw Lewis structures for the following molecules. Indicate nonzero formal charges and whether each is trigonal planar or trigonal pyramidal.
 - a) PF_3
 - b) COCl_2
 - c) BF_3

4. Draw Lewis structures for the following ions. Indicate nonzero formal charge and whether each is planar or trigonal pyramidal.
 - a) ClO_3^{1-}
 - b) CO_3^{2-}
 - c) PO_3^{3-}

5. Describe the shapes of the following:
 - a) ClF_3
 - b) XeF_4
 - c) ClF_5

6. The Lewis structures of the sulfate and phosphate ions that obey the octet rule contain large, positive formal charges on the central atoms and an excess of negative formal charges on the oxygen atoms. Assume that S and P use expanded valence shells and draw Lewis structures for the ions that contain no formal charge on the central atoms.

7. What is the hybridization on the central atoms in Exercise 1?

8. What is the hybridization on the central atoms in Exercise 2?

9. What is the hybridization on the central atoms in Exercise 3?

10. What is the hybridization on the central atoms in Exercise 4?

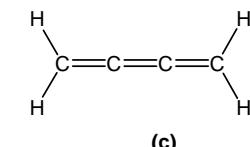
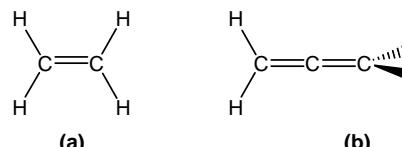
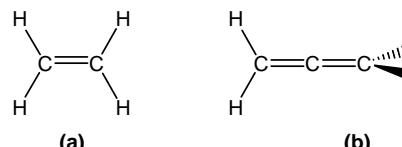
11. We use the approximate bond angles of 120° and 109° around central atoms with three and four electron groups, respectively. However, lone pairs affect bond angles differently than do bonding pairs. With this in mind, rank the following species in order of increasing H-N-H bond angles: NH_2^+ , NH_3 , and NH_4^+ .

12. List the following in order of increasing bond angles: SO_2 , CO_2 and H_2O .

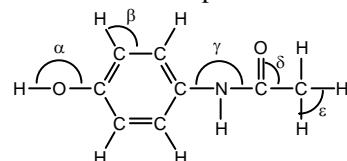
13. The nitrite ion (NO_2^{1-}) can add an H^{1+} ion (proton) to become nitrous acid. Based on the formal charges in the Lewis structure of the anion (Exercise 1a), draw the Lewis structure of nitrous acid, HNO_2 .

14. The carbonate ion (CO_3^{2-}) can add two H^{1+} ions to become carbonic acid. Based on the formal charges in the Lewis structure of the anion (Exercise 4b), draw the Lewis structure of carbonic acid, H_2CO_3 .

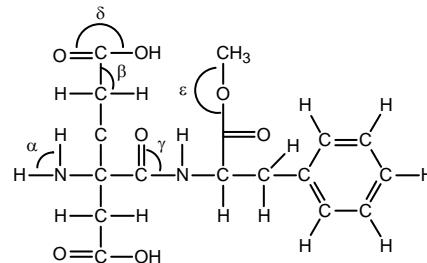
15. Explain why molecules A and C are planar while molecule B is not.



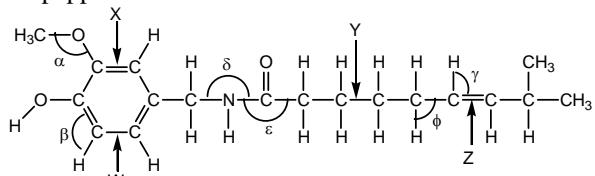
16. Acetaminophen is an analgesic (pain killer) that is often purchased under the name Tylenol®. What are the approximate bond angles labeled α , β , γ , δ and ε in the acetaminophen structure shown below?



17. Aspartame is the active ingredient in the sweetener NutraSweet®. What are the approximate bond angles α , β , γ , δ and ε in the aspartame structure shown below?



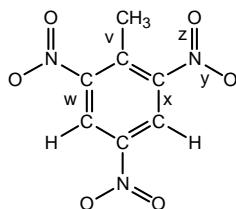
18. Consider the structure of capsaicin, the molecule responsible for the “heat” of chili peppers that is shown below.



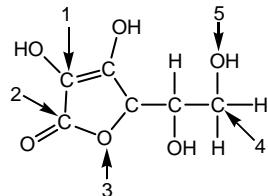
- a) What are the approximate bond angles labeled α , β , δ , ϵ , ϕ , and γ ?
 b) Explain the following statements.
 i) Bonds W and X are the same length.
 ii) Bond Z is shorter than bond X.
 iii) Bond Y is longer than bond W.

19. Consider the structure of the explosive TNT shown below to explain the following:

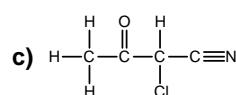
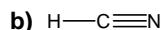
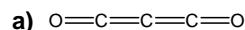
- a) Bond v is longer than bond w.
 b) Bonds w and x are of equal length.
 c) Bonds y and z are of equal length.



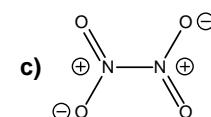
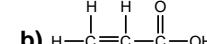
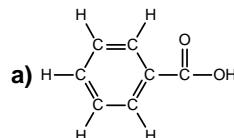
20. What are the hybridizations of the numbered atoms in the following structure of vitamin C?



21. How many σ bonds and how many π bonds are in each of the structures shown below? Note that lone pairs have been omitted for simplicity.



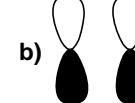
22. What are the numbers of σ and π bonds in each of the following? Note that lone pairs have been omitted for simplicity.



23. Indicate whether the following orbital interactions between s, p and d orbitals would result in σ bonds or in π bonds.



24. Indicate whether the following orbital interactions between p and d orbitals would result in σ bonds or in π bonds.



25. Draw two resonance structures for the acetate ion ($\text{CH}_3\text{COO}^{1-}$). Draw an MO diagram for the π system.

26. What is meant by a delocalized π system? Give an example of a molecule with a delocalized π bond and one with a localized π bond.

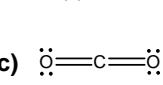
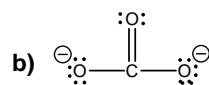
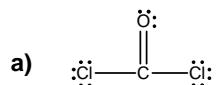
27. How many σ bonds and π bonds are found in a single bond, a double bond, and a triple bond?

28. How is the number of π bonds to a central atom related to its hybridization?

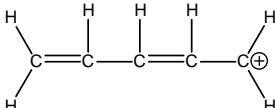
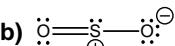
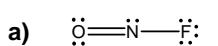
29. Indicate the hybridization of a central atom with the following electron groups:

- a) two σ bonds, one π bond and one lone pair
 b) three σ bonds, no π bonds, and one lone pair
 c) two σ bonds, two π bonds, and no lone pairs
 d) two σ bonds, no π bonds, and two lone pairs

30. Indicate whether the π bonds in the following are localized or delocalized. If the bonds are delocalized, draw the other resonance form(s).



31. Indicate whether the π bonds in the following are localized or delocalized. If the bonds are delocalized, draw the other resonance form(s).



32. All of the elements of the second period form fluorides. What is the hybridization on the central atom in each of the following: BeF₃, BF₃, CF₄, NF₃, and OF₂? Arrange the fluorides in order of increasing bond angles.

Hint: recall that lone pairs affect bond angles differently than bonding pairs.

33. What change in hybridization (if any) occurs on the carbon in each of the following reactions?

- a) CO₂ + H₂O \rightarrow H₂CO₃
 b) CH₄ + 2O₂ \rightarrow CO₂ + 2H₂O
 c) C₂H₂ + 2H₂ \rightarrow C₂H₆

34. What change in hybridization (if any) occurs on the sulfur in each of the following reactions?

- a) SO₃ + H₂O \rightarrow H₂SO₄
 b) SO₂ + 1/2O₂ \rightarrow SO₃
 c) SO₂ + 3H₂ \rightarrow H₂S + 2H₂O

35. Draw the result of mixing a p_x and a p_y orbital.

36. Use circles to represent the contributions of the AOs to represent the MOs of the following bonds:

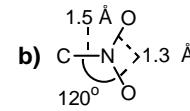
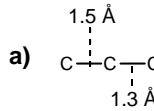
a) C-S

b) C-F

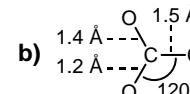
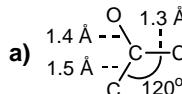
c) C-Sn

Instructions for 37 - 40 The relative positions of the atoms in a molecule can be obtained by a method known as x-ray diffraction. Lone pairs are not observed and hydrogen atoms are so small that their positions are often unknown, but we can construct the Lewis structure of the molecule, including placement of the lone pairs and hydrogen atoms from the bond lengths, the bond angles, and a knowledge of the relationships between bonding and structure given in Chapters 5 and 6. Assume that all atoms in Exercises 37-40 obey the octet rule and have minimum formal charge to add hydrogen atoms, lone pairs, and/or multiple bonds as required to complete each skeletal structure. Draw all resonance forms in cases where more than one resonance form is important. Refer to the table of bond lengths on the back cover to determine bond orders, Table 5.4 (page 94) to determine the number of bonds to an atom with zero formal charge, and the bond angles to determine hybridizations. Carbon has zero formal charge in all cases.

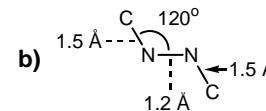
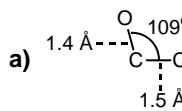
37. Add multiple bonds, lone pairs, and hydrogen atoms to the following molecules:



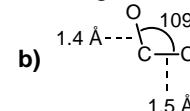
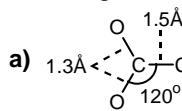
38. Add multiple bonds, lone pairs, and hydrogen atoms to the following molecules:



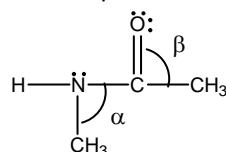
39. Add multiple bonds, lone pairs, and hydrogen atoms to the following molecules:



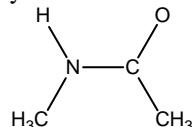
40. Add multiple bonds, lone pairs, and hydrogen atoms to each of the following anions that have -1 charges:



41. An *amide* is a compound that has a nitrogen next to a C=O group.
- a) Consider the Lewis structure of the amide $\text{CH}_3\text{NHCOCH}_3$ that contains no formal charge and is shown below. What are predicted values for angles α and β and what is the hybridization on the N atom?



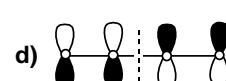
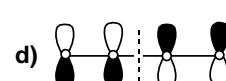
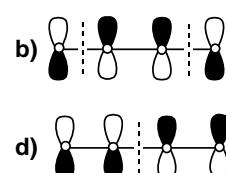
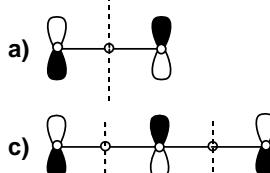
- b) The C-N-C bond angle is actually $\sim 120^\circ$ and the structure shown below is planar (except for the hydrogen atoms in the CH_3 groups). What is the hybridization of the N atom?



- c) Draw another Lewis structure that is important in the bonding description as determined from the structural information given in Part b. Indicate all nonzero formal charge in the structure. Are the π electrons localized or delocalized?

42. Use the rules for MO construction to draw an MO diagram for the pi system of linear A_5 . Label each MO as bonding, nonbonding, or antibonding. See Exercise 43c for one of the five orbitals.

43. Classify each of the following π MOs as bonding, nonbonding, or antibonding.



Use the appropriate MO diagram for the valence orbitals of the diatomic molecules of the elements of the second period shown below for Exercises 44-49. Note that the order of the $\pi(2p)$ and $\sigma(2p)$ orbitals for Li_2 through N_2 is reversed from that for O_2 and F_2 . To answer the questions, determine the number of valence electrons for each diatomic molecule and place them in the diagram.

$\sigma^*(2p)$	—	—	$\sigma^*(2p)$
$\pi^*(2p)$	— —	— —	$\pi^*(2p)$
$\sigma(2p)$	—	— —	$\pi(2p)$
$\pi(2p)$	— —	—	$\sigma(2p)$
$\sigma^*(2s)$	—	—	$\sigma^*(2s)$
$\sigma(2s)$	—	—	$\sigma(2s)$
$\text{Li}_2 - \text{N}_2$		$\text{O}_2 & \text{F}_2$	

44. What are the bond orders of the following bonds in the following diatomic molecules?

- a) Li_2 b) Be_2 c) B_2 d) C_2
 e) N_2 f) O_2 g) F_2 h) Ne_2

45. Which of the diatomic molecules in Exercise 44 should not form?

46. Which of the diatomic molecules in Exercise 44 have unpaired electrons?

47. Which has the strongest bond: O_2^{1-} , O_2 , or O_2^{1+} ? What is the bond order of the strongest bond?

48. The peroxide ion is O_2^{2-} . What is the O-O bond order in the peroxide ion?

49. Assume that the energy level order is the same for the bonding between nitrogen and oxygen in NO as it is between two O atoms in O_2 and construct an MO diagram for NO. NO has one unpaired electron. Is it more likely to gain an electron to form NO^{1-} or to lose an electron to form NO^{1+} ?

Chapter 7

States of Matter and Changes in State

7.0	<i>Introduction</i>	7.5	<i>Liquids</i>
7.1	<i>Gases</i>	7.6	<i>Changes in State</i>
7.2	<i>Kinetic Molecular Theory and Thermal Energy</i>	7.7	<i>Chapter Summary and Objectives</i>
7.3	<i>Intermolecular Forces</i>	7.8	<i>Exercises</i>
7.4	<i>Solids</i>		

7.0 INTRODUCTION

The substances we deal with every day exist in one of three states of matter: solid, liquid or gas. The molecules in the liquid and solid states are much closer to one another than are the molecules in the gas state, so the solid and liquid states are often called the *condensed states*. Substances are held in the condensed states by Coulombic forces between the molecules. Indeed, it is the strength of these forces that dictates the state of matter adopted by a substance at a given temperature and pressure.

We experience some substances in all three states: water is commonly found as solid ice, liquid water, and steam. However, many other substances are usually observed in only one state: copper, iron, sugar, and salt are found as solids; mercury as only a liquid; and oxygen, nitrogen, and helium as gases. Substances are seldom found as pure liquids because there is always some vapor above the liquid. Indeed, the odor associated with a liquid is due to vapor molecules that have escaped from the liquid. In this chapter, we examine the behavior of gases and the forces that are responsible for the condensed states. We then briefly discuss the liquid state, define the solid state, and conclude with a discussion of changes in state.

THE OBJECTIVES OF CHAPTER 7 ARE TO:

- characterize the different states of matter;
- describe the behavior of gases;
- explain the postulates of kinetic-molecular theory;
- define the absolute temperature scale;
- discuss the meaning of the term *thermal energy*;
- apply some of the general concepts of kinetic-molecular theory to phase equilibria;
- explain the origin of intermolecular forces;

- show how to determine if a molecule has a permanent dipole;
- describe the unique properties of water that result from hydrogen bonding;
- compare thermal energy to the energy of interaction for a solid, liquid, and gas;
- describe some properties of liquids and relate them to the strengths of the intermolecular interactions;
- describe the relative energies of the three states of matter;
- describe the various changes in state at a molecular level; and
- demonstrate the use of a phase diagram and how it is constructed.

7.1 GASES

Molecules in the **gaseous** state adopt the shape and the volume of their closed containers. If the volume of the container is changed, then the volume of the gas changes as well. The focus of this section is the variation of the volume (V) of a gas as its pressure (P), its temperature (T), and its amount (n) are changed.

PRESSURE AND BOYLE'S LAW

Studies of the composition of air and the properties of gases were greatly simplified in the mid 1600's when an Italian named Evangelista Torricelli (Galileo's secretary) invented the **barometer**. Scientists of the time realized that the earth was blanketed with a layer of gas that had a weight and therefore exerted a pressure, but they did not know how to measure the pressure. Torricelli discovered that when a glass tube, closed at one end and open at the other, is filled with mercury and immersed with the open end down into a pool of mercury, only part of the mercury drains from the tube (Figure 7.1). Furthermore, the height of the mercury column is independent of the length and cross-sectional area of the tube. He reasoned that it was the pressure exerted by the atmosphere that supported the column of mercury in the tube, thus the pressure exerted by the weight of mercury in the tube must equal the pressure exerted by the gases in the atmosphere.* Increases or decreases in pressure result in rises or drops in the height of the column, respectively. Consequently, the pressure is frequently given by the height of the column directly, and, in honor of the inventor of the barometer, a pressure that supports a mercury column to a height of 1 mm is called a **torr**.

The pressure exerted by the atmospheric gases at sea level is 14.7 lb/in². This means that a column of the atmosphere that goes from sea level to the top of the atmosphere (~30 km) and has a cross-sectional area 1 square inch weighs 14.7 pounds. Atmospheric

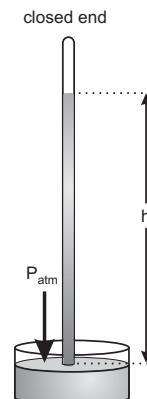


Figure 7.1 A barometer

The pressure exerted by the weight of the mercury column of height h equals the pressure exerted by the weight of the atmosphere.

* Pressure is a force per unit area, $P = F/A$. In a barometer, the force is the weight of the mercury in the inverted tube, and A is the cross-sectional area of the tube.

pressure is sufficient to support a column of mercury, like that shown in Figure 7.1, to a height of 760 mm. The following equalities relate the units for measuring gas pressures.

$$14.7 \text{ lb/in}^2 = 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01 \times 10^5 \text{ Pa}$$

Eq. 7.1

Pa is the pascal, the SI unit of pressure ($1 \text{ Pa} = 1 \text{ kg/m} \cdot \text{s}^2$).

The device used to measure the pressure of a gas in the laboratory is called a **manometer**. One side of the manometer shown in Figure 7.2 is open to the atmosphere, while the other is attached to the gas whose pressure is to be measured. Consequently, the atmospheric pressure (P_{atm}) is pushing on the right side and the unknown gas pressure (P) is pushing on the left. When the two pressures are the same, the two mercury columns in the manometer are at the same height, and $h = 0$. However, when the two pressures are not the same, the side with the greater pressure exerts the greater force, which causes the mercury column on that side to drop and the column on the other side to rise. *The difference in the pressures of the two sides is given by the difference in the two mercury levels, h .* The gas in Figure 7.2 exerts a pressure greater than barometric pressure because its mercury column is lower than the column on the atmosphere side, so $P = P_{\text{atm}} + h$.

Example 7.1

- a) What is the pressure of a gas, in atmospheres, if it can support a mercury column to a height of 407 mm?

$$407 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.536 \text{ atm}$$

- b) A pressure of 0.68 atm will support a column of mercury to what height?

$$0.68 \text{ atm} \times \frac{760 \text{ mm Hg}}{1 \text{ atm}} = 5.2 \times 10^2 \text{ mm}$$

- c) What is the pressure of the gas shown in the margin if barometric pressure is 757 torr? Express the answer in torr and atmospheres.

The column is lower on the side open to the atmosphere, which means that the pressure of the gas is less than barometric (atmospheric) pressure. Thus,

$$P = P_{\text{atm}} - h = 757 - 285 = 472 \text{ mm Hg} = 472 \text{ torr.}$$

We use the conversion factor taken from Equation 7.1 to obtain atmospheres.

$$472 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.621 \text{ atm}$$

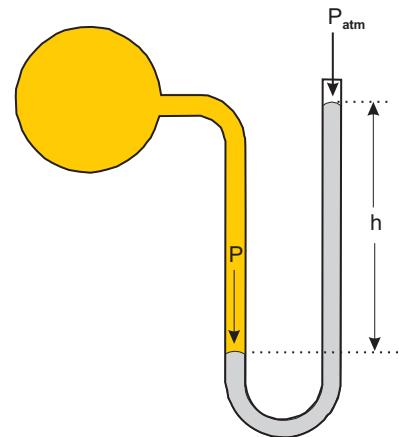
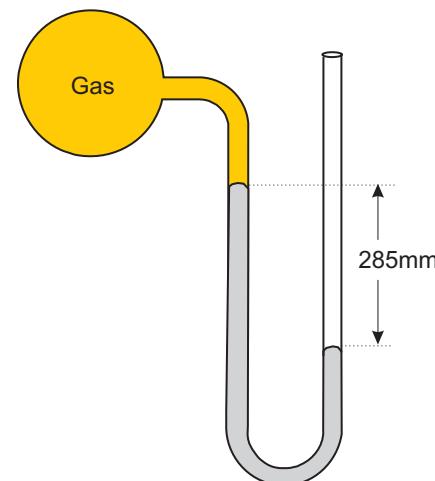


Figure 7.2 A manometer

A manometer is used to measure the pressure of a gas. In the above experiment, the pressure of the gas (P) is greater than barometric pressure (P_{atm}) by h mm of Hg; i.e., $P = P_{\text{atm}} + h$.



Example 7.1c

The volume of a given amount of gas at a constant temperature varies with its pressure, and shortly after the invention of the barometer, Robert Boyle found the relationship, which is now called **Boyle's law**:

The volume of a gas varies inversely with its pressure; or the pressure-volume product of a gas is constant as long as the amount and temperature of the gas are constant.

$$PV = k(n,T)$$

Eq. 7.2

$k(n,T)$ is a function of the number of moles (n) and the temperature (T) of the gas. Figure 7.3 shows the volume of one mole of gas as a function of its pressure at 0°C .

ABSOLUTE TEMPERATURE AND CHARLES' LAW

Experiments with gases in the late 1700's and early 1800's determined the relationship between the volume of a gas and its temperature. As shown in Figure 7.4, the volume of a given amount of gas at constant pressure increases linearly with its temperature. Although the slope of the straight line varies with the number of moles and pressure of the gas, extrapolation of all lines to the temperature of zero volume yields the same temperature, -273.15°C (degrees Celcius). At lower temperatures the volume of the gas would be negative, which is not physically possible, so we conclude that temperatures can be no lower than -273.15°C . The absolute temperature or Kelvin scale was defined based on this absolute minimum in temperature.

$$K = ^\circ\text{C} + 273.15$$

Eq. 7.3

Equation 7.3 shows that you add 273.15 to a temperature in degrees Celsius to convert it to the absolute scale. For example, water freezes at 0°C , which is 273 K,* and boils at 100°C , which is 373 K. Room temperature is usually assumed to be 25°C , which is 298 K. *The absolute temperature must be used in all equations involving the temperature of a chemical system.* However, either the Celsius or absolute scales can be used in equations involving a change in the temperature of a system because the unit size is the same in both scales. Once the new temperature scale was defined, the relationship between the volume and temperature of a gas, which is known as **Charles' law**, could be stated as

The volume of a gas is directly proportional to its temperature expressed in kelvins.

$$V = k(n,P)T$$

Eq. 7.4

$k(n,P)$ is a constant that depends upon the number of moles of gas (n) and its pressure (P).

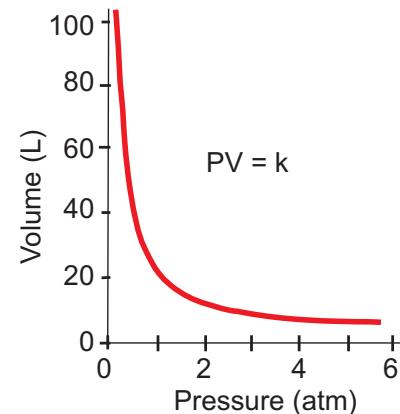


Figure 7.3 Boyle's Law

The volume of one mole of gas at 0°C plotted versus its pressure in atmospheres. $k = 22.4 \text{ L-atm}$ for 1 mole of gas at 0°C , but it is a function of both the number of moles and the temperature.

* Note that the degree symbol ($^\circ$) is used for degrees Celsius (0°C) but not for kelvins (273 K).

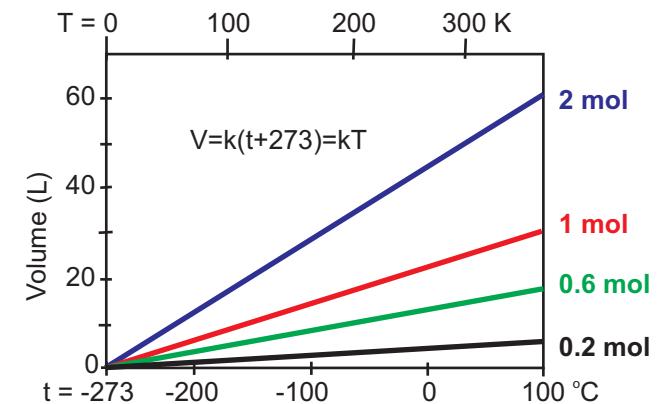


Figure 7.4 Charles' Law

The volume of the specified number of moles of gas plotted as a function of its temperature. The bottom scale is the temperature (t) in degrees Celsius, while the top scale is the temperature (T) in kelvins.

THE IDEAL GAS LAW

In Chapter 1, we discussed **Avogadro's law**,

Equal volumes of gases measured under the same conditions of temperature and pressure contain equal numbers of molecules; or the volume of a gas at constant temperature and pressure is directly proportional to the number of moles of gas.

$$V = k(P,T)n$$

Eq. 7.5

n is the number of moles of gas, and k(P,T) is a proportionality constant that depends upon the pressure and the temperature of the gas.

We have three equations that relate the volume of a gas to the pressure, temperature, and number of moles of the gas. Boyle's, Charles', and Avogadro's Laws can all be combined into one **ideal gas law**.

The volume of a gas is proportional to the number of moles of the gas and its absolute temperature and inversely proportional to its pressure.

$$PV = nRT$$

Eq. 7.6

R is the proportionality constant, known as the ideal gas law constant ($R = 0.0820578 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). The use of the ideal gas law is reviewed in detail in Appendix B, but we present one example of its use here.

Example 7.2

A weather balloon with a volume of $1.0 \times 10^3 \text{ L}$ will collect data at a height of 10 km, where the temperature is -50°C and the pressure is 120 torr. How many grams of helium should be placed in the balloon to completely fill it under these conditions?

The pressure in atmospheres is

$$\frac{120 \text{ torr}}{760 \text{ torr/atm}} = 0.158 \text{ atm}$$

The temperature in kelvins is $T = -50 + 273 = 223 \text{ K}$, and the volume is $1.0 \times 10^3 \text{ L}$. We are asked for the amount of gas, represented by n in the ideal gas law, so we solve Equation 7.6 for n and substitute the given values of P, V and T to obtain the number of moles of helium needed.

$$n = \frac{PV}{RT} = \frac{(0.158 \text{ atm})(1.0 \times 10^3 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(223 \text{ K})} = 8.6 \text{ mol}$$

The molar mass of helium is 4.0 g/mol, so the mass of helium required is

$$8.6 \text{ mol} \times \frac{4.0 \text{ g}}{\text{mol}} = 34 \text{ g He}$$

MIXTURES OF GASES

If molecules are to react, they must come into contact with one another. That is, reactants must be mixed. Consequently, an understanding of mixtures is essential to an understanding of how reactions occur. In this section, we discuss mixtures of gases.

Each component of a gaseous mixture exerts its own pressure, called its **partial pressure**. The partial pressure of component A, which is written P_A , can be obtained from the ideal gas law

$$P_A = \frac{n_A RT}{V} = \left(\frac{n_A}{V} \right) RT \quad \text{Eq 7.7}$$

The composition of a mixture of gases is the same throughout, so a mixture is said to be **homogeneous**. Homogeneous mixtures are also called **solutions**. Solutions are characterized by the **concentrations** (the number of particles per unit volume) of their components. The molarity of a solution is the most common type of concentration in the laboratory. The **molar concentration** of A, which is given the symbol $[A]$, is defined as the number of moles of A per liter of the solution:

$$[A] = \frac{n_A}{V} \quad \text{Eq 7.8}$$

n_A is the number of moles of A in V liters of solution. $[A] = 1 \text{ M}$ is read as “the concentration of A is 1 molar.” Substitution of Equation 7.8 into Equation 7.7 yields the relationship of the partial pressure of a gas to its molar concentration.

$$P_A = [A]RT \quad \text{Eq 7.9}$$

The total pressure of a mixture is related to the partial pressures by **Dalton's Law of partial pressures**:

The total pressure in a mixture of gases is the sum of the partial pressures of all gases in the mixture; i.e., $P_{\text{TOT}} = \sum_i P_i$, where P_i is the partial pressure of the i^{th} gas.

Thus, the total pressure in a mixture of A and B is $P_{\text{total}} = P_A + P_B$, which can be related to the number of moles or concentrations of the components with the use of the ideal gas law

$$P_{\text{total}} = P_A + P_B = \frac{n_A RT}{V} + \frac{n_B RT}{V} = RT \frac{(n_A + n_B)}{V} = RT ([A] + [B])$$

The total pressure of a mixture of non-interacting gases depends only upon the partial pressures or the temperature and concentrations of its components; it is independent of their identities.

Example 7.3

What is the molar concentration of fluorine in a 4.0-L flask that contains 4.2 g of fluorine?

Use Equation 7.8, which shows that the molar concentration of fluorine is equal to the number of moles of fluorine divided by the volume of the container. Thus, we start by determining the number of moles of fluorine. Fluorine is a diatomic gas (F_2), so $M_m = 2(19.0) = 38.0 \text{ g}\cdot\text{mol}^{-1}$ and the number of moles is

$$n = 4.2 \text{ g } F_2 \times \frac{1 \text{ mol } F_2}{38.0 \text{ g } F_2} = 0.11 \text{ mol } F_2$$

Now, we can determine the concentration of F_2 with Equation 7.8.

$$[F_2] = \frac{0.11 \text{ mol } F_2}{4.0 \text{ L}} = 0.028 \text{ mol}\cdot\text{L}^{-1} \text{ or } 0.028 \text{ M}$$

The concentration of fluorine in the container is 0.028 M (read 0.028 molar).

Example 7.4

0.12 mol Ne and 0.19 mol He are placed in a 6.0-L flask at 55 °C. What is the total pressure in the flask, and what are the partial pressures of the two gases?

We first determine the two partial pressures with the ideal gas law. The temperature of the mixture is $T = 55 + 273 = 328 \text{ K}$. The volume of each gas in a mixture is equal to the volume of the container, so $V = 6.0 \text{ L}$.

$$P_{\text{Ne}} = \frac{n_{\text{Ne}}RT}{V} = \frac{(0.12 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(328 \text{ K})}{6.0 \text{ L}} = 0.54 \text{ atm}$$

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{(0.19 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(328 \text{ K})}{6.0 \text{ L}} = 0.85 \text{ atm}$$

The total pressure is the sum of the partial pressures: $P_{\text{total}} = 0.54 + 0.85 = 1.39 \text{ atm}$. Alternatively, the total pressure can be obtained by applying the ideal gas law directly to the mixture. $n_{\text{total}} = 0.12 \text{ mol Ne} + 0.19 \text{ mol He} = 0.31 \text{ mol}$.

$$P_{\text{total}} = \frac{n_{\text{total}}RT}{V} = \frac{(0.31 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(328 \text{ K})}{6.0 \text{ L}} = 1.39 \text{ atm}$$

7.2 KINETIC-MOLECULAR THEORY AND THERMAL ENERGY

The behavior of ideal gases* is explained by **kinetic-molecular theory**, which is based on the following postulates:

1. The volume of the molecules is negligible compared to the volume of their container. This means that, on average, the distances between the molecules of the gas are large compared to their size.
2. The particles undergo constant, random motion.
3. There are no attractive forces between the particles.*
4. The average kinetic energy (energy of motion) of the particles is proportional only to the absolute temperature.

The fourth postulate states that the temperature of a system is a measure of the average kinetic energy (energy of motion) of the molecules in the system, so hotter atoms and molecules have more kinetic energy than do colder ones. The only motion available to single atoms is translation,[†] so hotter atoms move faster than do colder atoms. For example, the average speed of a He atom on a cold day ($0\text{ }^{\circ}\text{C} = 32\text{ }^{\circ}\text{F}$) is about 1.3×10^3 m/s, while it is close to 1.4×10^3 m/s on a hot day ($32\text{ }^{\circ}\text{C} = 90\text{ }^{\circ}\text{F}$). Thus, a He atom travels 12 football fields per second! However, motion is more complicated for molecules, because they can also rotate, and vibrate (atoms vibrate against their bonds). Thus, hotter molecules move faster, spin faster, and vibrate faster than cooler molecules.

The average kinetic energy of the molecules in a system is often referred to as the **thermal energy** of the system. Thermal energy is the average energy, so some molecules have more energy and are moving faster, while others have less energy and are moving slower. All of the energies related to molecules or ions that we have encountered to this point have been potential energies arising from electrostatic interactions. The thermal energy of the molecules is energy that can be used to overcome these interactions and to drive chemical reactivity. For example, if you supply enough thermal energy (get the molecule hot enough), the motions become so energetic that bonds break, which is what happens when you char meat under a broiler. In addition, as we explain later in this chapter, when the thermal energy exceeds the potential energy that holds the molecules in a crystal, the crystal melts. The thermal energy of the molecules also dictates how fast they react with one another. When the temperature of a reaction is increased, the rate at which it occurs also increases as the molecules collide more frequently and with more energy.

Thermal energies of solids and liquids are not easily defined, but *chemists usually approximate the thermal energy as RT* , where R is the ideal gas law constant. However, in

* Most gases do interact at high pressures and/or low temperatures. The interactions affect their pressure and volume to produce deviations $PV = nRT$. Such gases are no longer ideal gases. Only non-ideal gases can condense to become liquids.

[†] Translation is motion in a straight line. Atoms and molecules can both translate, but molecules can also rotate and vibrate. We will consider the different ways molecules can distribute their kinetic energy in more detail in Chapter 9.

calculations in which energy is involved, the value used is $R = 8.31451 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Room temperature is $\sim 300 \text{ K}$, so thermal energy at room temperature is approximately

$$\Delta E_{\text{thermal}} \sim RT = (8.3 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300 \text{ K}) = 2.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Thus, processes requiring hundreds of $\text{kJ}\cdot\text{mol}^{-1}$ occur only rarely at room temperature, while those requiring less than $\sim 10 \text{ kJ}\cdot\text{mol}^{-1}$ occur frequently. RT is only an approximation for thermal energy, but it does demonstrate that *the thermal energy of a system depends only upon its temperature*.

Example 7.5

- a) What is the approximate thermal energy of molecules in boiling water?

Water boils at 100°C , so $T = 100^\circ\text{C} + 273 = 373 \text{ K}$

We approximate the thermal energy of the liquid as RT and write:

$$RT = (8.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(373 \text{ K}) = 3.1 \times 10^3 \text{ J}\cdot\text{mol}^{-1}$$

Thus, the thermal energy is about $3 \text{ kJ}\cdot\text{mol}^{-1}$

- b) To what temperature should a sample be heated so that its thermal energy is $\sim 100 \text{ kJ}\cdot\text{mol}^{-1}$?

$$E = (100 \text{ kJ}\cdot\text{mol}^{-1})(10^3 \text{ J}\cdot\text{kJ}^{-1}) = 1.0 \times 10^5 \text{ J}\cdot\text{mol}^{-1}$$

$$T = \frac{E}{R} = \frac{1.0 \times 10^5 \text{ J}\cdot\text{mol}^{-1}}{8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}} = 1.2 \times 10^4 \text{ K} = 12,000 \text{ K}$$

7.3 INTERMOLECULAR FORCES

Particles in the gas phase are relatively far apart, so their attractive forces are negligible compared to their thermal energy. However, the attractive forces between particles in the condensed states are strong enough to hold the particles in contact with one another. Ionic compounds are always solids at room temperature because their cations and anions are held in the solid network by strong electrostatic attractions called ionic bonds. However, molecular substances can occur as gases (O_2), liquids (H_2O), or solids (sugar) at room conditions. This diversity in states arises from a diversity in the strengths of the forces between the molecules. Whereas the strength of ionic bonds determines the physical properties of a salt crystal, the physical properties of molecular substances are not related to the strength of their covalent bonds. In molecular substances, we must distinguish between two different kinds of forces:

Intramolecular forces exist within a molecule. They are the bonds between atoms that hold the atoms together in the molecule.

Intermolecular forces exist between molecules. They are the forces between different molecules that keep the molecules in the liquid and solid states.

The N≡N bond is a very strong bond, so the intramolecular force between the nitrogen atoms in an N₂ molecule is very strong. However, N₂ is a gas at room conditions because the intermolecular forces between different N₂ molecules are very weak.

Intermolecular forces, like all interactions in chemistry, are electrostatic. Thus, condensed phases in molecular substances result because there is an attraction between regions of opposite charge on the molecules. However, these charges are smaller, more diffuse, and farther apart than those in bonds, so the force of attraction between different molecules is much less than that between the atoms in a bond. Bond energies lie between 100 and 1000 kJ/mol, but the strengths of most intermolecular interactions are less than 10 kJ/mol. Consider that the bond formed with Super Glue® is an intramolecular (bonding) interaction, while *static cling* is an intermolecular interaction.

Although molecules are electrically neutral, many have regions of nonzero charge due to asymmetric distributions of their valence electrons that produce regions with above normal electron density that are slightly negative (δ^-) and regions of depleted electron density that are slightly positive (δ^+). Such molecules contain two poles, one positive (δ^+) and one negative (δ^-). The presence of two poles in the molecule results in a **molecular dipole**, much like the bond dipole discussed in Section 5.2. In this section, we discuss the origin of these dipoles and the forces they create.

DISPERSION FORCES

Consider the three molecules X, Y, and Z in Figure 7.5. In Figure 7.5a, they have a symmetric charge distribution, so they have no dipoles. However, random electron motion in molecule Y (Figure 7.5b) results in a temporary dipole because, for an instant, there are more electrons on the left side producing a partial negative charge. Movement of electrons to the left leaves the right side slightly electron deficient producing a partial positive charge there. The negative end (red) has increased electron density, which repels electrons in molecule X. The positive end (blue) is electron deficient, so it attracts the electrons in molecule Z. In Figure 7.5c, dipoles in molecules X and Z have been induced by the random dipole generated in molecule Y. The presence of these **induced dipoles** results in intermolecular interactions between the molecules (dotted lines in Figure 7.5c). The force

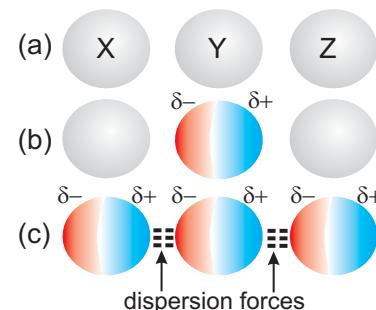


Figure 7.5 Dispersion forces

Regions of negative charge are shown in red, while regions of positive charge are shown in blue.

(a) Molecules X, Y and Z have symmetrical charge distributions and are not interacting.

(b) Random electron movement produces a temporary dipole in Y.

(c) The temporary dipole in Y induces dipoles in X and Z. The attraction between induced dipoles is called a dispersion force.

of attraction of the opposite charges created by the induced dipoles is called a **dispersion force**. Dispersion forces are the most common forces between molecules, because *dispersion forces exist in all molecular substances*. Dispersion forces are most important in molecules with large electron clouds, where electrons have more freedom of motion. Thus, dispersion forces typically increase with molecular size or molar mass.

DIPOLE-DIPOLE (DIPOLAR) FORCES

Most molecules contain atoms with partial positive charge and atoms with partial negative charge as a result of the electronegativity differences that produce polar bonds. If the centers of positive and negative charge do not coincide, two poles are produced and the molecule has a **permanent dipole**. The magnitude of the dipole depends upon both the size and the separation of the two centers of charge; if the centers of charge coincide, their separation is zero and they have no permanent dipole. Molecules with permanent dipoles are said to be a **polar**, while those that do not have permanent dipoles are said to be **nonpolar**. Interactions between the centers of opposite charge of the permanent dipoles of different molecules are called **dipolar forces** or **dipole-dipole forces**. *Dipolar forces act in addition to dispersion forces*. For example, the dispersion forces in HCl and F₂ are expected to be nearly the same because they have similar molar masses (38 and 37 g/mol, respectively). However, HCl is polar, and as shown in Figure 7.6, the partial positive charge on the hydrogen atom of one HCl molecule interacts with the partial negative charge on the chlorine atom of an adjacent molecule to produce a dipolar force between the molecules. This force is in addition to the dispersion forces, so the intermolecular forces are greater in HCl than in F₂, which makes HCl gas much easier to liquefy.

While electronegativity differences are important in determining the charge on the two centers, geometry determines their separation. For example, hydrogen is less electronegative than oxygen, so each hydrogen atom in a water molecule carries some positive charge, while the oxygen atom carries some negative charge. The magnitude of the charge on the oxygen must be twice that on each hydrogen atom because a water molecule is neutral, so the partial charges must sum to zero. The center of positive charge lies midway between the two H atoms, and because water is bent (Figure 7.7), it does not coincide with the center of negative charge on the oxygen atom. The combination of large electronegativity differences and a ~104° bond angle makes water a very polar molecule. As shown in Figure 7.7, the molecular dipole is often shown as an arrow pointing from the center of positive charge toward the center of negative charge.

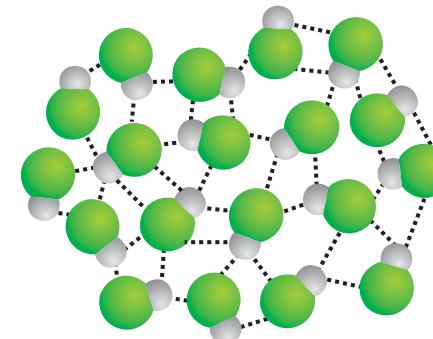


Figure 7.6 Dipolar interactions in a polar molecule

Dipolar interactions in HCl, which are represented with dashed lines, are between the Cl atom of one molecule (negative end of dipole) and the H atom of another molecule (positive end of dipole).

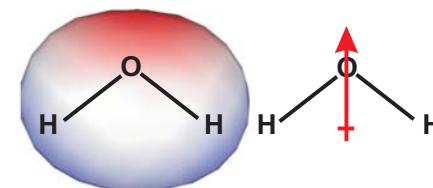


Figure 7.7 Dipole of water

Regions of charge are due to electronegativity differences between the bound atoms. The center of positive charge (blue region) lies between the two hydrogen atoms, while the center of negative charge (red region) resides on the oxygen atom. The molecular dipole is represented by an arrow pointing from the center of positive charge toward the center of negative charge.

Example 7.6

Which has the greater dipole, CO₂ or SO₂?

The electronegativities of both sulfur and carbon are 2.5, while that of oxygen is 3.5. Thus, the carbon and sulfur atoms carry similar positive charges, as do the oxygen atoms in the two molecules. The centers of positive charge lie on the carbon and sulfur atoms, while the centers of negative charge lie on the centers of the lines that connect the two oxygen atoms. The relative positions of the centers of positive and negative charge depend upon the molecular shapes, which are shown in Figure 7.8.

CO₂ is linear, so the center of negative charge (the midpoint of the O-O line) lies on top of the center of positive charge. Since the centers of positive and negative charge coincide, CO₂ has no permanent dipole and is a nonpolar molecule. Sulfur dioxide is bent, so the line connecting the two oxygen atoms no longer passes through the sulfur. Consequently, the center of negative charge does not coincide with the center of positive charge, and SO₂ has a permanent dipole, *i.e.*, it is a polar molecule.

Molecular polarity can also be viewed as the vector sum of the bond dipoles as shown in Figure 7.9. The two bond dipoles in CO₂ are of the same magnitude, but they cancel because they point in opposite direction. In SO₂, the two bond dipole vectors are not opposed and add to give the resultant molecular dipole.

Intermolecular **dipole-dipole (dipolar)** forces result from the attraction between the oppositely charged poles of polar molecules: *the more polar the molecule, the stronger the force*. The difference between dispersion forces and dipolar forces is that the dipole in dipolar interactions is permanent rather than induced or temporary. Molecules with permanent dipoles also exert dispersion forces. Thus, SO₂ molecules experience both dipole-dipole and dispersion interactions, while CO₂ molecules interact only through dispersion forces.

HYDROGEN BONDING

The **hydrogen bond** is an especially strong case of a dipolar interaction in compounds with N-H, O-H or F-H bonds. The strength of this force results from two factors:

1. The large electronegativity differences between electropositive H and the very electronegative N, O, and F atoms result in large partial charges on the atoms.
2. The small size of the elements allows the H atom on one molecule to get very close to the N, O, or F atom of an adjacent molecule.

The close proximity of relatively large charges produces a strong intermolecular interaction.

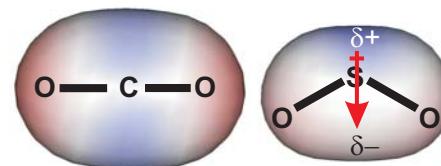


Figure 7.8 Charge distribution in CO₂ and SO₂

CO₂ is linear, so the centers of positive (blue) and negative (red) charge coincide (both are on the carbon atom), which makes CO₂ nonpolar. The centers of positive and negative charge do not coincide in SO₂, so it is a polar molecule. The resulting dipole is represented by an arrow pointing from the center of positive charge to the center of negative charge.

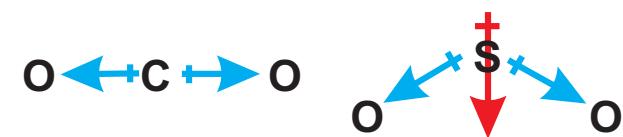


Figure 7.9 Molecular dipoles are the sums of bond dipoles

CO₂ is linear, so the bond dipoles (blue arrows) cancel, making it nonpolar, but SO₂ is bent, so the bond dipoles add to produce a permanent dipole (red arrow).

Hydrogen bonding strongly affects the properties of water. When water freezes, the molecules orient themselves so as to maximize the hydrogen-bonding interactions. The result is that each oxygen atom is surrounded by four hydrogen atoms: two covalently bound H atoms that make up the water molecule and two atoms from two other water molecules, which are hydrogen bonded through oxygen lone pairs. The resulting structure contains six-sided channels running throughout (Figure 7.10). These channels play an important role in determining the properties of ice.

- As water freezes, the hydrogen bonds are optimized, which establishes the channels. Introduction of the void space into the structure results in an expansion of the water, which is why cars and outdoor plumbing must be protected during the winter.
- The liquid is the denser phase, so ice melts when a pressure is applied.
- Ice floats because it is less dense than the liquid. Thus, aquatic life can survive the winter because ponds freeze on the surface, which insulates the water below.
- The channels are six-sided, so ice crystals grow in hexagonal patterns, which is why snowflakes are six-sided.

Hydrogen bonding interactions can also dictate the structure of large molecules. In Chapter 13, we discuss the double helix structure of DNA, which is the result of the molecule coiling so as to maximize the strength of hydrogen bonding interactions.

Covalent bonds are much stronger than any of the intermolecular interactions, but, as shown in Table 7.1, the strengths of the intermolecular interactions overlap. All molecules interact through dispersion forces, others through both dispersion and dipolar forces, and some through dispersion, dipolar, and hydrogen bonding. Thus, water molecules interact through all three types of forces, but the dispersion forces in water are quite small and the hydrogen bonding interactions dominate and make water a liquid at room conditions. I_2 molecules, on the other hand, interact only through dispersion forces, but those forces are so strong that I_2 is a solid at room conditions.

7.4 SOLIDS*

Intermolecular forces in the solid state are much greater than thermal energy, so the particles[†] in a solid take fixed positions relative to one another that maximize their interactions. Molecules in the gas phase are characterized by random motion, while particles in the solid state are characterized by fixed positions with molecular motion restricted to small oscillations about these positions. Thus, **solids** have their own shape and volume, which are independent of the container.

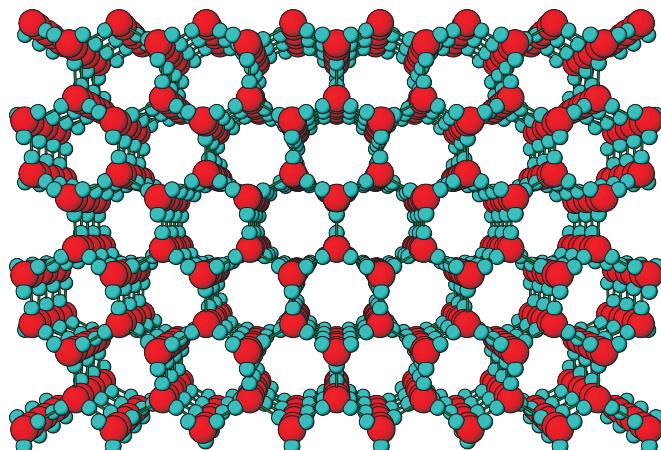


Figure 7.10 Structure of ice

The six-sided channels are responsible for the solid being less dense than the liquid. Water molecules are shown with space filling models (red spheres = O and blue spheres = H).

Table 7.1 Relative Strengths of Interactions

Interaction	Energy of interaction (kJ/mol)
Covalent Bond	100-1000
H-bond	10-50
Dipolar	5-25
Dispersion	1-50

* Solids are introduced only briefly here, the structure and properties of solids are taken up in much more detail in Chapter 8.

[†] The term “particles” is used for atoms, molecules, or ions.

7.5 LIQUIDS

The energy of attraction between molecules in the liquid state is comparable to their thermal energy, so the molecules remain relatively close to one another while undergoing random, but restricted, motion. **Liquids** adopt the shape of the bottom of the container but maintain their own volume, which depends only slightly on the temperature. Most of the properties of liquids depend upon the strengths of their intermolecular forces. We consider two examples here: viscosity and surface tension.

Viscosity is the resistance of liquids to flow. In order for a liquid to flow, molecules must slide past one another, so intermolecular interactions must be broken and reformed. If thermal energy is relatively low compared to the energy of interaction, the molecules cannot readily break the interactions, so the flow is retarded and the liquid is said to be *viscous*. Thus, viscosity decreases as the liquid is heated. For example, oil is quite viscous when cold, but flows easily when hot. Viscosity also depends upon the shape of the molecule: viscosity increases as the ease with which molecules become entangled increases.

Molecules on the surface of a liquid are at a higher potential energy than those in the interior because surface molecules are not involved in as many energy-lowering intermolecular interactions (Figure 7.11). Thus, water ‘beads’ into distorted spheres when it is placed on a surface with which it does not interact because doing so minimizes its surface area and the number of higher-energy surface molecules. Alternatively, the contraction into spheres can be viewed as a result of the net inward force exerted on the surface molecules (Figure 7.11) that is absent in the bulk because the competing forces cancel in the bulk. The energy required to increase the surface area of a liquid by a fixed amount is called the **surface tension** of the liquid. The units of surface tension are J/m^2 . *Surface tension increases with increasing intermolecular forces.*

Forces between like molecules are called **cohesive**, while those between unlike molecules are said to be **adhesive**. Viscosity and surface tension both result from cohesive forces. However, when a liquid is placed in a container, there may also be adhesive forces between the liquid and the walls of the container, and the balance between the cohesive forces that tend to ‘bead’ the liquid and the cohesive forces that tend to ‘wet’ the walls of the container dictates the curved shape of the top of the liquid, which is known as the **meniscus**. Glass contains many Si-O bonds, so water can hydrogen bond to the oxygens on the surface of the wall. The strong adhesive forces between water and glass tend to

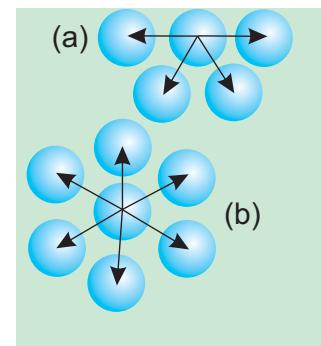


Figure 7.11 Interactions in the liquid

a) Molecules on the surface experience attractive forces from the bulk but not from above, so there is a net inward force, which causes the liquid to minimize its surface area. b) Molecules in the bulk of a liquid experience forces in all directions, so there is no net force on the molecule.

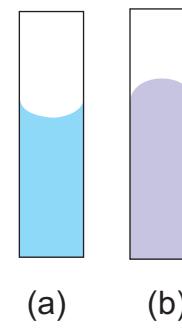


Figure 7.12 Meniscus shapes

a) Molecules that have strong adhesive forces increase interactions with the walls by forming a concave meniscus.
b) Molecules with weak adhesive forces maximize their cohesive forces by forming a convex meniscus.

draw the liquid up the walls of the glass and produce the concave shape of the meniscus (Figure 7.12a). Mercury atoms do not interact well with glass, so the adhesive forces are very weak. Consequently, mercury forms a convex meniscus (Figure 7.12b) to maximize Hg-Hg interactions and minimize interactions with the walls of the container.

7.6 CHANGES IN STATE

Molecules in a solid orient themselves to maximize their interactions, which lowers their potential energy. Indeed, solids have the lowest potential energy of the three states of matter. Molecules in the liquid state are close to one another, but they are not restricted to positions that maximize their interactions, so their potential energy is slightly higher than that of a solid. Molecules in the gas phase are far apart, so they interact only weakly, if at all, and their potential energy is the highest of the three states of matter. Figure 7.13a summarizes the relative energies of the three states of matter.

When heat is added to a substance, the energy increase of the substance can be in the form of either kinetic or potential energy. Increases in kinetic energy result in increases in the thermal energy or temperature of the substance. However, once certain temperatures are reached, the heat is used to increase the potential energy of the substance, not the kinetic energy. Increases in potential energy result in changes in states; solids melt or sublime to the higher energy liquid and gas states and liquids evaporate to the gas state. (Figure 7.13b). However, the state of matter is also a function of pressure; solids also melt and liquids boil as a result of pressure changes. In this section, we examine how the phases of a substance vary with both its temperature and its pressure.

SOLID-LIQUID TRANSITION

The particles in a solid occupy fixed positions that optimize their interactions with one another, and their kinetic energy is in the form of oscillations about these positions. As the temperature is increased, the speed and amplitude of the oscillations increase. Eventually, the oscillations become so agitated and their amplitude so great that the separation between particles becomes sufficiently large that the forces between them are no longer strong enough to keep the particles in their fixed positions. At this point, the structure of the solid collapses into a liquid as the substance melts. The forces that held the particles in their fixed positions in the solid still exist in the liquid, but they are weaker because the particles are farther apart.

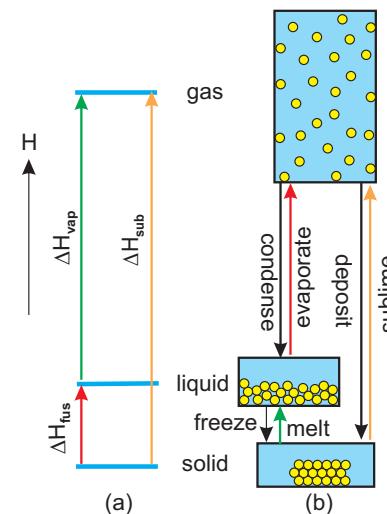


Figure 7.13 Definitions and energies of phase changes

(a) The energy of a gas is much greater than the energy of a liquid, which is greater than the energy of a solid. Heat, ΔH , must be supplied to carry out a change from a lower energy state to a higher energy state. ΔH_{fus} is the heat of fusion, ΔH_{vap} is the heat of vaporization, and ΔH_{sub} is the heat of sublimation. (b) A molecular view of the various changes in state.

The **melting or freezing point** is the temperature at which the solid and liquid coexist in a mixture called a **melt**. The melt remains at equilibrium so long as no heat is added or removed; the melting and freezing processes continue, but they occur at the same rate; *i.e.*, the solid melts at the same rate as the liquid freezes. Two processes that continue in opposite directions at the same rate and involve no net change in the system are said to be in **dynamic equilibrium**. Almost all chemical processes reach dynamic equilibrium. Dynamic equilibria are represented with double arrows to indicate that the forward and reverse processes continue at equilibrium. Thus, the solid-liquid equilibrium is expressed as solid \rightleftharpoons liquid.

The melting point is a measure of the thermal energy required to overcome the forces holding the particles in their fixed positions in the solid,* so it is an indication of the strength of those forces. We conclude that *substances with high melting points interact strongly with one another*. For example, ionic compounds have high melting points because the forces that must be overcome to break down the solid structure are ionic bonds, which are very strong interactions.

The **heat of fusion**, ΔH_{fus} , is the amount of heat required to melt a substance at its melting point. It is the potential energy difference between the solid and liquid states (Figure 7.13a). Heat added to a melt is used to melt the solid, and as long as there is solid present, there is no temperature rise, *i.e.*, the heat is used to increase the potential energies of the molecules not their kinetic energies.

A solid can also be made to melt or a liquid made to freeze by pressure changes, but large pressure changes are typically required to produce small changes in the melting point. The sign of the slope of the pressure versus temperature line (Figure 7.14) indicates the relative densities of the solid and liquid states because *increasing the pressure on an equilibrium mixture involving different states always moves the mixture toward the more dense state*. The solid is denser than the liquid for most substances, so increasing the pressure usually freezes the liquid to produce the denser solid phase (Figure 7.14a). However, the liquid is more dense than the solid in some compounds, such as water, so increasing the pressure of a solid-liquid mixture of these compounds causes the solid to melt, producing the more dense liquid phase (Figure 7.14b).†

* The forces between particles can be intermolecular forces or ionic or covalent bonds.

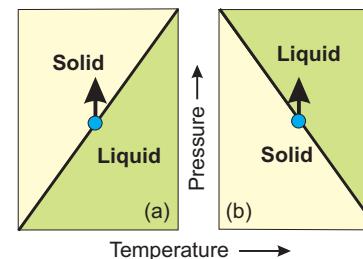


Figure 7.14 Solid-liquid equilibrium

The more dense phase is always above the pressure versus temperature line for the equilibrium. Increasing the pressure freezes the substance in (a), but it melts it in (b).

† One theory holds that ice skating is possible because ice melts when pressure is applied. Consider that an ice cube that has just been removed from the freezer is not slippery, but it becomes so only after melting slightly. The slick surface is the result of a thin layer of water on the ice, not the ice itself. Thus, the pressure that is exerted from the force of a skater's weight concentrated on the thin blades produces a pressure that is sufficient to melt the ice and produce the thin layer of water, which makes the surface slippery.

LIQUID-VAPOR TRANSITION

Once the entire solid has melted, additional heating causes the temperature of the liquid to rise, and the movement of the molecules becomes more chaotic as their thermal energy increases. However, thermal energy is the *average* kinetic energy, and not all molecules in the liquid have the same kinetic energy. Consequently, a small fraction of molecules have enough kinetic energy to break their intermolecular interactions. Those at the surface do so by escaping into the gas phase and **evaporation** (liquid → vapor) begins.

Molecules in the gas phase collide with one another, and intermolecular interactions can be established when they do. However, if the molecules have sufficient kinetic energy, they break the interaction and move on. Occasionally, colliding molecules do not have sufficient kinetic energy to escape their interaction, and they stick to one another and **condensation** (vapor → liquid) begins. As the collision frequency increases, so too does the rate of condensation. The frequency of the molecular collisions depends upon the concentration of the gas, which is proportional to its partial pressure (Section 7.1). Hence, there is a pressure at any given temperature at which the rates of evaporation and condensation are equal, and the system reaches another dynamic equilibrium: liquid \rightleftharpoons gas. The pressure of the gas at which the liquid and vapor are in equilibrium is called the **vapor pressure (P^o)** at that temperature. If the temperature is increased, the fraction of molecules in the liquid with sufficient kinetic energy to escape into the gas also increases, which increases the rate of evaporation. However, as more molecules escape into the vapor, the rate of condensation begins to increase as well. Eventually, the two rates become equal again and equilibrium is re-established. However, both rates have increased as has the vapor pressure. Thus, the vapor pressure of a substance increases with its temperature. The vapor pressure of water as a function of temperature is shown in Table 7.2 and Figure 7.15.

Weather reports state the partial pressure of water in the atmosphere as a relative humidity or dew point. The **relative humidity** is 100% times the ratio of the observed partial pressure of water in the atmosphere to the vapor pressure of water at that temperature. The **dew point** is the temperature at which the atmospheric water would begin to condense; *i.e.*, the temperature at which the vapor pressure of H₂O equals its partial pressure in the atmosphere. For example, consider a day on which the temperature is 25 °C and the partial pressure of H₂O is 12.8 torr. We note from Table 7.2 that the vapor pressure of water is 12.8 torr at 15 °C, so 15 °C is the dew point. The vapor pressure of

Table 7.2 Vapor pressure (P^o) of water at various temperatures

T (°C)	P ^o (torr)	T(°C)	P ^o (torr)
0	4.6	50	92.5
5	6.5	55	118.0
10	9.2	60	149.4
15	12.8	65	187.5
20	17.5	70	233.7
25	23.8	75	289.1
30	31.8	80	355.1
35	41.2	85	433.6
40	55.3	90	525.8
45	71.9	95	633.9

water at 25 °C is 23.8 torr, so the relative humidity = $(12.8/23.8)(100\%) = 53.8\%$.

The vapor pressure of a compound at a given temperature depends upon the strengths of its intermolecular interactions. *Compounds with stronger intermolecular interactions have lower vapor pressures than those that interact only weakly* because the stronger interactions cause them to condense more easily. Figure 7.15 shows the vapor pressure of CCl₄ and H₂O as a function of temperature. The vapor pressure of H₂O is less than that of CCl₄ at every temperature, so the intermolecular interactions are stronger in H₂O. Although the dispersion forces are greater in CCl₄, water also has dipolar and hydrogen bonding forces, which results in its relatively low vapor pressure.

Molecules with sufficient kinetic energy escape into the gas phase if they are on the surface of the liquid, but what about those that are not on the surface? The highly energetic molecules in the bulk of the liquid also attempt to escape into the gas by aggregating into bubbles, but the bubbles can withstand pressures no greater than the vapor pressure of the gas at that temperature, so the bubbles cannot form if the external pressure exceeds the vapor pressure. However, the bubbles are sustained at the temperature where the vapor pressure of the liquid equals the external pressure. This temperature is known as the **boiling point**. A liquid can be made to boil at any temperature by reducing the external pressure to the vapor pressure of the liquid at that temperature, so Table 7.2 can also be viewed as the boiling points of water as a function of pressure. Thus, the boiling point of water at 4.6 torr is 0 °C, and at 23.8 torr, it is 25 °C. The boiling point of a substance at 1 atm is known as the **normal boiling point**. When the boiling point of a substance is given without reference to an external pressure, it is assumed to be the normal boiling point. The normal boiling point of water is 100 °C.*

Normal boiling points are good indicators of relative strengths of intermolecular forces because molecules with stronger intermolecular interactions have higher normal boiling points. For example, dispersion forces are the only intermolecular forces acting in the halogens and noble gases, and the fact that their normal boiling points increase with molar mass (Figure 7.16) is strong support for our conclusion that dispersion forces increase with molar mass. Fluorine is a gas at room temperature (boiling point = 85 K), while the much larger iodine molecule is a solid at room temperature (boiling point = 457 K). Helium has the weakest intermolecular interaction of any substance and the lowest boiling point, 4 K.

It is more difficult to quantify dipolar interactions because they never occur in the absence of dispersion forces. However, the dispersion forces in CO and N₂ should be very similar because they are isoelectronic[†] and have the same molar mass, but CO is polar

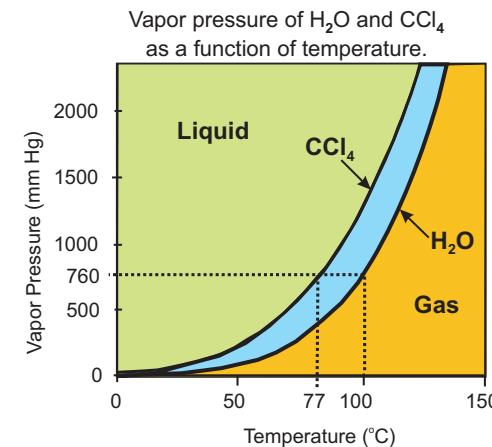


Figure 7.15 Vapor pressures of water and carbon tetrachloride as a function of temperature

Both are liquids at temperatures and pressures in the green region. CCl₄ is gas but H₂O is a liquid in the blue region, and both are gases in the orange-brown region.

* The boiling point of water in mile-high Denver is only about 95 °C due to the reduced pressure at that elevation.

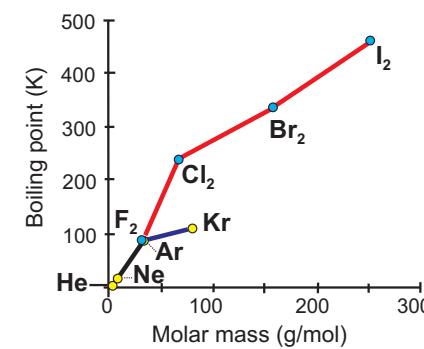


Figure 7.16 Boiling points of the halogens and the noble gases

[†] They each have 14 valence electrons and a triple bond.

while N₂ is not. The normal boiling points are 77 K for N₂ and 81 K for CO, so the impact of the dipole is not very great in this case. The difference between F₂ and HCl, which have very similar molar masses, is more dramatic. The boiling point of polar HCl is over 100 K higher than that of nonpolar F₂ even though the molar mass of HCl is slightly less.

The effect of hydrogen bonding can be seen by comparing the boiling points of the hydrogen compounds of the 4A, 5A, 6A, and 7A elements (Figure 7.17). As expected, the boiling points decrease with decreasing molar mass (weaker dispersion forces). This behavior continues for the 4A elements through the lightest member (CH₄), which has the lowest boiling point of the group. However, the lightest member of each of the other groups has the highest boiling point in its series because of hydrogen bonding. Thus, based on the boiling points of H₂Te, H₂Se and H₂S, water should be a gas at room conditions, with a boiling point of around 200 K (-70 °C). Instead, water is a liquid at room conditions and a solid at 200 K. This is due solely to the effects of H-bonding. Similar conclusions can be drawn for HF and NH₃.

We referred to Figure 7.15 as a plot of vapor pressure versus temperature, but it can also be viewed as a plot of boiling point versus pressure. The boiling points of CCl₄ and H₂O at 1 atm are 77 °C and 100 °C, respectively. The relative boiling points indicate the same relative intermolecular forces as did the vapor pressures: the forces are stronger in water than in carbon tetrachloride. Both have moderate intermolecular interactions as both are liquids with low vapor pressures at room temperature. Those forces are strong dispersion forces in CCl₄, and even stronger hydrogen bonds in water.

Evaporation requires energy because molecules in the gas phase are at a much greater potential energy than those in the liquid, so liquids cool as they evaporate.[†] The amount of energy required to convert a liquid to a vapor at a given temperature is referred to as the **heat of vaporization**, ΔH_{vap} , at that temperature. Just as a solid cannot be warmed above its melting point, a liquid cannot be heated above its boiling point. Thus, a vigorously boiling pot of water is at the same temperature as a slowly boiling one. All of the heat that is added at the boiling point is used to evaporate the water not raise the temperature. When the liquid is gone, the additional heat increases the temperature of the gas.

Gases become increasingly difficult to liquefy as their thermal energy increases. In fact, there is a temperature, called the **critical temperature**, beyond which the liquid cannot exist. The pressure required to liquefy a substance at its critical temperature is called the **critical pressure**. The critical temperature and critical pressure define the **critical point**. Beyond the critical point, the substance behaves like a gas, but its density is

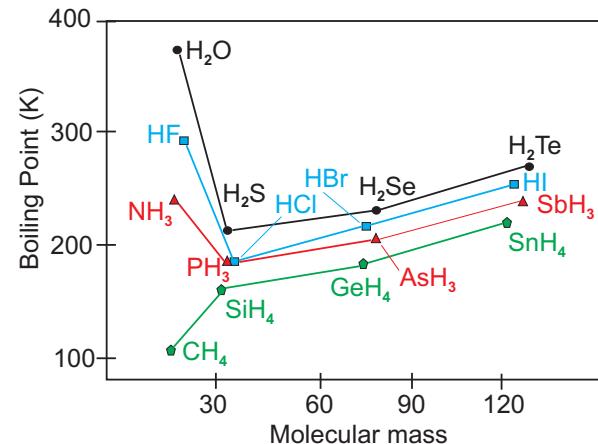


Figure 7.17 Boiling points of the Group 4A - 7A hydrides

Boiling points of the hydrogen compounds of the Group 4A (green), 5A (red), 6A (black) and 7A (blue) elements

[†] Warm blooded animals use evaporation to cool themselves by using body heat to evaporate a liquid. In the case of humans, it is the evaporation of perspiration. In dogs, it is the evaporation of saliva from the tongue.

more like a liquid. This unusual material is called a **supercritical fluid**. The unusual properties of supercritical fluids make them excellent solvents. For example, supercritical CO₂ is used as a solvent in the dry cleaning industry because it is gentle on material and is easily removed by reducing the pressure to convert the CO₂ back to a gas.

Example 7.7

a) Which substance has the higher boiling point, CH₄ or CCl₄?

Dispersion forces are the only forces at work in these molecules because neither molecule is polar and neither can exhibit hydrogen bonding. Dispersion forces increase with molecular size or mass. Thus, CCl₄ ($M_m = 154$ g/mol) boils at a higher temperature than CH₄ ($M_m = 16$ g/mol). The observed boiling points are: CCl₄ = +77 °C; CH₄ = -164 °C.

b) Which compound has the higher boiling point, PF₃ or Kr?

The formula weights are 88 and 84, respectively, so the dispersion forces are expected to be very similar. The difference between these substances is that PF₃ is a polar molecule (see structure in margin), so it exhibits dipole-dipole forces as well. Consequently, the boiling point of PF₃ is higher. The boiling points are: PF₃ = -102 °C; Kr = -152 °C.

c) Which has the higher vapor pressure at 298K, CH₃-CH₂-OH or H₃C-O-CH₃?

Both compounds are polar and have identical molar masses, but CH₃-CH₂-OH has an O-H bond. Thus, CH₃-CH₂-OH molecules can hydrogen bond to one another, while H₃C-O-CH₃ molecules cannot. At room temperature, far fewer CH₃-CH₂-OH molecules are able to escape into the vapor state, so its vapor pressure is much lower than that of H₃C-O-CH₃.

d) Which substance has the higher normal boiling point, CH₃-NH₂ or CH₃-F?

Hydrogen bonding in CH₃-NH₂ raises its boiling point above that of CH₃-F, which does not form hydrogen bonds. The observed boiling points are: CH₃NH₂ = -6 °C and CH₃-F = -78 °C. Note that CH₃F has both hydrogen and fluorine atoms but, because they are not bound to one another, there is no hydrogen bonding.



PF₃

SOLID-VAPOR TRANSITION

Under certain conditions, a solid can be in equilibrium with its vapor: solid ⇌ vapor. The solid-vapor equilibrium is also dynamic and occurs when the rate of **sublimation** (solid → vapor) equals the rate of **deposition** (vapor → solid). Any solid, such as garlic, that has an odor is subliming because gas molecules are the ones that interact with the olfactory receptors in the nose to produce the sense of smell. Carbon dioxide cannot be a liquid at normal conditions, so solid CO₂ (dry ice) sublimes, but it does not melt at normal

conditions. The energy required to convert a substance from the solid to the gas is known as the **heat of sublimation**, ΔH_{sub} . Figure 7.18 shows the pressure of the gas in equilibrium with the solid as a function of temperature.

PHASE DIAGRAMS

A phase diagram shows the phase of a substance as a function of temperature and pressure. It is simply a combination of diagrams like those shown in Figures 7.14, 7.15, and 7.18. A partial phase diagram of water is shown in Figure 7.19. The line separating the liquid and solid phases is similar to that shown in Figure 7.14b and indicates the pressure dependence of the melting point. The line separating the liquid and the gas phases is the same one displayed in Figure 7.15 and shows the vapor pressure of the liquid as a function of temperature (or the boiling point as a function of pressure). The line separating the solid and the gas is the same line shown in Figure 7.18 and shows the sublimation pressure as a function of temperature.

Consider the labeled points in the phase diagram for water shown in Figure 7.19. At room conditions, which are typically taken to be 25°C and 1 atm pressure (Point C), water is a liquid with a vapor pressure of 0.031 atm. Point A is an equilibrium mixture of solid and liquid (a melt) at 1 atm, so the temperature at that point (0°C) is the normal melting point. Recall that increasing the pressure over a mixture always drives the mixture to the denser phase. Increasing the pressure at Point A moves the liquid-solid mixture into the liquid phase, so the liquid phase of water is denser than the solid phase. The liquid and gas phases are in equilibrium at Point D. The pressure is 1 atm, so the temperature (100°C) is the normal boiling point of water. All three phases are in equilibrium at Point B, so it is the **triple point**.^{*} The triple point of water occurs at 0.01°C and 0.006 atm. The critical point of water (Point E) occurs at 374.4°C and 217.7 atm.

Some key features of the phase diagram of carbon dioxide are represented in Figure 7.20. At room conditions (Point C), CO_2 is a gas. Unlike water, liquid CO_2 does not exist at 1 atm, so there is no normal boiling or melting point. Reducing the temperature at 1 atm results in deposition at -78°C (Point A), the temperature of ‘dry ice’. Carbon dioxide can be liquefied by increasing the pressure at 25°C to 67 atm (Point D). The triple point of carbon dioxide (Point B) occurs at 5.1 atm and -56°C . Note that the slope of the solid \rightleftharpoons liquid line indicates that solid CO_2 is denser than liquid CO_2 . The critical point of CO_2 (Point E) is at 31.1°C and 73.0 atm. CO_2 is a supercritical fluid at points above and to the right of Point E.

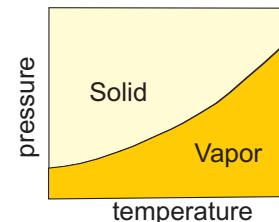


Figure 7.18 Solid-vapor equilibrium

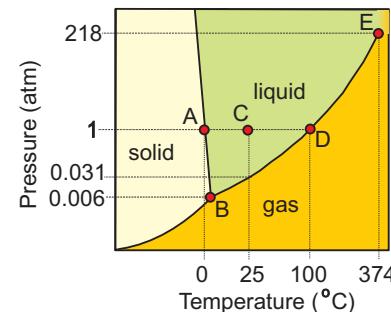


Figure 7.19 Phase diagram of water

The temperature and pressure axes are not drawn to scale.

* All three phases are in equilibrium at the triple point, so a mixture of the solid and liquid can boil under these conditions. In the case of water, ice water boils at 0.01°C and 0.006 atm, i.e., at its triple point.

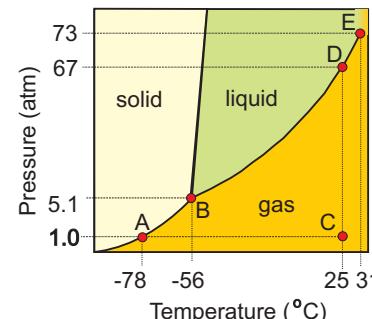


Figure 7.20 Phase diagram of CO_2 (dry ice)

The temperature and pressure axes are not drawn to scale.

7.7 CHAPTER SUMMARY AND OBJECTIVES

The state of matter (phase) in which a substance is found depends on a combination of temperature, pressure, and the strength of the intermolecular forces. Substances are gases when their thermal energy is much greater than their energy of interaction; they are liquids when their thermal energy and their energy of interaction are comparable; and they are solids when their energy of interaction is much greater than their thermal energy.

The volume of a gas depends upon its pressure, its temperature, and on the number of moles present. The pressure of a gas can be determined by the height of a mercury column that it will support. As a result, gas pressures are often given in mm Hg or torr. At sea level, the pressure is 760 torr, which is the same as 1 atmosphere. The relationship between the pressure, volume, temperature, and number of moles of gas is $PV = nRT$, the ideal gas law. Mixtures of gases are homogeneous, so they are solutions. The molar concentration of a component of a solution is defined as the number of moles of the component per liter of solution. The molar concentration of A is defined as $[A] = n_A/V$. Each component of a mixture of gases exerts its own pressure, called the partial pressure, which is directly proportional to its molar concentration ($P_A = RT[A]$). Dalton's law of partial pressures states that the total pressure in a mixture of gases is the sum of the partial pressures of the component gases. The average thermal energy of a system of molecules is approximated as RT , which is about 2.5 kJ/mol at room temperature. Thermal or kinetic energy is a measure of the how fast the molecules are moving, rotating, and vibrating.

Intermolecular forces are much weaker than covalent bonds and are responsible for holding the molecules in the liquid and solid states. They are of three types: dispersion forces, present in all compounds; dipole-dipole forces, found only in polar molecules; and hydrogen bonds, which dramatically change the properties of molecules with N-H, O-H and F-H bonds.

The potential energy of a molecule increases (becomes less negative) in going from solid to liquid to gas. Thus, the phase of a substance can be changed by the addition of energy: a solid can be melted to a liquid or sublimed to a gas, and a liquid can be vaporized to a gas by the addition of heat. A substance at its melting point undergoes a dynamic equilibrium between solid and liquid phases, which is represented as solid \rightleftharpoons liquid. The liquid \rightleftharpoons vapor equilibrium is also a dynamic equilibrium. The pressure of the vapor in equilibrium with a liquid is referred to as the vapor pressure. The boiling point of a liquid is the temperature at which the vapor pressure equals the external pressure and is,

therefore, a function of pressure. Typically, when the boiling point of a substance is given, it is the normal boiling point (that is, the temperature at which the vapor pressure is 1 atm). The critical temperature is the maximum temperature at which the liquid can exist, and the pressure required to liquefy a gas at the critical temperature is called the critical pressure. Finally, the solid \rightleftharpoons vapor equilibrium is reached when the rate of sublimation (solid \rightarrow vapor) equals the rate of deposition (solid \leftarrow vapor). A graph that shows the phase of a substance as a function of its temperature and pressure is called a phase diagram.

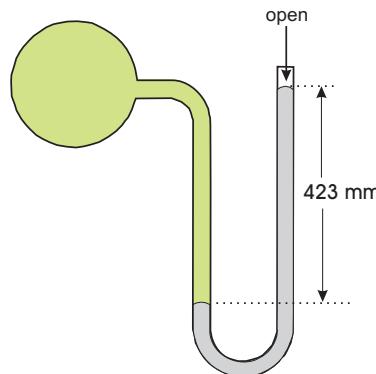
After studying the material presented in this chapter, you should be able to:

1. determine the pressure of a gas given the relative heights of the mercury columns in a manometer and the barometric pressure (Section 7.1);
2. convert from degrees Celsius to kelvins (Section 7.1);
3. use the ideal gas law, $PV = nRT$, to determine one unknown given the other variables (Section 7.1);
4. determine the partial pressures of each of the gases in a mixture of gases (Section 7.1);
5. define "molar concentration" and determine the molarity of a gas (Section 7.1);
6. explain the postulates of kinetic-molecular theory (Section 7.2);
7. estimate the thermal energy of a system from its temperature (Section 7.2);
8. distinguish between intermolecular and intramolecular forces (Section 7.3);
9. describe a temporary dipole and how it leads to dispersion forces (Section 7.3);
10. use Lewis structures to predict if a molecule contains a permanent dipole (Section 7.3);
11. explain the effects that hydrogen bonding has on water (Section 7.3);
12. describe the general features of a solid (Section 7.4);
13. define viscosity and surface tension and explain how they vary with the strength of the intermolecular interactions (Section 7.5);
14. define meniscus and explain why it can be either convex or concave (Section 7.5);
15. define the heats of fusion, vaporization, and sublimation (Section 7.6);
16. define melting point, vapor pressure, boiling point, critical point and explain how they vary with intermolecular forces (Section 7.6);
17. describe changes in state at a molecular level (Section 7.6); and
18. interpret a phase diagram (Section 7.6).

7.8 EXERCISES

See Appendix B for more exercises on the gas laws.

- A weather report indicates a barometric pressure of 29.2 in. What is this pressure expressed in torr?
- What is the volume of the He in the following apparatus if it contains 0.25 g of He at 20 °C, and the barometric pressure is 758 torr?

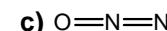
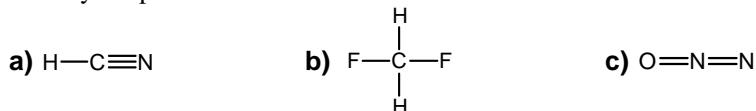


- If the gas in Exercise 2 is heated to 35 °C, what would be the separation between the two mercury levels?
- Convert the following temperatures to the Kelvin scale:
 a) 58 °C b) -263.08 °C c) 42.1 °C d) -185 °C
- Convert the following temperatures to the Celsius scale:
 a) 4 K b) 350 K c) 186.4 K d) 657 K
- What mass of He is required to fill a 5.2-L balloon at 23 °C and 746 torr?
- What is the pressure inside a 7.20-L container filled with 0.254 moles of CO₂ at 35 °C?
- To what temperature must a 12.0-L container filled with 1.65 g of Ne be heated to obtain a pressure of 1.60 atm?
- The pressure of air in a tire at 10 °C is 22 psi. After several miles of driving at high speed, the pressure is 28 psi. Assume the volume of the tire is unchanged and calculate the temperature of the air in the tire.

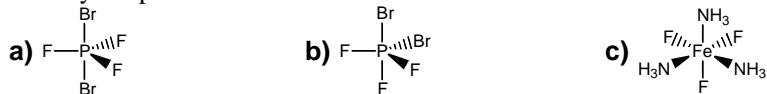
- What are the concentrations in mol/L of the gases in Exercises 6, 7, and 8?
- Determine the concentrations of the following gases in moles/L:
 a) 3.0 moles of gas at 900 K and 2.6 atm
 b) 6.2 L of a gas at 250 °C and 800 torr
 c) 4.0 g of Ne in a 0.56 L container at 200 °C
- 2.0 mol CO₂ and 1.2 mol O₂ are mixed at 75 °C in a 12-L container. What are the partial pressures of the two gases and the total pressure inside the container expressed in atmospheres?
- What are the partial pressures in torr of O₂ and N₂ and the total pressure in a 3.5-L flask at 77 °C that contains 4.0 g O₂ and 7.0 g N₂?
- The total pressure of a mixture of He, Ne, and Ar is 622 torr in a 2.75-L flask at 400 K. If the partial pressure of He and Ne are 175 torr and 326 torr, respectively, how many moles of Ar are in the flask?
- What is the approximate thermal energy in kJ/mol of molecules at each of the following temperatures?
 a) -200 °C b) 300 °C c) 75 °C
- At what temperatures would molecules have the following thermal energies?
 a) 5 kJ/mol b) 25 kJ/mol c) 2.5 J/mol
- How does the thermal energy compare to the energy of attraction between molecules in a solid and in a gas?
- Rank the strengths of the intermolecular interactions of I₂, CCl₄, and CH₄ given that iodine is a solid, carbon tetrachloride is a liquid and methane (CH₄) is a gas at room conditions.
- Explain why the boiling point of a substance increases as the pressure increases.
- What can be concluded about the structures of the solid and liquid states of a compound if the melting point increases as pressure is applied?
- Explain why bubbles form when a liquid boils.

22. Rapidly cooling a vapor in equilibrium with its liquid causes the liquid to boil. Explain.
23. Which has a greater potential energy at 270 K, ice or water vapor? Explain.
24. Explain why the odor of mothballs (solid naphthalene) becomes stronger when the temperature increases.
25. Why are ionic substances solids under normal conditions?
26. Why are the noble gases all gases under normal conditions?
27. Explain why many gases are liquefied by increasing the pressure.
28. Give three properties of water that can be attributed to hydrogen bonding and the six-sided channels that form when water freezes.
29. Explain how snow can disappear without melting.
30. Explain how perspiration is used to cool the body.
31. Explain why the temperature of a solid \rightleftharpoons liquid mixture does not change when it is heated.
32. Explain why water expands when it freezes.
33. What is a dynamic equilibrium? Give two examples of dynamic equilibria.
34. Define the term “heat of vaporization”. The heat of vaporization of water at 100 °C is 40.7 kJ/mol. Write the chemical equation for the process to which this number applies.
35. Define the term “heat of fusion”. The heat of fusion of water at 0 °C is 6.0 kJ/mol. Write the chemical equation for the process to which this number applies.
36. Refer to Figure 7.15 to determine whether CCl₄ is a liquid or a gas under the following conditions of temperature and pressure.
 a) 50 °C and 500 torr b) 77 °C; 500 torr c) 100 °C; 800 torr
37. Refer to Figure 7.15 to determine whether H₂O is a liquid or a gas under the following conditions of temperature and pressure.
 a) 50 °C and 500 torr b) 77 °C; 500 torr c) 100 °C; 800 torr

38. Identify the polar molecules.



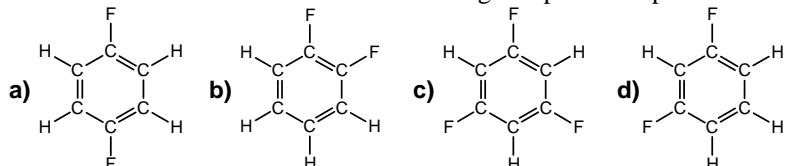
39. Identify the polar molecules.



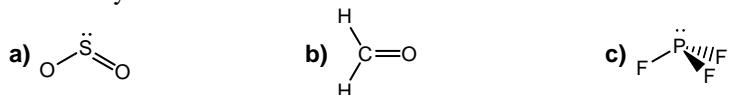
40. Indicate the polar substance in each pair.



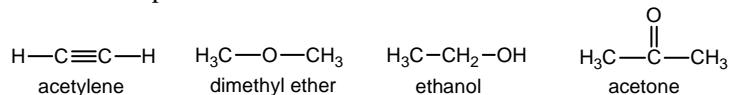
41. Indicate whether or not each of the following compounds is polar.



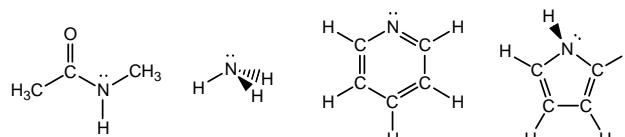
42. Use the arrow notation to indicate the direction of the dipole of the molecules below. Note that, for simplicity, lone pairs are shown on central atoms only.



43. In which of the following molecules is hydrogen bonding between like molecules important?

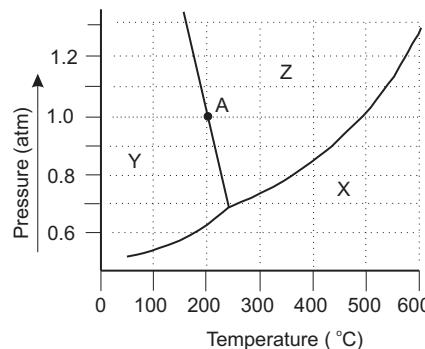


44. In which of the following molecules is hydrogen bonding between like molecules important?



45. Indicate which of the following substances has the higher boiling point and the type of force that is most responsible for the difference:
- a) CCl_4 or CF_4 b) $\text{CH}_3\text{-CH}_3$ or $\text{CH}_3\text{-NH}_2$
 c) H_2Se or Kr d) KF or HF
46. Indicate which of the following molecules has the higher boiling point and the force that is most responsible for the difference:
- a) NH_3 or PH_3 b) $\text{C}_2\text{H}_5\text{OH}$ or CH_3OCH_3
 c) C_4H_8 or $\text{C}_{10}\text{H}_{20}$ d) HCl or F_2
47. There are three different molecules with the formula $\text{C}_2\text{H}_2\text{F}_2$ that differ in the relative positions of the hydrogen and fluorine atoms around the two carbons. The different molecules are called isomers; they are not resonance structures because the positions of the atoms are different. Draw the Lewis structures of the three isomers of $\text{C}_2\text{H}_2\text{F}_2$ and indicate whether each is polar.
48. Indicate all of the forces that exist between molecules in the condensed states of the following:
- a) NCl_3 b) SO_3 c) SO_2 d) HBr e) HOCl
49. Indicate all of the forces that exist between molecules in the condensed states of the following:
- a) CCl_4 b) CH_2O c) CO_2 d) HF e) $\text{H}_3\text{C-OH}$

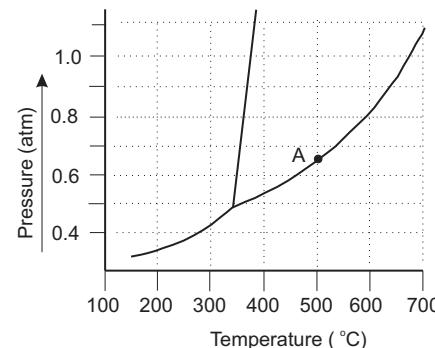
Use the following phase diagram to answer Exercises 50 and 51.



50. Identify the states represented by the regions labeled X, Y, and Z.

51. Consider the preceding phase diagram.
- a) What are the normal boiling and melting points of the substance?
 b) In what state of matter does the substance exist under room conditions?
 c) What is the vapor pressure of the substance at $300\text{ }^\circ\text{C}$?
 d) What transition in state occurs when the pressure at point A is increased?
 e) What transition in state occurs when the temperature at point A is increased?

52. Consider the following phase diagram.



- a) What are the normal boiling and melting points of the substance?
 b) In what state of matter does the substance exist under room conditions?
 c) What is the vapor pressure of the substance at $600\text{ }^\circ\text{C}$?
 d) What process occurs at point A when the pressure is reduced?
 e) What process occurs at point A when the temperature is decreased?
 f) Which is more dense, the solid or the liquid?

Chapter 8

Solid Materials

<i>8.0 Introduction</i>	<i>8.7 Ionic Solids and Ionic Radii</i>
<i>8.1 Unit Cells</i>	<i>8.8 Covalent Solids</i>
<i>8.2 Cubic Unit Cells and Metallic Radii</i>	<i>8.9 Molecular Solids and Atomic Radii</i>
<i>8.3 Unit Cell Stoichiometry</i>	<i>8.10 Comparison of Solid Types</i>
<i>8.4 Coordination Number & Geometry</i>	<i>8.11 Chapter Summary and Objectives</i>
<i>8.5 Density and Packing Efficiency</i>	<i>8.12 Exercises</i>
<i>8.6 Band Theory of Simple Metals</i>	

8.0 INTRODUCTION

Thus far, our study has focused on the structure and properties of individual atoms and molecules, but most of our experience is with materials, large collections of interacting particles. Although materials are constructed from individual atoms, ions, or molecules, the interactions between these particles can result in a material whose bulk properties are quite different from the atomic or molecular properties of its constituents. Indeed, material scientists and chemists design and build materials to meet a wide variety of needs. In this chapter, we discuss the structure of solids and relate the properties of some solids to their structure.

THE OBJECTIVES OF CHAPTER 8 ARE TO:

- show how atoms and ions pack to form metallic and ionic solids;
- describe metallic bonding and electrical conductivity in terms of band theory;
- explain the properties of some important materials in terms of their structure;
- show how the sizes of atoms and ions are determined;
- distinguish between the various types of solids;
- explain how the properties of some covalent solids are related to their structures; and
- relate the properties of a substance to the type of solid it forms.

8.1 UNIT CELLS

Solid materials can be classified as either crystalline or amorphous. **Crystalline** solids have very well defined and ordered repeating patterns of the particles making up the solid. This ordered arrangement extends throughout the entire crystal, so there is *long-range order* in crystalline solids. By contrast, the ordered arrangement extends over only a short distance in amorphous solids, so there is only *local order* in amorphous solids.

The long-range order of crystalline solids results from a repeating pattern of particles. The particles may be atoms, ions, or groups of atoms, such as polyatomic ions or molecules. The repeating pattern forms a three-dimensional array known as the **crystalline lattice**. Because the same pattern is repeated throughout the crystal, the structure of the entire crystalline solid can be described effectively by describing the smallest repeating unit of the crystalline lattice, known as the **unit cell**. When the unit cell is repeated in all three directions, it generates the entire crystal. Figure 8.1 describes a two-dimensional lattice of **A**'s and **B**'s. A unit cell of this two-dimensional lattice can be viewed as a square with **A**'s in the corners and a **B** in the center of the cell or with **B**'s in the corners and an **A** in the center. The two unit cells are highlighted in yellow in Figure 8.1. Translation of either unit cell by the length of a cell edge in any of the four directions produces an adjacent cell. Continued operations of translation generate the complete lattice. A typical crystal might have a unit cell edge of about 10^6 mm (10 \AA). This requires 10^6 (one million) unit cells, stacked end to end, to reach across a crystal that is only 1 mm on edge. A three-dimensional lattice is formed by repeating a three-dimensional unit cell in three directions.

All unit cells can be uniquely characterized by the three edge lengths (a , b , and c) and the three angles (α , β , and γ) as defined in Figure 8.2. They must be six-sided polygons that completely fill space; that is, no holes are present when the unit cell polygons are packed in three-dimensions. As a result, there are only seven different types of unit cells. We limit our discussion to the simplest type of unit cell, the **cubic unit cell**. The cubic unit cell is one in which $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. There are three types of cubic unit cells: simple cubic (*sc*), body-centered cubic (*bcc*), and face-centered cubic (*fcc*).

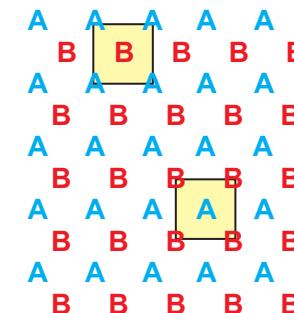


Figure 8.1 A simple two-dimensional lattice

Two different, but equivalent, unit cells are highlighted in yellow. In one, **A**'s are at the corners, and a **B** is in the center. In the other, **B**'s are on the corners, and an **A** is in the center.

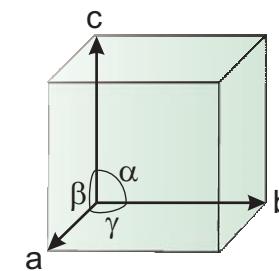


Figure 8.2 Parameters used to define lattice types

8.2 CUBIC UNIT CELLS AND METALLIC RADII

For simplicity, the following discussion is based on metallic solids because all of the atoms in a metal are identical. There are three types of cubic unit cells that differ in the locations of the sites that are occupied by the atoms.

Simple-cubic (sc) unit cell: The atoms reside only on the eight corners (Figure 8.3a).

Body-centered cubic (bcc) unit cell: the atoms occupy the eight corners and the center of the cell body (Figure 8.3b).

Face-centered cubic (fcc) unit cell: The atoms occupy the eight corners and the six face centers (Figure 8.3c).

The relative positions of the atoms in a unit cell are determined by scattering x-rays from the atoms with a technique called x-ray diffraction. One application of this method is the determination of atomic radii, which are inferred from the distances between the atoms by assuming that the atoms touch along one line in the unit cell. In this method, the radius of an atom is related to the unit cell edge length (**a**). As shown in Figure 8.4, the line of contact in metallic solids is along the edge of a *sc* unit cell, along the face diagonal (*fd*) of a *fcc* unit cell, and along the body diagonal (*bd*) of a *bcc* unit cell. The edge of the *sc* unit cell equals two atomic radii, while the lengths of the *fd* and *bd* of the *fcc* and *bcc* unit cells are each equal to four atomic radii. Setting the edge length equal to the $2r$ in the *sc* unit cell, and applying the Pythagorean Theorem to the triangles shown in Figures 8.4b and 8.4c, we obtain the relationships between the atomic radius (**r**) and the edge length (**a**).

$$\text{a) sc unit cells: } r = \frac{a}{2}$$

$$\text{b) fcc unit cells: } r = \frac{\sqrt{2}a}{4}$$

$$\text{c) bcc unit cells: } r = \frac{\sqrt{3}a}{4}$$

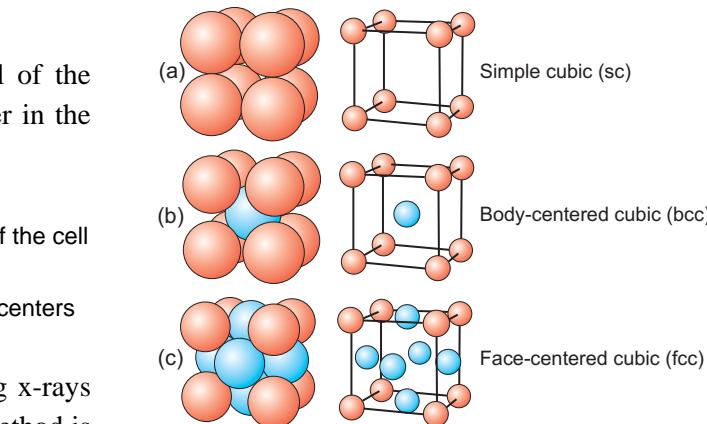


Figure 8.3 Cubic unit cells

Different colors are used to distinguish between the different lattice sites, not different atom types.

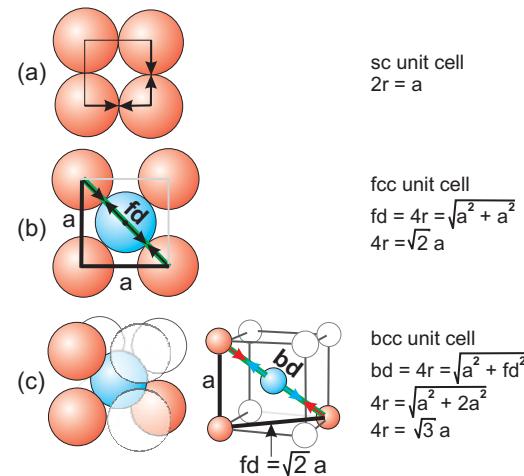


Figure 8.4 Atom contact in cubic unit cells

Atom contact is along the edge of a *sc* cell (a), along the face diagonal (*fd*) of a *fcc* cell (b), and along the body diagonal (*bd*) of a *bcc* cell (c). The arrows along the diagonals represent the atomic radii of which they are composed.

Example 8.1

γ -iron adopts a fcc crystal structure with an edge length of 3.56 Å. What is the metallic radius of iron inferred from this structure?

Use Equation 8.1b for fcc unit cells and the known edge length.

$$r = \frac{\sqrt{2}}{4} a = (0.354)(3.56) = 1.26 \text{ \AA}$$

8.3 UNIT CELL STOICHIOMETRY

The stoichiometry of a compound can be determined from the composition of its unit cell. However, recall that unit cells pack to completely fill space, so they must share faces, corners, and edges with other unit cells. Consequently, atoms sitting on these sites are shared by more than one unit cell. For example, consider the two-dimensional lattice of **A**'s and **B**'s in Figure 8.1. The **A**'s on the corners of a cell are each shared by four unit cells, so each **A** on a corner contributes only $\frac{1}{4}$ **A** to any one unit cell. As a result, the four corner **A**'s combine to contribute only one **A** to the overall stoichiometry ($4 \text{ corners} \times \frac{1}{4} \text{ A per corner} = 1 \text{ A}$). The **B** in the center of the cell is completely within the cell, so it contributes a full **B** to the overall stoichiometry of the cell. Consequently, the stoichiometry of the unit cell is **AB**. The same stoichiometry is achieved using the cell with **B**'s on the corner and an **A** in the center. Figure 8.5 shows that an atom (the yellow sphere) is shared by two unit cells when it occupies a face center (Figure 8.5a), by four unit cells (Figure 8.5b) when it sits on an edge, and by eight unit cells when it is located on a corner (Figure 8.5c).

The contribution of each atom position in the unit cell (*uc*) to the overall unit cell stoichiometry can be summarized as follows:

- Each atom located totally within the cell contributes 1 atom to the unit cell.
- Atoms on the faces contribute a total of 3 atoms to the unit cell. A cube has six faces, but only $\frac{1}{2}$ of each atom is in any one unit cell (Figure 8.5a); $(\frac{1}{2})(6) = 3$ atoms.
- Atoms on the edges contribute a total of 3 atoms to the unit cell. A cube has twelve edges, but only $\frac{1}{4}$ of each atom on an edge is in any one cell (Figure 8.5b); $(\frac{1}{4})(12) = 3$ atoms.
- Atoms on the corners contribute at total of 1 atom to the unit cell. A cube has eight corners, but only $\frac{1}{8}$ of each atom is in any one unit cell (Figure 8.5c); $(\frac{1}{8})(8) = 1$ atom.

Example 8.2

How many atoms are in each of the three cubic unit cells?

a) **Simple cubic (sc)**

Atoms are on the eight corners only, so there is only one atom in a simple cubic unit cell.

b) **Body-centered cubic (bcc)**

Atoms on the eight corners contribute one atom and the atom in the body center contributes another atom, so there are two atoms in a body-centered cubic unit cell.

c) **Face-centered cubic (fcc)**

Atoms are on the eight corners contribute one atom and those in the six face centers contribute three more atoms, so there are four atoms in a face-centered cubic unit cell.

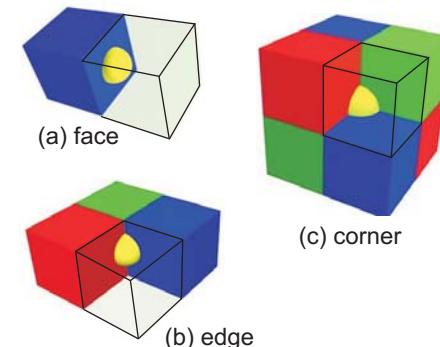


Figure 8.5 Atoms in more than one unit cell

- Atoms on the faces are shared by two unit cells.
- Atoms on an edge are shared by four unit cells.
- Atoms on a corner are shared by eight unit cells.

8.4 COORDINATION NUMBER AND GEOMETRY

An understanding of the unit cell of a crystalline solid also provides an understanding of the local environment of each atom or ion. The **coordination number (CN)** and the **coordination geometry** of an ion or atom indicate the number and geometry of atoms or ions that surround it in the crystal lattice, which indicates the nature of the bonding in a crystal. Figure 8.6 shows the most common coordination numbers adopted by atoms (represented by the red spheres). Four particles coordinated to a central particle with CN = 4 generally exhibit tetrahedral geometry (Figure 8.6a). The atoms in a simple cubic unit cell have octahedral coordination geometry and CN = 6 (Figure 8.6b). Atoms in a body-centered cubic unit cell have CN = 8 (Figure 8.6c). Each atom in a face-centered cubic unit cell has CN = 12 (Figure 8.6d), which can be viewed as three planes of particles: the top (green spheres) and bottom (blue spheres) planes with three particles each and one plane in the middle that contains the central atom and six particles (yellow spheres) that form an equatorial belt around it. The packing of equal sized particles in this geometry represents the tightest possible packing arrangement for spheres and is frequently described as **closest packed**.

Example 8.3

Rutile is a titanium oxide mineral that crystallizes in the tetragonal ($a=b>c$, $\alpha=\beta=\gamma=90^\circ$) unit cell shown in the margin. What is the formula of the titanium oxide in rutile, and what are the coordination number and geometry of Ti in the mineral?

Determine the number of each type of atom in the uc.

$$N_{\text{Ti}} = \text{eight atoms on the corners} + \text{one atom in the cell} = (8)(\frac{1}{8}) + 1 = 2 \text{ Ti atoms}$$

$$N_{\text{O}} = \text{four atoms on faces} + \text{two atoms in the cell} = (4)(\frac{1}{2}) + 2 = 4 \text{ O atoms.}$$

Thus, the unit cell stoichiometry is Ti_2O_4 . The formula of the oxide is the simplest whole number ratio, which is TiO_2 , so there are two TiO_2 molecules in the unit cell.

All of the O atoms in the unit cell are nearest neighbors of the Ti atom in the center, so its coordination number is 6, and its coordination geometry is octahedral (Figure b). Note that the Ti atoms are arrayed in a body centered fashion, and the Ti atoms on the corners and in the center are equivalent, so the coordination number of all Ti atoms is six.

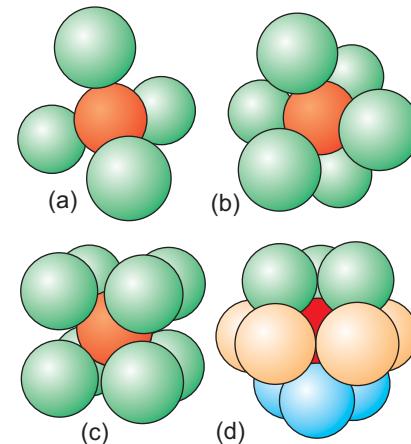
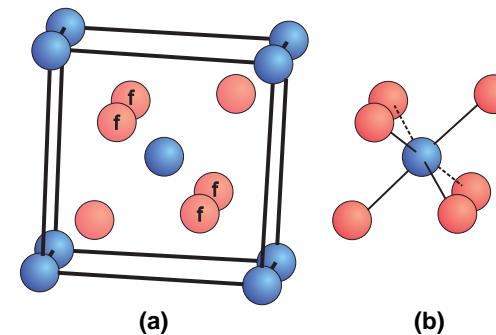


Figure 8.6 Coordination numbers (CN) and geometries

- a) CN = 4 is tetrahedral
- b) CN = 6 is octahedral
- c) CN = 8
- d) CN = 12 (closest packed)



Example 8.3 Unit cell of rutile

(a) Ti atoms (blue) are situated on the eight corners and in the body center. The O atoms (red) labeled with 'f' are in faces, while those that are not labeled are totally within the unit cell. (b) The octahedral coordination of the central Ti atom. Note it is a distorted octahedron because the bonds to the two O atoms in the cell are longer than those to the four O atoms in the faces.

8.5 DENSITY AND PACKING EFFICIENCY

Density (d) is the mass-to-volume ratio of a substance (Equation 8.2).

$$d = \frac{\text{mass of substance}}{\text{volume of substance}} = \frac{m}{V} \quad \text{Eq. 8.2}$$

Individual atoms get denser moving from left to right in a period as their mass increases and their size decreases, but the densities of elements in the bulk do not increase in such a regular fashion because the density of an element also depends upon the efficiency with which it packs in the solid state. The **packing efficiency (PE)** is the fraction of the volume (typically expressed as a percent) of the unit cell that is actually occupied by particles. The space that is not occupied by particles is called **void space**. Equation 8.3 gives the mathematical expression for packing efficiency expressed as a percent.

$$PE = \frac{\text{volume of particles}}{\text{volume of unit cell}} \times 100\% = \frac{NV_{\text{atom}}}{a^3} \times 100\% \quad \text{Eq. 8.3}$$

N is the number of atoms in the unit cell and a is the edge length of the cubic unit cell. V_{atom} is the volume of a spherical atom of radius r , so $V_{\text{atom}} = \frac{4}{3}\pi r^3$. Example 8.4 demonstrates how packing efficiencies are determined.

Example 8.4

What is the packing efficiency of a face-centered cubic unit cell?

We apply Equation 8.3 with $N = 4$ atoms for a fcc unit cell. We then use Equation 8.1b for the fcc unit cell ($r = 0.354a$) to get r in terms of a .

$$PE = \frac{NV_{\text{atom}}}{a^3} \times 100\% = \frac{(4)\left(\frac{4}{3}\pi r^3\right)}{a^3} \times 100\% = \frac{4\left(\frac{4}{3}\pi (0.354 a)^3\right)}{a^3} \times 100\% = 74\%$$

Note that the a^3 terms cancel, so the packing efficiency depends only on the type of unit cell and is independent of the atomic radius or the size of the unit cell.

As shown in Example 8.4, the packing efficiency of a unit cell depends only on the cell type; it is independent of edge length and atomic radius because both cancel in the calculation. Table 8.1 gives the packing efficiencies of the cubic unit cells and coordination numbers of the atoms in them. As might be expected, the packing efficiency increases as the number of atoms in the unit cell and the number of atoms that are packed around each atom (coordination number) increases.

Table 8.1 Packing efficiencies (PE), numbers of atoms in the unit cell (N), and coordination numbers (CN) of cubic lattices

Lattice Type	PE	N	CN
Simple	52%	1	6
Body-centered	68%	2	8
Face-centered	74%	4	12

Table 8.2 shows the unit cell types, metallic radii, and densities of selected metals that adopt cubic unit cells. Almost half of the volume of a *sc* unit cell is void space, so the *sc* unit cell is not a favorable way to pack and metals do not generally crystallize in *sc* lattices. Indeed, the only known example of a metal adopting the *sc* unit cell is a form of polonium. The densities of the Group 1A elements are all quite low due to the fact that their atoms are not very dense and because they pack in the less efficient *bcc* lattice. The impact of packing efficiency on the density can be seen by comparing K and Ca, which are next to one another in the periodic chart and have nearly identical metallic radii. Ca is almost 60% more dense because it crystallizes in the more efficient *fcc* unit cell. The effect can also be seen by comparing two forms of iron. Iron normally crystallizes with a *bcc* structure known as α -iron, but it also can be made to adopt a more efficiently packed *fcc* structure called γ -iron by adding small amounts of carbon and manganese or nickel and chromium. The tighter packing of γ -iron makes it so corrosion-resistant that it is known as *stainless steel*.*

Example 8.5

Determine the density of α -iron, which adopts a *bcc* crystal structure with $a = 2.86\text{\AA}$, and γ -iron, which adopts an *fcc* crystal structure with $a = 3.56\text{\AA}$.

To calculate the density (*d*) of a material, we must determine the mass (*m_{cell}*) and volume (*V_{cell}*) of the unit cell. *m_{cell}* is the number of atoms in the cell times the mass of each atom, and *V_{cell}* is *a*³. α -Iron is *bcc*, so there are two iron atoms/unit cell. Density has units of grams per cubic centimeter, so the side length, *a*, should be expressed in centimeters ($1\text{\AA} = 10^{-8}\text{ cm}$), so *a* = $2.86 \times 10^{-8}\text{ cm}$.

$$m_{\text{cell}} = 2 \text{ Fe atoms} \times \frac{1 \text{ mol Fe}}{6.022 \times 10^{23} \text{ Fe atoms}} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} = 1.855 \times 10^{-22} \text{ g}$$

$$V_{\text{cell}} = a^3 = (2.86 \times 10^{-8} \text{ cm})^3 = 2.34 \times 10^{-23} \text{ cm}^3$$

$$\text{density of } \alpha\text{-iron} = \frac{m_{\text{cell}}}{V_{\text{cell}}} = \frac{1.855 \times 10^{-22} \text{ g}}{2.34 \times 10^{-23} \text{ cm}^3} = 7.93 \text{ g/cm}^3$$

γ -Iron is *fcc*, so *N* = 4 iron atoms/unit cell. The side of the unit cell is $3.56\text{\AA} = 3.56 \times 10^{-8}\text{ cm}$. Making these substitutions yields

$$\text{density of } \gamma\text{-iron} = \frac{(4 \text{ atoms})(9.274 \times 10^{-23} \text{ g/atom})}{(3.56 \times 10^{-8} \text{ cm})^3} = 8.22 \text{ g/cm}^3$$

Table 8.2 Unit cell type, metallic radii, and densities of selected metals with cubic unit cells

metal	unit cell	radius (Å)	density (g/cm ³)
Ag	fcc	1.44	10.5
Al	fcc	1.43	2.70
Au	fcc	1.46	19.3
Ba	bcc	2.48	3.59
Ca	fcc	2.35	1.55
Cu	fcc	1.28	8.96
K	bcc	2.35	0.86
Li	bcc	1.55	0.53
Na	bcc	2.35	0.97
Ni	fcc	1.25	8.90
Pb	fcc	1.75	11.35
Pt	fcc	1.39	21.45
Rb	bcc	2.48	1.53
Sr	fcc	2.15	2.6

* There are numerous crystal structures reported for stainless steel, but only the most corrosion resistant is described here.

8.6 BAND THEORY OF SIMPLE METALS

The lattice sites of simple metals are occupied by metal atoms that are held together by **metallic bonds**. The strength of metallic bonds can vary substantially, so their properties vary over a wide range. For example, melting points of simple metals range from -39 °C for mercury, a liquid at room temperature, to 3410 °C for tungsten, while densities vary from about 0.5 g·cm⁻³ for lithium to 22.6 g·cm⁻³ for osmium. In the classical picture of metallic bonding, metal atoms lose all or some of their valence electrons to form positively charged ions and a ‘sea of electrons’ that is delocalized over the entire metal. The metal cations are immersed in that sea, and the electrostatic force exerted between the cations and the surrounding electrons holds the positively charged metal ions in place, just as the bonding electrons hold the two nuclei together in a covalent bond.

The molecular orbital description of the delocalized electrons in metallic bonds provides a more complete picture of metallic bonding as well as an explanation for the electrical conductivity of metals. The explanation, which is called **band theory**, applies the concepts presented in the molecular orbital discussion in Chapter 6 to a very large number of orbitals. In molecules, the number of atomic orbitals that are used to construct the MO’s is relatively small because the number of atoms involved is small, but recall that there are $\sim 10^6$ unit cells/mm in a solid, so the number of orbitals involved in a metal is enormous. Two effects of increasing the number of orbitals can be seen by comparing a system with two s orbitals with one of ten s orbitals as shown in Figure 8.7.

- 1) Increasing the number of orbitals increases their energy spread ($\Delta E_2 > \Delta E_1$).

Orbital X has nine bonding interactions, while orbital A has only one. Each bonding interaction lowers the energy of the orbital, so X is at lower energy. Orbital Z has nine antibonding interactions, while orbital B has only one.

Thus, Z is at a higher energy than B. We conclude that increasing the number of orbitals increases the energy difference between the highest and lowest energy orbitals; *i.e.*, the energy spread.

- 2) Increasing the number of orbitals reduces the energy separation between adjacent orbitals ($\Delta E_3 < \Delta E_1$). Orbital A is completely bonding, but orbital B is completely antibonding. They are very different types of orbitals, so their energies of very different. Orbital X has nine bonding interactions, while orbital Y has eight bonding interactions and one antibonding interaction.

Orbitals X and Y are both strongly bonding, so they are close in energy.

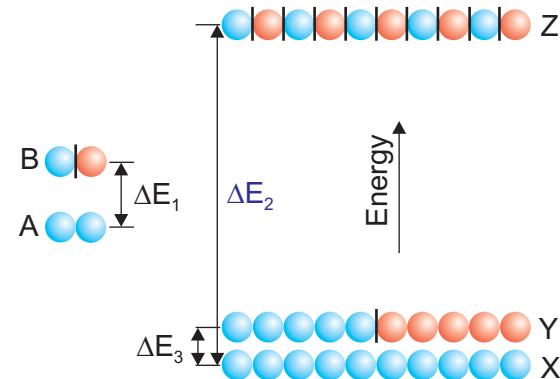


Figure 8.7 Energy levels in two- and ten-orbital systems

Only the two orbitals at lowest energy and the one at highest energy of the ten-orbital system are shown.

Figure 8.8 extends the discussion to the case of a very large number of orbitals that would describe the delocalized orbitals in a metal. The orbitals in the solid are constructed in the same way as those in a molecule, but they apply to a crystal rather than a molecule, so they are called **crystal orbitals** rather than molecular orbitals. As the number of orbitals increases, the adjacent orbitals become more similar, and the resulting energy levels get closer together. In a piece of metal, the number of atoms and atomic orbitals in each crystal orbital is enormous (on the order of Avogadro's number), so the energy levels are so close that they can no longer be distinguished. At this point, the energy levels are said to form an **energy band**. We will represent energy bands with rectangles to indicate that essentially any energy within the rectangle is accessible to the electron. However, the crystal orbitals in a band are filled in the same way as those in a molecule: from lowest energy up and two electrons per orbital. The occupancy of a band is usually the same as the occupancy of the atomic orbitals used to construct it. For example, a band constructed from filled atomic orbitals will be full, and one constructed from half-filled atomic orbitals will be half full. The band occupancy is represented by shading the occupied portion of the band. Thus, Figure 8.9 shows a half-filled band because only half of the band is shaded.

Electrical conductivity relies on the ability of the electrons to move through the crystal orbitals that are delocalized over the entire metal, but electrons are free to move only if there are empty orbitals available for them to move into. Thus, it is the highest energy electrons, those closest in energy to the empty orbitals that are responsible for electrical conductivity, and it is the energy separation between the highest occupied crystal orbital and the lowest unoccupied crystal orbital that dictates the conduction properties of the solid. Indeed, the highest occupied crystal orbital is such an important characteristic of the metal that it is given a name, the **Fermi level**.^{*} Crystal orbitals above the Fermi level are empty and those below it are full. In a partially filled band, such as the one shown in Figure 8.9, the energy separation at the Fermi level is essentially zero, so thermal energy is sufficient to move electrons from filled into empty orbitals, where they are mobile and can conduct electricity. Thus, substances with partially filled bands like the one shown in Figure 8.9 are **metallic conductors**.

The band structure in Figure 8.9 applies only to metals with half-filled atomic orbitals, but atoms with filled atomic orbitals also form bands. The band structure for an atom with no partially filled bands is shown in Figure 8.10. The highest energy filled band, which is filled with valence electrons, is called the **valence band**, while the lowest energy empty band is called the **conduction band**. The Fermi level is at the top of the valence band. The

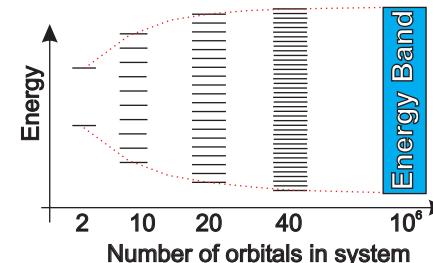


Figure 8.8 Energy diagrams for some many-atom systems

Energy diagrams for two-, ten-, twenty-, forty-, and 10^6 -orbital systems. The energy separation in the 10^6 orbital system is so small that an energy band is formed. The dotted, red line shows the behavior of the maximum and minimum energies in the systems. Note how they level off for systems with large numbers of orbitals.

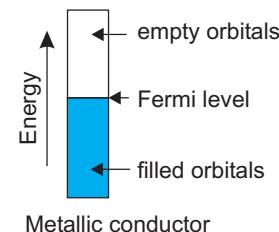


Figure 8.9 Band diagram for a metallic conductor

* The Fermi level is to crystal orbitals what the HOMO is to molecular orbitals.

energy difference between the top of the valence band and the bottom of the conduction band is called the **band gap**. Conduction can occur only if there are unfilled orbitals into which electrons can move, but there are no unfilled orbitals available in a filled valence band, so electrons must be excited from the valence band into the conduction band if the substance is to conduct. Thus, a material with the band structure in Figure 8.10 is an **insulator** if the band gap is much greater than thermal energy and no electrons occupy the conduction band. However, if the band gap is not much greater than thermal energy, some electrons do populate the conduction band and the material becomes a conductor. Increasing the temperature (thermal energy) of a material with a small to moderate band gap increases its conductivity by increasing the population of the conduction band. A substance whose conductivity increases with temperature is called a **semiconductor**.* Silicon and germanium have moderate band gaps (100 and 67 kJ/mol, respectively) and are semiconductors, while diamond, which has a much larger band gap (502 kJ/mol), is an insulator.

Some metals, such as zinc, that have filled valence shells can still be metallic conductors if there is overlap between the highest energy filled band and the lowest energy unoccupied band. In zinc, the band formed from the filled 4s orbitals and the band formed from the empty 4p orbitals overlap. High energy electrons in the filled band move into crystal orbitals at lower energy in the unoccupied band to produce two partially filled bands as shown in Figure 8.11. The presence of two partially filled bands makes zinc a metallic conductor even though all of its valence orbitals are full.

8.7 IONIC SOLIDS AND IONIC RADII

To this point, we have focused on crystals in which all of the particles are identical, but ionic substances are composed of two or more different ions, so their structures consist of at least two different types of particles. The ions in an ionic crystal can be treated as charged spheres that pack to maximize cation-anion interactions. In a sodium chloride crystal, each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions. The result is an extended solid of alternating sodium and chloride ions with no unique NaCl molecules. Breaking or melting an ionic crystal requires breaking a large number of strong interactions (ionic bonds). Consequently, ionic substances are generally hard and have high melting points (600–2000 °C). The strength of the interaction depends upon the magnitude of the charges on the ions and the separation between them. Thus,

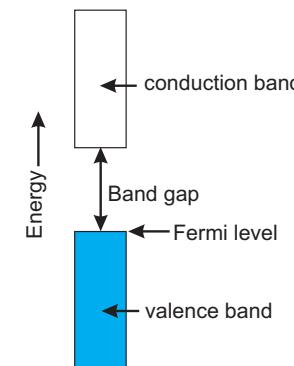


Figure 8.10 Conductivity and the band gap

The band diagram is that of a semiconductor if the band gap is small or that of an insulator if the band gap is large.

- * The conductivities of metallic conductors decrease slightly at elevated temperatures due to the increased thermal motion of the atoms.

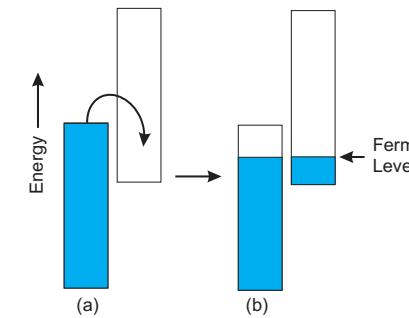


Figure 8.11 Metallic conductor produced by the overlap of a filled and an empty band

- (a) High-energy electrons in a filled band seek lower energy orbitals in the empty band.
- (b) At equilibrium, both bands are partially filled, so the substance is a metallic conductor.

melting points are highest for ionic substances with small, highly charged ions that are closely packed.

The distance between two adjacent ions in a crystal is equal to the sum of their **ionic radii**. For example, the distance between Li^{1+} and I^{-} ions in a crystal of LiI is 2.96 Å, so we can write $r_{\text{Li}} + r_{\text{I}} = 2.96 \text{ \AA}$. Ionic radii have been determined by examining many such distances. The ionic radii of the alkali metal ions (Group 1A) and the halide ions (Group 7A) are given in Table 8.3.

Example 8.6

What is the ionic radius of Mg^{2+} , if the Mg-Cl distance in MgCl_2 is 2.53 Å?

Express the distance as the sum of the ionic radii: $2.53 = r_{\text{Mg}} + r_{\text{Cl}}$

Set $r_{\text{Cl}} = 1.67 \text{ \AA}$ from Table 8.3 and solve for the ionic radius of Mg^{2+}

$$r_{\text{Mg}} = 2.53 - 1.67 = 0.86 \text{ \AA}$$

Not all of the particles in an ionic solid are identical, but the same structural descriptions that are applied to metallic solids can be used to understand the crystal structure of many ionic compounds. For example, most of the alkali halides have a preference for a structure in which the anions pack in a face-centered cubic unit cell, as shown in Figure 8.12a. The three anions along a diagonal of a face touch in a fcc unit cell, but there is void space along each of the cell edges and in the body center. Much smaller cations can fit into these ‘holes’ as shown for LiI in Figure 8.12b. Each ion is surrounded by six ions of opposite charge, so both Li^{1+} and I^{-} ions have coordination numbers of six and octahedral coordination geometries. Using geometry, we can calculate that to fill these holes perfectly, the radius of the cation should be a little less than half the radius of the anion ($r_{\text{cation}} = 0.414 r_{\text{anion}}$). LiI nearly adopts the ideal structure ($r_{\text{Li}}/r_{\text{I}} = 0.44$) and has a very high packing efficiency. However, the Li^{1+} ions are slightly too large to fit into the holes, so the I^{-} ions are pushed apart slightly and do not make contact. Chloride ions are smaller than iodide ions, so their fcc arrangement has even smaller holes along the edge. As a result, they are pushed apart even farther to accommodate the Li^{1+} ions in crystalline LiCl (Figure 8.13). Example 8.7 determines the distance between chloride ions.

Sodium chloride adopts the same structure type as lithium chloride. In fact, this structure type is called the sodium chloride structure, and LiCl is said to crystallize in the **sodium chloride structure**. In sodium chloride, the sodium cation is considerably larger than the ideal hole created by closest packed chloride anions. As shown in Figure 8.14, the

Table 8.3 Ionic Radii of Group 1A and Group 7A Ions

Cation	Radius (Å)	Anion	Radius(Å)
Li^{1+}	0.90	F^{-}	1.19
Na^{1+}	1.16	Cl^{-}	1.67
K^{1+}	1.52	Br^{-}	1.82
Rb^{1+}	1.66	I^{-}	2.06
Cs^{1+}	1.81		

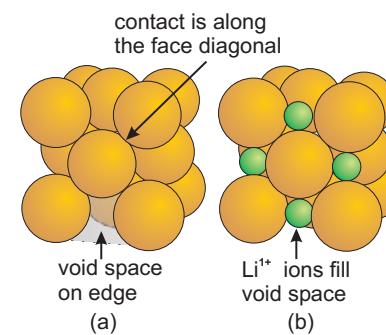


Figure 8.12 Filling void space with cations

(a) fcc structure of iodide ions with no cations. In this arrangement, the ions touch along the diagonal. (b) fcc structure of iodide ion with lithium ions inserted into the void spaces on the edge. The iodide ions no longer touch along the diagonal.

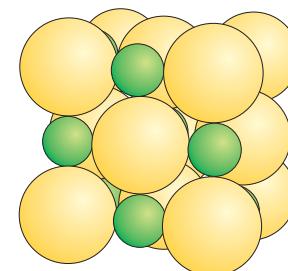


Figure 8.13 LiCl unit cell

chloride anions are moved even farther apart to accommodate the larger sodium ions. While this expansion of the packing in the unit cell lowers the packing efficiency, there is little energy cost because each ion is still in direct contact with six ions of opposite charge. The major change in this expanded structure is that the like charges (anion-anion and cation-cation) are further separated, which is energetically favorable.

The radius of a cesium ion is slightly greater than that of a chloride anion, so the fcc lattice is expanded considerably to introduce a great deal of void space. The resulting low packing efficiency is essentially the same as in a simple cube. Indeed, the similarity of the ionic radii results in a unit cell that has the appearance of a simple cube in which four of the corners are occupied by cations and four are occupied by anions, as shown in Figure 8.15a. Under special conditions, CsCl can be made to crystallize with this sodium chloride structure type, but under normal conditions, the packing efficiency of these nearly equally sized ions is optimized in the arrangement, as shown in Figure 8.15b. This structure, known as the **cesium chloride structure**, can be described as having chloride anions forming a simple cube with a cesium cation in the body center. The unit cell has the packing efficiency of a body-centered cubic unit cell, and it can be described as a simple cube of cesium cations with a chloride anion in the body center.

Example 8.7

Use ionic radii to determine the void space between chloride ions in LiCl.

The ionic radii from Table 8.3 are $r_{\text{Li}} = 0.90 \text{ \AA}$ and $r_{\text{Cl}} = 1.67 \text{ \AA}$. Li^{1+} and Cl^{1-} ions touch along the edge of the unit cell, so the length of the unit cell edge (a) is two Li^{1+} ionic radii plus two Cl^{1-} ionic radii (see figure in margin):

$$a = 2r_{\text{Li}} + 2r_{\text{Cl}} = 2(0.90) + 2(1.67) = 5.14 \text{ \AA}$$

The length of the face diagonal of LiCl is obtained from the edge length (a) and the Pythagorean theorem to be

$$fd^2 = a^2 + a^2 = 2a^2 \Rightarrow fd = \sqrt{2}a = \sqrt{2}(5.14) = 7.27 \text{ \AA}$$

Four chloride ionic radii is $4r_{\text{Cl}} = 4(1.67) = 6.68 \text{ \AA}$, so the actual face diagonal is $7.27 - 6.68 = 0.59 \text{ \AA}$ longer than the length of the chloride ions that lie on the diagonal. This difference is twice the void space between Cl^{1-} ions (red bars in figure). The void space between chloride ions in LiCl is $\sim 0.59/2$ or $\sim 0.3 \text{ \AA}$.

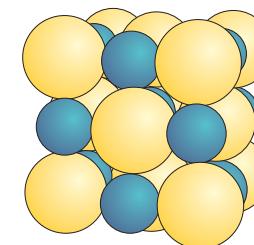


Figure 8.14 NaCl structure

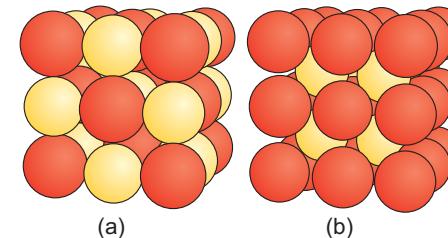
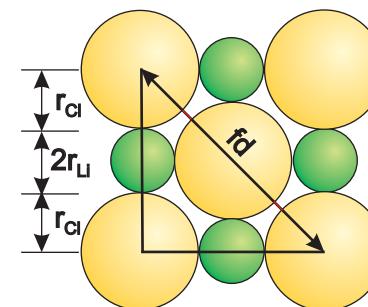


Figure 8.15 CsCl unit cells

(a) CsCl in the NaCl structure. (b) CsCl in the CsCl structure.



Example 8.7

The void space between chloride ions is highlighted in red. fd is the face diagonal of the LiCl unit cell. The Li^{1+} ion touches the Cl^{1-} along the edge, which forces the Cl^{1-} ions apart.

8.8 COVALENT SOLIDS

Covalent solids are very large networks of atoms held together by covalent bonds, which are very strong interactions. Consequently, covalent solids have very high melting points (600 - 2000 °C) and are very hard. Ionic bonds are largely non-directional as the opposite charges simply pack around one another as efficiently as possible, while covalent bonds are directional and lead to molecular structures as discussed in Chapter 6. Thus, the structures of extended solids formed from covalent bonds differ from those formed from ionic bonds. Some elements can exist in several structural forms called **allotropes**, which can have very different properties. For example, graphite and diamond are two allotropes of carbon, and we begin our discussion of covalent solids by examining some structure-property relationships in these well known materials and in some other less known but interesting forms of carbon.

The carbon atoms in **graphite** are sp^2 hybridized and form a two-dimensional σ -bonding framework as shown in Figure 8.16a. The sheets then stack as shown in Figure 8.16b to produce the solid material. Graphite is used in electrodes, lubricants, and pencils. These uses can all be understood in terms of the bonding and structure of the material. Its conducting ability (electrodes) arises because the p orbital of each atom that is not used in hybridization is part of a π system that is delocalized over the entire sheet. The number of atoms involved in the system is quite large, so the delocalized π system produces bands. One of the bands is half-filled, so graphite is a metallic conductor, but only in the plane of the sheet, not between sheets. The distance between sheets is fairly large (3.4 Å), which is indicative of relatively weak intermolecular interaction between layers. Consequently, the layers are easily moved over one another, which makes graphite an excellent lubricant. The layers can even be removed completely with rubbing, which makes it ideal for the “lead” in pencils.

Fullerenes are carbon compounds with structures based on the graphite structure. The most common fullerene is C_{60} (Figure 8.17), which is called buckminsterfullerene (or buckyball) after the architect of the geodesic dome. Buckyball was discovered in the early 1980’s. It contains 20 hexagons and 12 pentagons and is the shape of a soccer ball. The hexagons are the same units that form the basis of graphite, but the pentagons are required for closure. A great deal of research was done on fullerenes to develop new technologies. For example, efforts were made to use it as a molecular ball-bearing lubricant, and to encapsulate smaller molecules in its cavity, so the molecules could be released slowly into

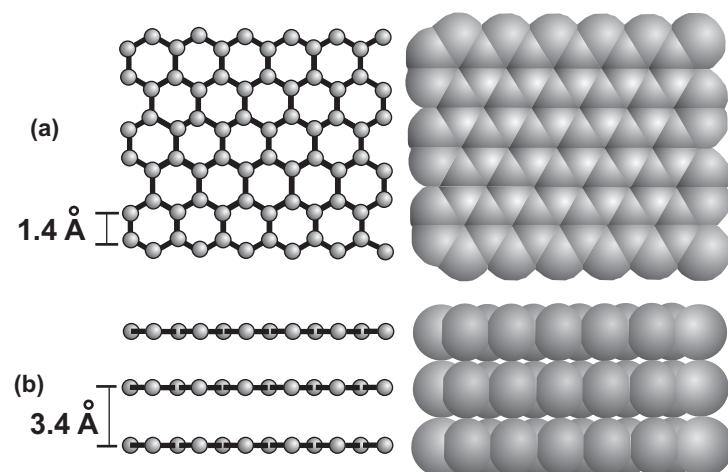


Figure 8.16 Ball-and-stick and space-filling models of graphite

(a) Face of a portion of one sheet that shows the two-dimensional σ -bonding framework and the 1.4 Å bond length.
(b) Three adjacent sheets of graphite showing how the sheets stack in the solid material with a 3.4 Å separation between sheets. Note that the atoms of adjacent sheets just touch in the space-filling model.

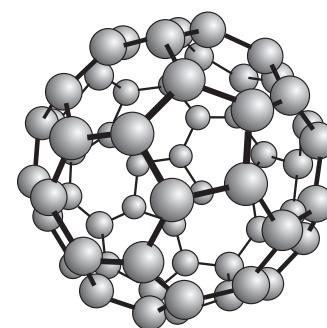


Figure 8.17 C_{60} or “Buckyball”

the body. Buckyball is also a superconductor, and efforts have been made to take advantage of this property as well. However, no practical uses of buckyball have yet been developed.

A **carbon nanotube** is a rolled-up sheet of graphite (Figure 8.18) that is only nanometers in diameter but up to a centimeter long. Nanotubes are very strong, and, depending on how the graphite sheets are rolled (straight across or at a slight diagonal), they are conductors or semiconductors. Single nanotubes have been used to make molecular wires, diodes, and transistors, and groups of nanotubes have been integrated into logic circuits, fundamental computer components. These devices are a hundred times smaller than those on present-day computer chips. Nanotubes are a basic building block in the new field of molecular electronics. Indeed, a new technology, one based on devices that measure less than a 1000 nanometers, is currently being developed. This new technology is referred to as **nanotechnology**.

Diamond (Figure 8.19) is constructed from sp^3 hybridized carbon atoms. The resulting three-dimensional framework has a much lower packing efficiency (34%) than found for metals or ionic compounds. The strength of its C-C bonds combined with its rigid structure makes diamond the hardest substance known. The electrons of the covalent bonds are delocalized over the entire structure, which results in a completely filled valence band and an empty conduction band. Although diamond is an insulator because its band gap is very large, the diamond structure type is adopted by silicon and germanium, two of the most common semiconductors.

While differences in the structures of covalent and ionic compounds are expected, there are definite similarities in some structures. For example, the carbon atoms in a diamond unit cell adopt the lattice positions of a face-centered cubic cell and an additional four positions of tetrahedral coordination that lie totally within the cell. Remember that there are four atoms in the face-centered cubic unit cell, and each atom totally within the unit cell contributes another one full atom to the cell stoichiometry. Consequently, there are a total of eight carbon atoms in the diamond unit cell. This unit cell type is the basis of several important covalent solids. The *zinc blende structure* results when the corners and face-centers are occupied by one type of atom, but the four sites within the cell are occupied by another. Figure 8.20 shows the structure of ZnS, which is the prototype for the **zinc blende structure** (zinc blende is the mineral name for zinc sulfide). GaP, a useful semiconductor, also adopts this structure type. In fact, this is the structure type of the most common semiconductors, including GaAs and InP. The similarity in properties

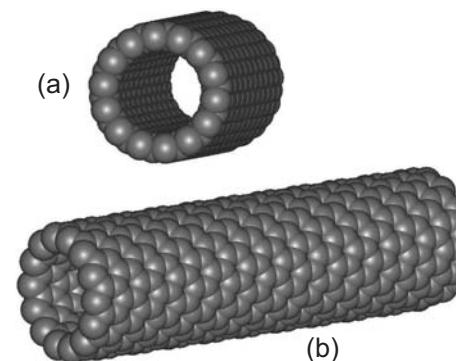


Figure 8.18 Carbon nanotube

Space-filling model of tube is viewed down its axis (a) and along its side (b).

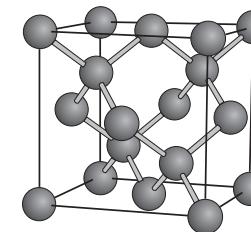


Figure 8.19 Diamond

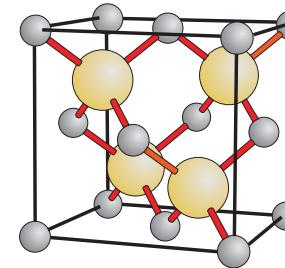


Figure 8.20 Zinc blende (ZnS)

Zinc atoms are grey and sulfur atoms are yellow.

between the solids formed from the Group 4 atoms (C, Si, and Ge) and those formed from compounds of Group 3 and Group 5 atoms results because the two sets of solids are isoelectronic; *i.e.*, a pair of atoms in either solid contains a total of eight valence electrons.

Figure 8.21 shows a high-temperature form of SiO_2 . In this structure, the silicon atoms also adopt the diamond-type structure shown in Figure 8.19; but, in this structure, there is an oxygen atom located between each pair of silicon atoms. This comparison of diamond, common semiconductors, and a high-temperature form of SiO_2 demonstrates how variation of the composition of materials that adopt similar structures can dramatically change the properties of materials.

Natural **zeolites*** are aluminosilicates, extended networks built from tetrahedral AlO_4 and SiO_4 anions that are bridged by oxygen atoms (each oxygen atom is part of two units). The structure of zeolites is filled with channels (Figure 8.22a) and cavities or pores (Figure 8.22b) that are only a few angstroms wide. The aluminosilicate framework is composed of anions, so natural zeolites are commonly found with sodium cations inside the cavities. Small molecules can also get into the channels, where they interact with the oxygen atoms in the aluminosilicate framework. The interaction keeps them from leaving, so zeolites are used as **molecular sieves**. One common use of molecular sieves is as a drying agent. Water molecules are small enough to enter the cavities where they interact so strongly with the walls via hydrogen bonding that they do not exit, so when sieves are added to a wet liquid, they extract any water that is present. The sieves are filtered out of the liquid to leave an anhydrous (no water) liquid behind. The sieves can be reactivated by placing them in a hot oven where the thermal energy is sufficient for the water molecules to break their interactions with the framework. The ability of zeolites to function as molecular sieves also makes them excellent blood clotting agents that are used by the military and rescue professionals. When a zeolite powder is applied to a wound, it draws the water out of the blood, which concentrates the clotting agents and speeds the clotting process.

The sodium ions, which are only loosely bound in the cavities, are easily displaced by other ions, so zeolites are also used in **ion-exchangers**. For example, when ‘hard water’ (water containing dissolved Ca^{2+} and Mg^{2+} ions) is passed through a zeolite column, the Ca^{2+} and Mg^{2+} ions displace the Na^{1+} ions in the zeolite because the more highly charged ions interact more strongly with the anionic framework. The water that leaves the column contains Na^{1+} ions instead of Ca^{2+} and Mg^{2+} ions, so it is “softened.” Some laundry detergents contain zeolites that are used to soften the wash water during the wash cycle.

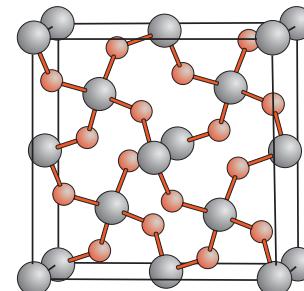


Figure 8.21 β -crystobalite

A form of SiO_2 found at temperatures above 1500 °C. Silicon is shown as grey spheres and oxygen as red spheres.

* The word “zeolite” comes from the Greek word for “boiling stone” because steam was observed escaping from the mineral when it was heated.

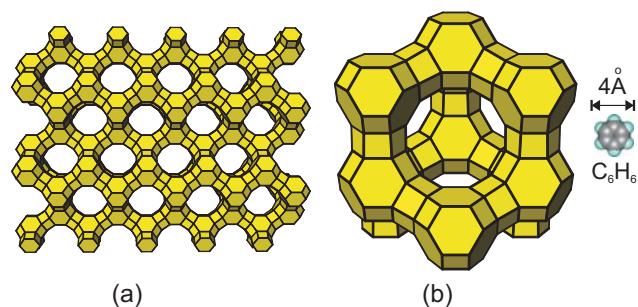


Figure 8.22 Zeolite

Each line has an Al or Si atom at the end and an O atom in the middle. Openings that are too small to be entered by smaller molecules are closed to emphasize the channel (a) and pore (b) structures. A benzene molecule is shown for size comparison.

Chemistry can also take place inside the pores. Indeed, some reactions that occur with difficulty on their own occur with relative ease within the cavities of a zeolite. The enhanced reactivity results because interactions with the aluminosilicate framework can make substances more reactive, *i.e.*, zeolites can function as **catalysts**.^{*} Indeed, the largest use of zeolites is to catalyze reactions that convert some of the less useful molecules found in petroleum into more useful ones. The pore size dictates the size of both the reactants and the products, so chemists can select to react only certain molecules in a mixture by selecting a zeolite with the appropriate pore size to exclude larger molecules. Chemists also create zeolites with chemical groups attached to them that enhance certain reactions; *i.e.*, they *functionalize* zeolites.

Clays are the most abundant minerals found in soils, rocks and waters. Like zeolites, they are usually aluminosilicates. However, Mg is substituted for Al in many clays, and Fe fills certain of the Al sites in some clays to give them a red color. All clays exhibit a two-dimensional layered lattice structure rather than the porous network structure of zeolites. The two major types of clays, kaolinite and smectic clays pictured in Figures 8.23a and 8.23b, respectively, differ in the organization of tetrahedral (SiO_4) and octahedral (AlO_6 or MgO_6) building blocks. The differences in their structures result in dramatically different properties for these two types of clays.

Kaolinite clays, Figure 8.23a, consist of aluminosilicate sheets composed of a silicate layer (SiO_4 tetrahedra shown in blue) and an aluminate layer (AlO_6 octahedra shown in green). In their sedimentary formation, kaolinite clays may have water between the aluminosilicate layers. However, upon heating (firing) the water is driven out from between the layers, leaving only OH bonds on the surface formed by the aluminate layers. These terminal OH groups form strong hydrogen bonds to the oxygen atoms of the silicate portion of the neighboring layer providing a rigid material, which is why kaolinite clay is the main component of china clay.

Smectic (or swelling) clays, Figure 8.23b, consist of sheets composed of a layer of aluminate octahedra sandwiched between two layers of silicate tetrahedra. Other cations surrounded by water (hydrated metal ions), represented by the larger gray spheres in the figure, often fill the space between these layers. There are fewer OH groups in this type of structure, and those that are present are ‘buried’ in the aluminate layer between the two silicate layers, which effectively shields them from forming inter-layer hydrogen bonds. As a result, the layers in a smectic clay are not tightly held together, and other ions and molecules can penetrate in between these layers and force the sheets apart. This property

* Catalysts are materials that speed the rate of reaction. They will be discussed in Chapter 9.

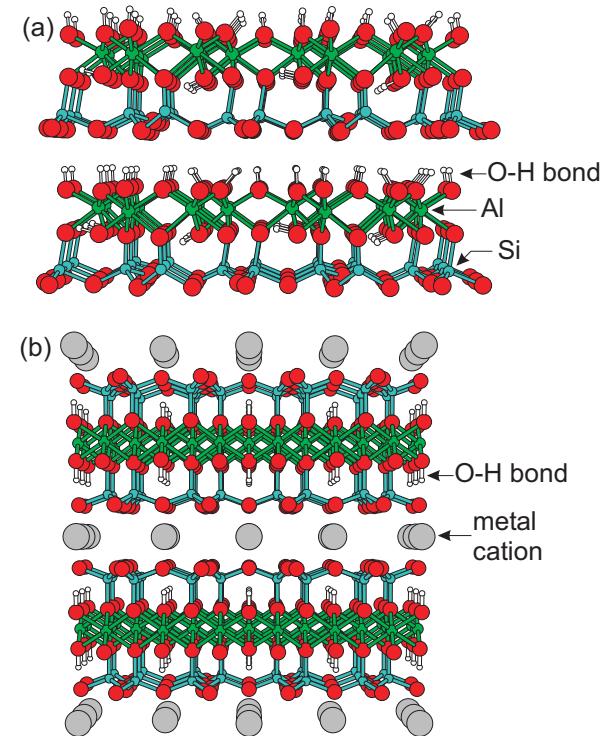


Figure 8.23 (a) Kaolinite and (b) Smectic clays

Si atoms and Si-O bonds are blue, Al atoms and Al-O bonds are green, O atoms are red, and H atoms and O-H bonds are white.

makes them chemically important in separations and catalysis for the same reasons as zeolites. The major difference between them is that the 3-D network of zeolites provides greater size and shape selectivity than does the 2-D structure of clays. Interestingly, when smectic clay is fired, the water can also be driven out of the crystal lattice. However without strong hydrogen bonding between the layers, the fired materials result in the flaky material, mica, rather than the more robust china or porcelain.

8.9 MOLECULAR SOLIDS AND ATOMIC RADII

Unlike ionic or network covalent solids, individual molecules are easily identified in **molecular solids** (Figure 8.24). Adjacent molecules interact through intermolecular forces (dotted lines in figure), while atoms within a molecule interact through much stronger covalent bonds (red rods in figure). Molecules are easily identified because the distance between atoms on adjacent molecules, which is called the **van der Waals distance** (d_{vdw}), is much greater than the distance between atoms within a molecule, which is called the bond length (L). The situation is much different in a network covalent solid such as SiO₂ (Figure 8.21) where all Si-O distances between adjacent atoms are the same, and there are no identifiable SiO₂ molecules.

The intermolecular forces that hold molecules in the solid state are much weaker than those responsible for ionic or covalent solids, so molecular solids tend to have lower melting points and are softer than the other solids. However, their properties can be quite diverse, as evidenced by the fact that hydrogen, water, table sugar (C₁₂H₂₂O₁₁), dry ice, and iodine form molecular solids, which have melting points that range from -259 °C for H₂ to 186 °C for sugar, a range of over 400 °C. In addition, the intermolecular forces are typically tens of kilojoules, while covalent bond strengths are hundreds of kilojoules. Thus, covalent bonds are not broken when a substance melts, so molecules retain their identity in the liquid state.

There are two X-X distances shown in Figure 8.24, and each defines a different atomic radius. The **covalent radius** of X is defined as one-half of the X-X bond length ($L = 2r_{cov}$), and the **van der Waals radius** of X is defined as one-half of the X-X van der Waals distance. The van der Waals radius of an atom is viewed as its “interaction distance.” Two atoms closer than the sum of their van der Waals radii are assumed to be interacting. The radii of the atomic spheres used in space-filling models are proportional to their van der Waals radii. The definition of the van der Waals radius is clarified in Figure 8.25, which is

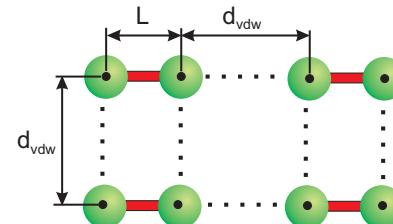


Figure 8.24 Four molecules in crystalline X₂

Ball-and-stick models are used for X₂. The molecules are identifiable because the van der Waals distance (d_{vdw}) is much greater than the bond length (L). Dotted lines represent weak intermolecular forces, while heavy red lines are used to show the covalent bonds.

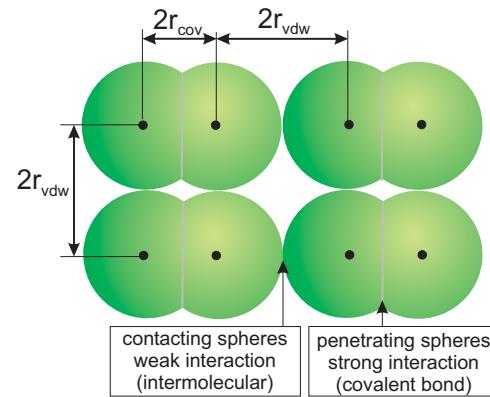


Figure 8.25 van der Waals radius (r_{vdw})

Space-filling models for four X₂ molecules in crystalline X₂ are used to distinguish between the covalent and van der Waals radii of X.

identical to Figure 8.24 except that space-filling representations are used rather than ball-and-stick. Note that the atomic spheres of X penetrate one another in an X_2 molecule, which means that the two atoms are much closer than the sum of their van der Waals radii. Two atoms much closer than the sum of their van der Waals radii are interacting strongly, so there is a bond between the two X atoms. The spheres on adjacent molecules are touching but not penetrating, so the X atoms of different X_2 molecules interact only weakly. Figure 8.26 compares the ball-and-stick, covalent radius, and space-filling representations of X_2 . In the ball-and-stick representation, the spheres indicate the positions but not the sizes of the atoms. When atomic size is represented with covalent radii, bonds are indicated by the contact of spheres, but when atomic size is given by van der Waals radii (space-filling), bonds are indicated by the penetration of spheres. Table 8.4 gives the covalent and van der Waals radii of selected nonmetals.

Example 8.8

- a) What is van der Waals distance in graphite (Figure 8.16), and what is the van der Waals radius of carbon as determined from this distance?

The carbon atoms in adjacent layers are touching but not penetrating, so the van der Waals distance is the distance between layers, which is 3.4 Å. The van der Waals radius is one-half of the van der Waals distance, so the van der Waals radius of a carbon atom is 1.7 Å, in agreement with its entry in Table 8.4.

- b) How does the C-C bond length in graphite compare to that predicted from the covalent radii in Table 8.4?

The C-C bond length predicted from Table 8.4 is twice the covalent radius of carbon, so $L = 2r_c = 2(0.77) = 1.54\text{ \AA}$. The observed C-C length in graphite is 1.4 Å. The reason for the difference is that the covalent radii are determined for single bonds, but the C-C bond order in graphite is 1.5 due to the delocalized π system.

Example 8.9

Use the covalent radii in Table 8.4 to determine the Ge-Cl bond length.

The bond length is the sum of the covalent radii of the bound atoms. Obtain the two covalent radii from Table 8.4 and sum them to get the bond length.

$$L(\text{Ge-Cl}) = r_{\text{cov}}(\text{Ge}) + r_{\text{cov}}(\text{Cl}) = 1.22 + 0.99 = 2.21 \text{ \AA}$$

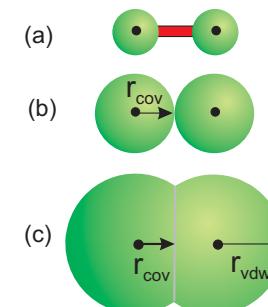


Figure 8.26 Representations of X_2

- (a) **Ball-and-stick representation:** The sizes of the spheres are not usually meaningful.
- (b) **Covalent radii:** When atoms are represented by their covalent radii, bonds are represented by contact of the two spheres.
- (c) **Space-filling model:** The atomic size is represented by the van der Waals radius and bonds by the penetration of the atomic spheres.

8.10 COMPARISON OF SOLID TYPES

Table 8.5 A summary of the key properties of the different types of solids.

Type	Particles	Forces	Strength*	Examples
Metallic	Atoms	Metallic bonds	Variable	Na, Cu, Ag, Fe
Ionic	Ions	Ionic bonds	Strong	NaCl, NH ₄ Cl
Network covalent	Atoms	Covalent bonds	Strong	C, ZnS, SiO ₂
Molecular	Molecules	Intermolecular	Weak to moderate	H ₂ O, sugar, SO ₂

* The strength of interaction is indicative of the melting point of the solid and how hard it is because these forces must be overcome to melt the solid or to break it.

Example 8.10

Which compound in each pair has the higher melting point?

a) MgO or NaF

Both contain a metal and a nonmetal and are therefore ionic. The strength of the interaction in ionic solids increases with the charge on the ions, so we predict that the interaction of the Mg²⁺ ion with the O²⁻ should be much greater than that between Na¹⁺ and F¹⁻. The melting points are 2800 °C for MgO and 988 °C for NaF.

b) NaCl or Cl₂

NaCl is ionic, but Cl₂ is molecular. Ionic substances usually have higher melting points than molecular substances, so NaCl is expected to have the higher melting point. Indeed, NaCl is a solid at room conditions, while Cl₂ is a gas.

c) SiO₂ or SO₂

Neither contains a metal, so it might appear that they are both molecular solids, however, SiO₂ (quartz) is a covalent solid with no identifiable SiO₂ molecules. Consequently, covalent bonds must be broken to melt SiO₂. SO₂, on the other hand, is molecular and only relatively weak intermolecular forces must be broken to melt it. SiO₂ melts at 1700 °C, while SO₂ melts at -73 °C.

Table 8.4 Covalent and van der Waals radii in Å of selected nonmetals

H				
r _{cov}	0.32			
r _{vdw}	1.2			
C N O F				
r _{cov}	0.77	0.75	0.73	0.72
r _{vdw}	1.70	1.5	1.40	1.35
Si P S Cl				
r _{cov}	1.11	1.06	1.02	0.99
r _{vdw}	2.10	1.9	1.85	1.80
Ge As Se Br				
r _{cov}	1.22	1.20	1.17	1.14
r _{vdw}	2.0	2.00	1.95	

8.11 CHAPTER SUMMARY AND OBJECTIVES

Atoms in a metal pack like spheres to form the solid state. The basic unit that defines the way in which they pack is called the unit cell. There are seven types of unit cells, but we considered only the cubic unit cell, which consists of three types: simple cubic (*sc*), body-centered cubic (*bcc*) and face-centered cubic (*fcc*). Each type of unit cell is characterized by the number of atoms present in the unit cell, the coordination number of the atoms in the cell, and the packing efficiency of the cell. The *fcc* is the most tightly packed, with a packing efficiency of 74%.

Atoms are held in a metal by metallic bonding. Metallic bonding is best understood in terms of crystal orbitals and bands rather than atomic orbitals and levels. Metallic conductors are metals that have partially filled bands. A band filled with valence electrons is called the valence band, while the empty band above it is called the conduction band. The energy separation between the valence and conduction bands is called the band gap. Materials with small band gaps are semiconductors because their conductivity increases with temperature, while those with large band gaps are insulators.

The sodium chloride structure is a cubic structure in which the sodium ions can be viewed as occupying the void space in a closest packed arrangement of chloride ions (*fcc*). It is the structure adopted by the alkali halides when the ion sizes are sufficiently different to allow the smaller ion to fit into the void space without distorting the closest packed arrangement too much. When the anion and cation radii are similar, the sodium chloride structure is a very inefficient way to pack the ions, so ionic solids in which the radii are similar crystallize in the cesium chloride structure, which can be viewed as a *bcc* arrangement in which the cation is in the center and the anions are at the corners.

Network covalent solids are networks of atoms held together by covalent bonds. The structure of the solid is responsible for many of its properties. Thus, graphite is a lubricant because it consists of weakly interacting sheets that can slide over one another, while diamond is very hard due to the three-dimensional nature of its covalent bonds. Buckyball, C₆₀, has the same shape as a soccer ball and many interesting properties. Nanotubes are formed from sheets like those in graphite that have been rolled up. Their conductivity has led to their use as molecular wires and transistors. Zeolites are porous materials made from Al, Si, and O. The pores are large enough for other molecules to enter and do chemistry. Clays have a similar building block to zeolites, but clays are composed of sheets rather than pores and channels.

Molecular solids are composed of molecules or atoms that interact only through intermolecular interactions. These interactions vary considerably from the weakest dispersion force in He to fairly strong hydrogen bonds. Consequently, molecular solids can be solids, liquids, or gases at room conditions.

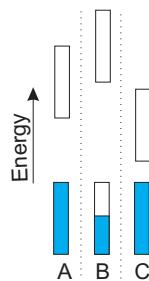
Atomic radii can be given as the metallic radius, the covalent radius, or the van der Waals radius. Metallic radii are deduced from the distance between metal atoms that are touching in a metallic solid. Covalent radii are defined from bond lengths because the length of a covalent bond is the sum of the covalent radii of the bound atoms. The van der Waals radius is one-half of the van der Waals distance (distance between two adjacent molecules in the crystal of an element). The spheres used to represent the atoms in space-filling models are based on their van der Waals radii. Thus, a covalent bond can be represented as the contact of two spheres with radii equal to the covalent radii of the atoms or as the penetration of two spheres with radii equal to the van der Waals radii.

After studying the material presented in this chapter, you should be able to:

1. identify and define unit cells (Section 8.1);
2. draw the sc, bcc and fcc unit cells (Section 8.2);
3. determine the metallic radius of an atom from the edge length of the unit cell and cell type (Section 8.2);
4. determine the formula of a substance based on the unit cell occupancy (Section 8.3);
5. determine the coordination number of an atom or ion in a crystal lattice (Section 8.4);
6. explain packing efficiency and why it is important and calculate the density of a solid from its unit cell dimensions (Section 8.5);
7. differentiate between a conductor, a semiconductor, and an insulator on the basis of their band structures (Section 8.6);
8. determine the distances between ions in a crystal given their ionic radii and the crystal type (Section 8.7);
9. differentiate between the sodium chloride and cesium chloride structures and explain why one structure would be preferred over the other (Section 8.7);
10. distinguish between the following forms of carbon: graphite, diamond, buckyball, and nanotubes (Section 8.8);
11. describe the diamond and zinc blende structures adopted by several covalent solids (Section 8.8);
12. describe the structure and function of zeolites and clays (Section 8.8);
13. define the van der Waals distance (Section 8.9);
14. distinguish between covalent and van der Waals radii and determine a bond length from the covalent radii of the atoms (Section 8.9); and
15. predict relative melting points from the types of solids (Section 8.10).

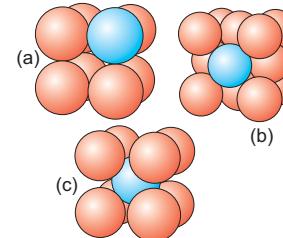
8.12 EXERCISES

1. What is a unit cell?
2. How many unit cells are shown in Figure 8.15a?
3. How many unit cells are shown in Figure 8.15b?
4. What distinguishes a crystalline solid from an amorphous solid?
5. What is the Fermi level?
6. How do valence bands differ from conduction bands?
7. What is a band gap?
8. Use band theory to explain the difference between a conductor, a semiconductor, and an insulator.
9. The band structures of a conductor, a semiconductor and an insulator are shown below. Identify each.



10. Suggest a reason why the band gap decreases in the order $C > Si > Ge$. Refer to Figure 2.6 and the valence electron configurations of the atoms.
11. Gold crystallizes in a face-centered cubic geometry that is 4.08 \AA on each side.
 - a) Draw a picture showing the face of the unit cell. What atomic radius of gold is required for this geometry?
 - b) How many gold atoms are present in the unit cell?
 - c) What is the volume of the unit cell in \AA^3 ?
 - d) What is the volume occupied by the atoms in the unit cell?
 - e) Based on your results to c and d, what is the packing efficiency of the unit cell? How does this compare with the packing efficiency expected for a fcc unit cell?

12. Use the three unit cells shown below to answer the questions.



- a) Which arrangement has the best packing efficiency?
 - b) What is the coordination number of the blue sphere in each case?
 - c) What fraction of each blue sphere is in each unit cell?
 - d) How many spheres are in each unit cell?
 13. Calcium titanate, which is composed of calcium, titanium, and oxygen, crystallizes in the *perovskite* structure shown below. Ca (green spheres) resides on the corners of the unit cell, Ti (blue sphere) resides in the body center, and O (red spheres) resides on each of the cell faces. What is the formula of calcium titanate?
- The figure shows a 3D representation of the perovskite crystal structure unit cell. It is a cube with green spheres at the corners, a blue sphere at the center, and red spheres on the faces.
- $\text{Ca} = \textcolor{green}{\bullet}$ $\text{Ti} = \textcolor{blue}{\bullet}$ $\text{O} = \textcolor{red}{\bullet}$
14. Calculate Avogadro's number given that silver crystallizes in a face-centered cubic unit cell with a 4.09 \AA side and has a density of 10.5 g/cm^3 .
 15. Calculate the atomic radius and density of copper if it crystallizes in a fcc unit cell that is 3.61 \AA on a side.
 16. Metallic nickel crystallizes in a fcc unit cell. What is its density if its atomic radius is 1.24 \AA .
 17. How does the cesium chloride structure differ from a body-centered-cubic structure?

18. KF crystallizes in the sodium chloride structure with a 5.39 Å unit cell edge. Calculate the density of KF.
19. Use the method employed in Example 8.4 to calculate the packing efficiency of a simple cubic unit cell.
20. Use the ionic radii in Table 8.3 to calculate the packing efficiencies of the following salts. Assume direct contact between anions and cations is along the edge of the unit cell.
- a) LiI b) NaCl
21. Consider the structure of CsCl shown in Figure 8.15a
- a) Do the ions touch along the edge, face diagonal, or body diagonal?
- b) Use the ionic radii in Table 8.3 to determine the unit cell edge length.
- c) What is the volume of the unit cell?
- d) What is the volume occupied by the ions?
- e) What is the packing efficiency of the unit cell? How does this packing efficiency compare to that of a simple cubic unit cell?
22. Consider the structure of CsCl shown in Figure 8.15b.
- a) Do the ions touch along the edge, face diagonal, or body diagonal?
- b) What is the length of the body diagonal?
- c) What is the edge length of the unit cell?
- d) What is the void space on the edge formed by the chloride ions?
- e) What is the volume of the unit cell?
- f) What volume is occupied by the ions?
- g) What is the packing efficiency of the unit cell? How does it compare to the packing efficiency of a bcc unit cell?
23. Explain at the molecular level why graphite can be used as a lubricant but diamond cannot.
24. What is buckyball? How is its structure related to that of graphite?
25. Describe nanotubes and explain why they are important. How is the structure of a nanotube related to that of graphite?

26. Describe the features that make zeolites so useful and explain how they function as water softeners and molecular sieves.
27. What are clays? Why do some clays swell in the presence of water while others do not?
28. Indicate the substance in each pair that has the higher melting point. Explain your choice.
- a) AlF₃ or PF₃ b) NaCl or BeO c) Si or Kr
29. Indicate the substance with the higher melting point in each pair. Explain your choice.
- a) CsBr or AlN b) CaF₂ or CS₂ c) ZnS or H₂S
30. Each of the following substances is a solid at room temperature. Indicate whether each is a molecular, metallic, ionic, or covalent solid.
- a) C₁₂H₂₂O₁₁ b) MgO c) ZnS
31. Each of the following substances is a solid at room temperature. Indicate whether each is a molecular, metallic, ionic, or covalent solid.
- a) Si b) Ag c) I₂

Chapter 9

Reaction Energetics

<i>9.0 Introduction</i>	<i>9.7 Free Energy and Reaction Spontaneity</i>
<i>9.1 The First Law of Thermodynamics</i>	<i>9.8 Standard Free Energy and the Extent of Reaction</i>
<i>9.2 Enthalpy</i>	<i>9.9 Activation Energy</i>
<i>9.3 Enthalpies of Combustion</i>	<i>9.10 Rates of Reaction and the Rate Law</i>
<i>9.4 Bond Energies</i>	<i>9.11 Equilibrium and the Equilibrium Constant</i>
<i>9.5 Entropy</i>	<i>9.12 LeChâtelier's Principle</i>
<i>9.6 The Second Law of Thermodynamics</i>	<i>9.13 Chapter Summary and Objectives</i>
	<i>9.14 Exercises</i>

9.0 INTRODUCTION

The energy released in chemical reactions plays an important role in our lives as it is used to heat our homes, run our cars, power our factories, and even keep our bodies functioning. We now expand our understanding of the flow of energy and its utilization in a study of **thermodynamics**, the study of energy and its transformations, and **thermochemistry**, the branch of thermodynamics that focuses on the energy involved in chemical reactions. Thermodynamics is concerned only with energy differences between the initial and final states of a process, not with how the initial state is converted into the final state. Similarly, thermochemistry deals with the energy difference between the reactants and products, not with how the reaction takes place. The process by which the reactants are transformed into the products is the domain of **chemical kinetics**, the study of the rates and mechanisms of chemical reactions. In this chapter, thermodynamics and kinetics are combined under the broader term **reaction energetics** in our study of why and how reactions occur.

THE OBJECTIVES OF CHAPTER 9 ARE TO:

- explain the principles of the first and second laws of thermodynamics;
- define the enthalpy of reaction and relate it to bond energies;
- define entropy;
- explain how the order of a system can be used as a predictor for its entropy;
- describe the thermodynamic driving force behind a reaction;
- describe the energy changes required to convert reactants to products;
- discuss the rate law of a reaction;
- write rate laws for elementary processes;
- describe the equilibrium process and define the equilibrium constant; and
- describe Le Châtelier's principle and apply it to systems at equilibrium.

9.1 THE FIRST LAW OF THERMODYNAMICS

Thermodynamics is similar to bookkeeping. In thermodynamics the flow of energy is monitored, while in bookkeeping, the flow of money is monitored. The direction of flow is given by the sign of the change. By convention, the change in a variable is denoted by placing a delta (Δ) in front of the variable. In addition, *change is always defined as the variable's final value minus its initial value*: $\Delta X = X_{\text{final}} - X_{\text{initial}}$. If ΔX is positive, $X_{\text{final}} > X_{\text{initial}}$, and X increases. If ΔX is negative, $X_{\text{final}} < X_{\text{initial}}$ and X decreases.

Consider an example of cash flow in which you write a check for \$50 to a friend who uses the same bank. The first step in "setting up the books" is to define the reference account, which has a balance of **B**. The sign of the balance change, ΔB , gives the direction of money flow in that account. For example, if your account is the reference account then $\Delta B = -\$50$. The minus sign signifies that money flowed out of your account. If your friend's account is the reference, $\Delta B = +\$50$ as money flowed into that account. Finally, if the bank is the reference, $\Delta B = 0$ as no money entered or left the bank; the money you exchanged with your friend stayed in the bank.

A thermodynamic problem would be set up the same way. Suppose that 50 J of energy is transferred from **A** to **B**. The first step is to define the thermodynamic **system**, which is that portion of the universe under investigation (the reference). If **A** is the system, then the energy change is $\Delta E = -50 \text{ J}$ because the energy flows out of **A**. That portion of the universe that exchanges energy with the system is called the **surroundings**. System **B** would be the surroundings in this example. No subscript is used for system quantities, but the subscript 'sur' is used to denote surroundings quantities, so $\Delta E_{\text{sur}} = +50 \text{ J}$ because 50 J of energy flows into the surroundings **B**. The system and its surroundings combine to form the thermodynamic **universe**, which is denoted with a subscript 'univ.' Thus, we would write the $\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}} = -50 \text{ J} + 50 \text{ J} = 0$. If we had chosen **B** as the system, then **A** would have been the surroundings, then $\Delta E = +50 \text{ J}$ and $\Delta E_{\text{sur}} = -50 \text{ J}$. Note that $\Delta E_{\text{univ}} = 0$ either way. If your account had been defined as the system in the accounting example above, your friend's account would be the surroundings and the bank would have been the universe. The money flow would then be $\Delta B_{\text{univ}} = \Delta B + \Delta B_{\text{sur}} = -\$50 + \$50 = 0$.

The flow of energy is predicted by the **first law of thermodynamics**, which states that

Energy is neither created nor destroyed in any process.*

By definition, all energy change in a thermodynamic problem must remain within the thermodynamic universe. If no energy can enter or leave the thermodynamic universe, and

* Actually, the term **mass-energy** should be used instead of energy because mass and energy can be converted into one another by $E = mc^2$. In nuclear reactions, where large amounts of energy are involved, there are substantial changes in mass. However, the mass changes in chemical processes are undetectable because the energy changes are so small.

energy can neither be created nor destroyed, then the energy of the thermodynamic universe must remain constant. Consequently, we can use Equation 9.1 as another statement of the first law.

$$\Delta E_{\text{univ}} = 0 \text{ for all processes}$$

Eq. 9.1

To better understand how energy is transferred between a system and its surroundings, we substitute $\Delta E + \Delta E_{\text{sur}}$ for ΔE_{univ} in Equation 9.1 to obtain following:

$$\Delta E + \Delta E_{\text{sur}} = 0$$

The above can be solved for the energy change of the system.

$$\Delta E = -\Delta E_{\text{sur}}$$

Eq. 9.2

Equation 9.2 indicates that *the only way that the energy of a system can be changed is by exchanging energy with its surroundings*.

Heat and work are the two most common ways of exchanging energy between a system and its surroundings. **Heat** (q) is that form of energy that is transferred as a result of a temperature difference, and **work** (w) is that form of energy that is transferred when one object moves another. ***q is defined as the heat absorbed by the system***. When a system absorbs heat it absorbs energy, so its energy increases; *i.e.*, $q > 0$ means that heat flows into the system increasing the energy, but if $q < 0$ heat flows out of the system to decrease its energy. ***w is defined as the work done on the system***. When work is done on a system, the energy of the system increases; *i.e.*, $w > 0$ means that work is done on the system, which increases its energy, but $w < 0$ means that work is done by the system, which decreases its energy. Equation 9.3, which is another statement of the first law of thermodynamics, shows that the energy of a system increases when it absorbs heat (q) from or has work (w) done on it by its surroundings.

$$\Delta E = q + w^t$$

Eq. 9.3

The signs of q and w simply indicate the direction of energy flow. However, the direction of energy flow is frequently given verbally without using the sign explicitly. The common expressions used to state the direction are given in Table 9.1. For example, $w = -10 \text{ J}$ is usually read as 10 J of work was done by the system, and $q = -10 \text{ J}$ would be read 10 J of heat was given off by the system. Thus, if a question asks for the amount of heat that is given off, and $q = -10 \text{ J}$, the answer is +10 J. Processes for which $q > 0$ are said to be **endothermic** (heat into the system), and processes for which $q < 0$ are said to be **exothermic** (heat exits the system).

[†] ΔE depends only upon the initial and final states, so it is called a **state function**. However, q and w depend upon how the system goes from one state to the other. Consider that the energy of a system can be increased by 10 J ($\Delta E = 10 \text{ J}$) in an infinite number of ways. For example, $q = 10 \text{ J}$ and $w = 0$, $q = 5 \text{ J}$ and $w = 5 \text{ J}$, $q = 0$ and $w = 10 \text{ J}$, or $q = 15 \text{ J}$ and $w = -5 \text{ J}$, to name just a few. q and w depend on how the energy change is accomplished, not just the final and initial states, so they are not state functions. This is why no ' Δ ' is used in front of q or w .

Table 9.1 Expressions used for the direction of energy flow

$q > 0$	heat is <u>absorbed</u> by the system
$q < 0$	heat is <u>given off</u> or <u>evolved</u> by the system
$w > 0$	work is done <u>on</u> the system
$w < 0$	work is done <u>by</u> the system

Example 9.1

What is the energy change of a system that absorbs 500 J of heat and does 300 J of work?

The system absorbs 500 J ($q = +500$ J), so its energy increases by 500 J. However, doing 300 J of work ($w = -300$ J) requires the expenditure of 300 J. Thus, $\Delta E = q + w = 500\text{ J} - 300\text{ J} = +200$ J. The system increases in energy by 200 J.

9.2 ENTHALPY

Reactions are frequently carried out in vessels open to the atmosphere, so gases that are produced are lost to the atmosphere, keeping the pressure constant. The reactants are initially at room temperature and the products are *eventually* at room temperature, so the reaction can be viewed thermodynamically as being carried out at constant temperature.[†] Conditions of constant pressure and temperature are quite common, so our treatment of thermodynamics is limited to processes carried out under these conditions. The gases that escape to the atmosphere carry some of the energy change of the reaction with them. This energy is lost, so chemists typically discuss the heat of reaction rather than the energy of reaction. The heat of a reaction at constant pressure is so common that it is given a special name, the **enthalpy or heat of reaction**, ΔH .

Energy changes result because the potential energies of the products and reactants are different. The energy required for an endothermic reaction is used to convert reactants into products that are at higher potential energy (Figure 9.1a); *i.e.*, endothermic reactions are said to go “uphill” in enthalpy. The energy comes from the surroundings, which causes them to cool, so *the reaction container of an endothermic reaction, which is part of the surroundings, cools as the reaction proceeds*. The heat given off in an exothermic reaction is produced when the reactants are converted to products that are at lower potential energy (Figure 9.1b); *i.e.*, exothermic reactions are said to go “downhill” in enthalpy. The energy released in an exothermic reaction goes into the surroundings and causes them to warm. Thus, *the reaction container of an exothermic reaction warms as the reaction proceeds*.

STANDARD STATES

Thermodynamic properties, such as enthalpy, vary with the state and concentration of the substance, so care must be taken to make comparisons under similar conditions. Consequently, thermodynamic properties are typically reported for processes in which the reactants and products are all in their **standard states**, which are defined as follows:

[†] Thermodynamics is concerned only with the initial and final states. Thus, a reaction can be treated at constant T and P as long as the initial and final conditions are the same, even if the conditions vary during the reaction.

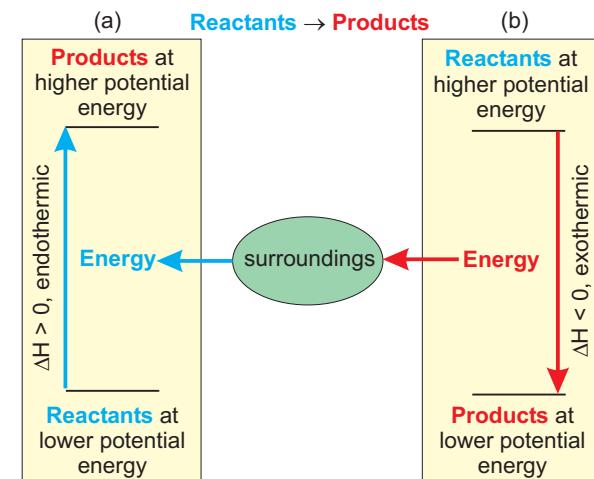


Figure 9.1 Sign of enthalpy change and energy flow

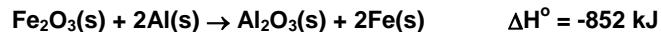
The enthalpy of the system a) increases in an endothermic reaction as energy is transferred from the surrounding to the system, and b) decreases in an exothermic reaction as energy is transferred from the system to the surroundings. Therefore, the surroundings cool in (a) and warm in (b).

- The standard state of a pure substance is its most stable form at 1 atm pressure and the specified temperature. Unless indicated otherwise, solids and liquids are considered to be pure. Gases can be assumed pure even in mixtures because the molecules in the gas interact only weakly. Thus, the standard state of a gas is a partial pressure of 1 atm.
- The standard state of a substance in solution is a concentration of 1 M* at 1 atm pressure and the specified temperature. Thus, the standard state of a sugar solution is a solution in which the sugar concentration is 1 M.

The enthalpy change of a reaction in which all of the reactants and products are in their standard states is called the **standard enthalpy of reaction** and given the symbol ΔH° . All enthalpy values given in this chapter are standard enthalpies.

There is no standard temperature, so the temperature should be specified. However, if no temperature is specified, then exactly 25 °C (298.15 K) should be assumed. While 25 °C is the commonly used temperature, it is not the standard state temperature. The standard state of a substance depends upon its temperature. For example, the standard state of water is a liquid at 1 atm and 25 °C, a solid at 1 atm and -25 °C, and a gas at 1 atm and 125 °C.

The state of each substance is important, so it is usually included in parentheses after the substance (s = solid; l = liquid; g = gas; aq = aqueous solution[†]). A thermochemical equation gives the enthalpy of reaction next to the balanced chemical equation. The following thermochemical equation for the *thermite* reaction at 298 K states that 852 kJ of heat are *liberated* ($\Delta H < 0$) when one mole of solid Fe₂O₃ reacts with two moles of solid Al to produce one mole of solid Al₂O₃ and two moles of solid Fe.

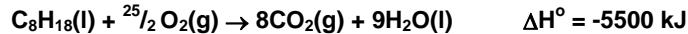


All substances are in their standard states at 298 K, so the superscript zero is included to indicate that the enthalpy change is the *standard* enthalpy of reaction.

PROPERTIES OF ENTHALPY

We frequently need to determine the enthalpy of a process from the tabulated enthalpy of a closely related process. The following two properties of enthalpy can help us do that:

- The enthalpy of reaction is directly proportional to the number of moles of each substance reacting.



Octane, C₈H₁₈, is a component of gasoline, so the above two equations indicate that the amount of energy released is doubled when the amount of gasoline is doubled.

* Recall from Chapter 7 that 1 M is read 'one molar' and implies one mole of the substance per liter of solution.

[†] Aqueous solutions are those in which water is the dominant substance.

- Reversing the direction of a reaction changes the sign of the enthalpy of reaction.



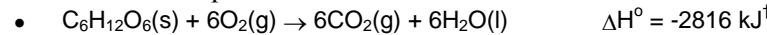
Thus, 6 kJ are absorbed ($\Delta H > 0$) when one mole of ice at its melting point, but 6 kJ are released ($\Delta H < 0$) when one mole of water freezes.

9.3 ENTHALPIES OF COMBUSTION

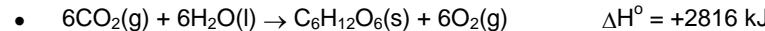
Combustion is the reaction of a substance with oxygen, and it is the major source of harnessed energy. It is the energy released in combustion reactions that fuels our vehicles, heats our homes, and powers our bodies. The products of combustion are usually, but not always, the oxides of the elements comprising the molecule being combusted.

The **enthalpy or heat of combustion** of a substance is defined as the heat absorbed when one mole of the substance reacts with oxygen at constant pressure.

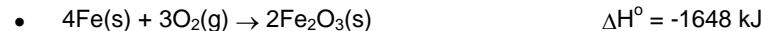
Combustion reactions are all exothermic, so heat is given off rather than absorbed, and enthalpies of combustion are negative in this text.* Consider the following thermochemical equations that deal with some common combustion reactions:



Our bodies derive energy from the combustion of glucose (a sugar).



Plants make glucose in photosynthesis by reversing the glucose combustion reaction. The energy required to make this endothermic reaction proceed is supplied by the sun.



Rusting of iron is the basis of corrosion.

* Care must be taken when using tables in other sources because they may list heats of combustion as positive. Just remember that heat is always liberated in a combustion reaction.

† When ΔH appears with a chemical equation, it has units of kJ because the amounts are specified by the equation. However, when an enthalpy is given without a chemical equation, the units are kJ/mol to specify that one mole of the substance is involved. For example, $\Delta H^\circ = -2816 \text{ kJ}$ for this reaction, but the heat of combustion of glucose would be given as -2816 kJ/mol in a table to specify the reaction of one mole of glucose.

Example 9.2

- a) The heat of combustion of sucrose (table sugar) is -5650 kJ/mol^\S . How much heat is released when one teaspoon of sucrose (~4.8 g) is burned?

$M_m (\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 342 \text{ g/mol}$, so one teaspoon (4.8 g) of sucrose contains

$$4.8 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342 \text{ g sucrose}} = 0.014 \text{ mol sucrose}$$

$\Delta H = (0.014 \text{ mol})(-5650 \text{ kJ/mol}) = -79 \text{ kJ}$, so 79 kJ of heat are released

- b) Verify the statement on the label of a bag of sugar that “one teaspoon of sugar contains 19 calories.”

The calorie (cal) is an older unit of energy that is still commonly used. It is the amount of

[§] No chemical equation is given, so the units are kJ/mol to specify that the enthalpy is for the combustion of one mole of sucrose.

heat required to raise the temperature of one gram of H₂O by 1 °C. 1 cal = 4.18 J. However, a dietary calorie, which appears on packaging of common food items, is actually a kcal (1000 cal). To convert from kJ to kcal, we use the fact that 4.18 kJ = 1 kcal:

$$(79 \text{ kJ})(1 \text{ kcal}/4.18 \text{ kJ}) = 19 \text{ kcal or 19 dietary calories}$$

9.4 BOND ENERGIES

The **bond** or **dissociation energy (D)** is the energy required to break one mole of bonds *in the gaseous state*. It is always positive.



Similarly, energy is always released when bonds are formed.



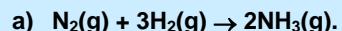
The enthalpy of a gas phase reaction is simply the difference between the amount of energy required to break the reactant bonds and the amount of energy released when the product bonds are formed,

$$\Delta H \sim \sum D(\text{broken bonds}) - \sum D(\text{formed bonds}) \quad \text{Eq. 9.4}$$

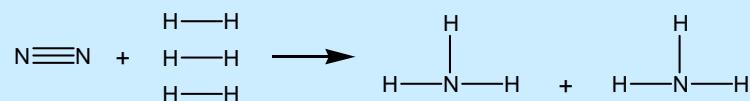
Enthalpies derived from Equation 9.4 are only approximate values when tabulated bond energies are used because the bond energy depends on the environment of the bond, while the values presented in tables like Table 9.2 are average values of many environments. For example, the O-H bond in F₃COH is slightly weaker than in (CH₃)₃COH, but we would use the tabulated, average value of 463 kJ/mol for each.

Example 9.3

Use the data in Table 9.2 to estimate ΔH for the following reactions.



Bond energies depend upon both the number and types of bonds. Thus, the first thing we must do is to draw the Lewis structures of the molecules.*



The N≡N bond and three H-H bonds must be broken, and six N-H bonds must be formed.

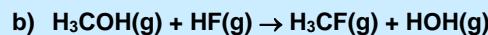
$$\Delta H \sim D(\text{N}\equiv\text{N}) + 3D(\text{H-H}) - 6D(\text{N-H}) = 941 \text{ kJ} + 3(436) \text{ kJ} - 6(391) \text{ kJ} = -97 \text{ kJ.} \dagger$$

Table 9.2 Some common bond energies (kJ/mol)

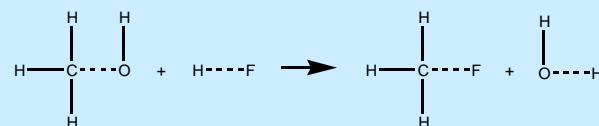
C-H	413	N-H	391	O-H	463	H-H	436
C-F	485	N-F	272	O-F	190	H-F	565
C-Cl	328	N-Cl	200	O-Cl	203	H-Cl	431
C-Br	276	N-Br	243	O-Br	235	H-Br	366
C-I	234			O-I	234	H-I	299
C-C	347	N-N	163	C-N	305	C-O	358
C=C	612	N=N	418	C=N	615	C=O	799
C≡C	820	N≡N	941	C≡N	891	C=O	1072
F-F	159	O-O	146				
Cl-Cl	243	O=O	495				
Br-Br	193						
I-I	151						

* Carbon-carbon bonds can be single, double, or triple bonds, but carbon always has four bonds to it.

† The tabulated value is -92 kJ, so this answer is off by about 5%, which is the approximation error in this example.



First, draw the Lewis structures. Examination of the Lewis structures reveals that neither the C-H bonds nor the O-H bond are affected by the reaction, so only the bonds shown as dotted lines are broken or formed.



Breaking the C-O and H-F bonds and forming the C-F and O-H bonds yields the following:

$$\Delta H \sim D(\text{C-O}) + D(\text{H-F}) - D(\text{C-F}) - D(\text{O-H}) = 358 + 565 - 485 - 463 = -25 \text{ kJ}$$

Breaking the three C-H bonds and the O-H bond and then reforming them would yield the same answer because the energy required to break them is identical to that released when they reform.

9.5 ENTROPY

A spontaneous process is one that, once started, takes place without intervention. For example, once a ball begins to roll down a hill, it does so spontaneously, but it can sit at the top of the hill and not roll down without some kind of intervention to get it started. However, it rolls uphill only with intervention even after the climb is started. As another example, gasoline reacts spontaneously with oxygen, yet gasoline can be stored in air because it needs intervention (a spark or flame) to get started. However, once the reaction is started, it continues spontaneously. As we shall see in Section 9.9, the initial intervention that is required to start a spontaneous reaction is called the activation energy for the reaction.

In this section, we show how to predict whether a process is spontaneous. Our first hypothesis might be that a process is spontaneous if it is exothermic. After all, we have made frequent use of the concept that systems strive to lower their potential energy. However, recall from Chapter 7 that the potential energy of the molecules in the gas phase is much greater than that in the liquid phase, yet liquids do evaporate spontaneously, so evaporation is a process that proceeds spontaneously to a higher potential energy. Clearly, there must be another factor, and the other factor is related to the manner in which molecules distribute their thermal energy.

Recall from Section 7.2 that thermal energy (RT) is a measure of the average kinetic energy (energy of motion) of the molecules in a system. Thus, we begin our treatment of

this second factor by considering how molecules move. The motion of molecules is a combination of three different types of movement (translation, rotation, and vibration) called **degrees of freedom**.

1. **Translation** is the straight line motion of the entire molecule through space, which can be described in terms of its x, y, and z components. Thus, all particles have three degrees of translational freedom. A molecule with N atoms must have $3N$ degrees of freedom, three of which are translational, because each of its atoms can move in three directions.
2. **Rotation** is the circular motion of a molecule about an axis fixed to the molecule. There are three axes in a molecule (X, Y, and Z), so there are three degrees of rotational freedom. However, energy cannot be stored in a rotation if all of the atoms lie on the axis, so linear molecules have only two rotational degrees of freedom.
3. **Vibration** is the motion of the atoms in a molecule relative to one another that causes small changes in bond lengths and/or bond angles. A molecule has $3N$ degrees of freedom, but six are due to translation and rotation, so non-linear molecules have $3N-6$ vibrational degrees of freedom. Linear molecules have $3N-5$ degrees because they have only two degrees of rotational freedom.

Figure 9.2 shows the six degrees of freedom of CO: 3 translational, 2 rotational, and $3N - 5 = 3(2) - 5 = 1$ vibrational.

Consider a system of ten books. There are $10! = 3,628,800^{\dagger}$ ways in which they can be distributed on a shelf, but only one is alphabetical. Thus, constraining (restricting or confining) the books to an alphabetical order greatly reduces the number of ways in which they can be distributed. Removing and returning books from the alphabetical arrangement without intervention (no librarian), would result in a random arrangement because a random arrangement is favored on strictly statistical grounds (3,628,799 random to 1 alphabetical). Similarly, energy is more likely to be found in systems that can distribute the energy in more ways. For this purely statistical reason, systems that have many ways in which to distribute their energy are favored over those that have only a few.

The number of ways in which the energy of a molecular system can be distributed decreases as constraints on molecular motion are added. For example, all of the thermal energy of an O atom is translational, while that of an O₂ molecule is a combination of translational, rotational, and vibrational. Thus, the energy of an O atom, whose energy is disbursed over only three degrees of freedom is more constrained than an O₂ molecule, whose energy can be spread over six degrees of freedom.* Freedom of movement not only applies to the number of degrees of freedom; it also applies to how freely a molecule can move in each degree of freedom. For example, a molecule in the gas phase has a great deal

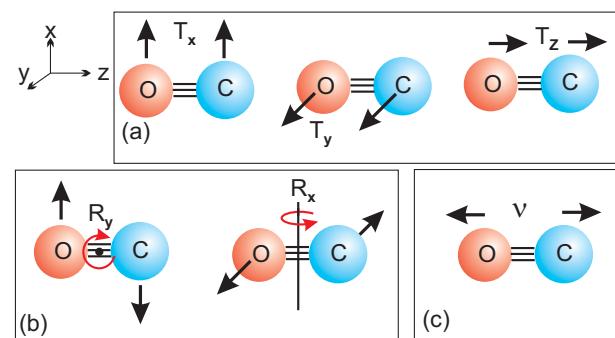


Figure 9.2 Six Degrees of Freedom of a Diatomic Molecule

a) Translations result when all atoms move in the same direction. T_x is a translation along the x-axis. b) Rotations occur when atoms move in opposite directions perpendicular to the bond. R_y is a rotation about the y-axis. There is no rotation about the bonding axis in a linear molecule. c) A vibration is caused by atoms moving in opposite directions along the bond axis. v is called a C=O stretch.

[†] $10!$ (spoken ten factorial) = $10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1$.

* Increasing the number of atoms always increases the number of degrees of freedom and the number of ways in which the energy can be distributed. Thus, O₃ has nine degrees of freedom and can distribute its energy in more ways than can O₂.

of translational freedom of motion as it flies through its container, but the translational motion of the same molecule in the solid is constrained to an oscillation about its lattice position. The constrained motion in the solid relative to the gas means that the molecules in the solid have far fewer ways in which to distribute their energy.

The number of ways in which the energy of a system can be distributed is such an important property of the system that a thermodynamic variable is defined to quantify it. The thermodynamic property is called **entropy** and given the symbol **S**. Systems with high entropies can distribute energy in more ways than those with low entropies.

The motion of molecules in the gas phase is much less constrained than in the liquid or solid states, and the number of ways a system of molecules can distribute its energy increases as constraints to molecular motion are removed. Therefore, the entropy of a system of molecules in the gas phase is much greater than that of the same system in a condensed state. Molecules in the liquid state have slightly more freedom of motion than those in the solid, so the entropy of a system of molecules in the liquid state is slightly greater than in the solid state. We will use the following relationship frequently:

$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$$

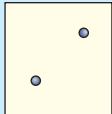
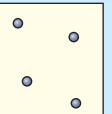
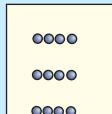
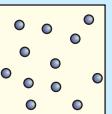
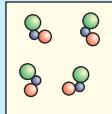
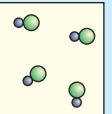
Constraints not only decrease the entropy of a system, they also tend to order the system. For example, motion is unconstrained in the gas phase, so the entropy of a gas is high. However, when intermolecular forces constrain the molecules, the molecules align to increase their interactions and, in so doing, produce the short-range order found in the liquid state. When the forces further constrain the system, the molecules align better so as to maximize their interactions. The increased constraints produce the long-range order found in the solid state. Thus, increasing the constraints on a system decreases its entropy and increases its order. We conclude that

Disordered systems have greater entropies than do ordered ones.

Indeed, entropy is commonly defined in terms of the order in a system. However, entropy is a measure of the number of ways in which the energy of a system can be distributed; the order in a system is simply a good predictive tool because ordered systems are more constrained and have lower entropies than disordered systems.

Example 9.4

Predict which system of molecules in each pair has the greater entropy.

 (a)	 (b)	Four atoms can distribute energy in more ways than two atoms, so system (b) has the greater entropy.
 (a)	 (b)	The order of the 12 atoms in (a) indicates that they are being constrained more than those with the random distribution in (b). Therefore, system (b) has the greater entropy
 (a)	 (b)	Each of the four molecules in (a) has $3(3) = 9$ degrees of freedom, but each molecule in (b) has only $2(3) = 6$ degrees. Therefore, the molecules in (a) can distribute their energy in more ways and have the higher entropy.

The two driving forces behind a process are the tendencies for systems to minimize their potential energy ($\Delta H < 0$) and to maximize the number of ways in which they can distribute their energy ($\Delta S > 0$). However, unless the entropy change is large, the tendency to minimize enthalpy is the dominant driving force. We have seen how to estimate enthalpy changes from bond energies, and we now show how to predict whether the entropy change is large and positive, large and negative, or negligible. The entropy change of a reaction is given as $\Delta S = S_{\text{products}} - S_{\text{reactants}}$, so $\Delta S > 0$ when the entropy of the products is greater than that of the reactants. At this point, we need only predict whether ΔS is large, and, if so, what is its sign.* To do this, we recall that $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$ to conclude that *entropy changes are large only in reactions in which the number of moles of gas changes*. We will ignore the effect of entropy changes that are not large because enthalpy changes almost always dominate such processes, and the sign of large entropy changes can be estimated with the following:

$\Delta S > 0$ for reactions that produce gas; $\Delta S < 0$ for reactions that consume gas; but

$\Delta S \sim 0$ (negligibly small) for reactions that do not involve a change in the number of moles of gas.

* ΔS can be calculated and the procedure is covered in Chapter 4 of Chemistry - A Quantitative Science.

The number of ways in which a system can distribute its energy increases with the amount of energy it has to distribute, so *the entropy of a system always increases with temperature*. Similarly, adding heat to a system always increases the entropy of the system. In our energy-book analogy, the alphabetized arrangement would represent the order expected in a constrained, low-entropy, low-temperature system, while the random arrangement would represent the unconstrained, high-entropy, high-temperature system. We now examine the effect of adding a small amount of heat to a system at high and low temperatures by examining the effect of adding one book to the alphabetized and random systems. The additional book increases the total number of books, so the number of ways they can be distributed increases ($\Delta S > 0$). However, the effect of placing a book randomly in the two systems is very different. The additional book would probably not go into its correct location in the alphabetized system, so the effect of the out-of-place book on the order of the system would be dramatic. Similarly, adding a small amount of heat to a system at low temperature has a dramatic effect on the entropy. However, another ‘out-of-place’ book in a random system would be hardly noticeable. Similarly, adding a small amount of heat to a system at high temperature has only a minor impact on the entropy. Adding 1 J of heat to a solid at 5 K (very ordered, low entropy) has a much more dramatic effect on the entropy than adding 1 J to a vapor at 500 K (highly disordered, high entropy). We conclude that the impact of adding heat to a system is greater if the initial energy of the system is low (low T). This relationship is expressed mathematically as follows:

$$\Delta S \geq \frac{q}{T} \text{ J}\cdot\text{K}^{-1} \quad \text{Eq. 9.5}$$

Equation 9.5 indicates that the entropy change accompanying the addition of q joules at a temperature T is greater than or equal to q/T , so ΔS has units of $\text{J}\cdot\text{K}^{-1}$. Whether *greater than* or *equal to* applies depends upon how the heat is added. If the heat is added slowly and the system remains at equilibrium,[†] the equals sign applies, but if the heat is added so quickly that equilibrium is not maintained, then the greater than sign applies. Also, note that $T\Delta S \geq q$, so $T\Delta S$ and q have the same units, which are those of energy.

[†] Processes that are carried out while maintaining equilibrium are said to be **reversible**. Indeed, a reversible process is one that is at equilibrium. Processes that do not maintain equilibrium are said to be **irreversible**.

Example 9.5

Predict the sign of ΔS° for each of the following processes:



There are 2 moles of gas on each side of the equation, so the number of moles of gas does not change. Thus, we predict that $\Delta S^\circ \sim 0$.

Tabulated value: $\Delta S^\circ = +21\text{ J}\cdot\text{K}^{-1}$



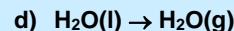
$\Delta S^\circ < 0$ because the number of moles of gas decreases (4 mol \rightarrow 2 mol).

Tabulated value: $\Delta S^\circ = -199\text{ J}\cdot\text{K}^{-1}$



$\Delta S^\circ \sim 0$ because there are no gases involved. All reactants and products are in the same state, so we cannot predict the sign, but we can predict that the magnitude is small.

Tabulated value: $\Delta S^\circ = +33\text{ J}\cdot\text{K}^{-1}$. Note that this is comparable to Part a where there was no change in the number of moles of gas but small compared to Part b where there was a change in the number of moles of gases.



$\Delta S^\circ > 0$ because a gas is produced.

Tabulated value: $\Delta S^\circ = +118\text{ J}\cdot\text{K}^{-1}$.

Example 9.6

Indicate which process in each pair increases the entropy of the system more:



The heat is added at the same temperature, so the greater entropy change occurs when the greater amount of heat is added. Consequently, adding 50 J results in a greater entropy change than adding 10 J at 300 K.



The amount of heat added is the same, so the greater entropy change occurs when the heat is added at the lower temperature. Consequently, adding 10 J results in a greater entropy change at 300 K.



$\Delta S = q/T$. $(50/800) > (10/300)$, so adding 50 J at 800 K causes a larger entropy change.



$\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}} \sim 0$ because no gases are involved.

$\Delta S_{\text{evaporation}} = S_{\text{gas}} - S_{\text{liquid}} \gg 0$ because gas is produced.

9.6 THE SECOND LAW OF THERMODYNAMICS

We now combine ΔS and ΔH into one thermodynamic property that can be used to predict spontaneity. We begin by realizing that processes that increase the number of ways in which energy can be distributed are statistically favored, but processes affect the entropy of both the system and its surroundings, and it is the dispersal of energy in both that is important. Indeed, the **second law of thermodynamics** defines spontaneity in terms of the entropy change in the universe.

The entropy of the universe increases ($\Delta S_{\text{univ}} > 0$) in all spontaneous processes.

Spontaneous processes are those that increase the entropy of the universe. Processes that reduce the entropy of a *system* can occur spontaneously, but only if they increase the entropy of the surroundings more than they decrease the entropy of the system. In Example 9.7, we show why heat flows spontaneously only from hot to cold.

Example 9.7

Show that heat flows spontaneously from a hot reservoir to a cold one.

The two heat sources at temperatures T_1 and T_2 in the figure in the margin are in thermal contact but are insulated from the rest of the universe. Heat can flow spontaneously from T_1 to T_2 only if the process increases the entropy of the universe. Because the two containers are insulated from their surroundings, they form their own universe, and we can write:

$$\Delta S_{\text{univ}} = \Delta S_1 + \Delta S_2 > 0.$$

ΔS_1 and ΔS_2 are the entropy changes in the two containers caused by the flow of heat.

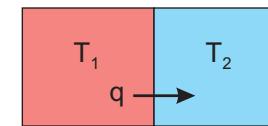
Using Equation 9.5, we can write:

$$\Delta S_1 = -q/T_1 \quad \text{and} \quad \Delta S_2 = +q/T_2$$

The negative sign indicates that heat is leaving the reservoir at temperature T_1 , and the positive sign indicates that heat is entering the reservoir at temperature T_2 . Substitution of these ΔS values into the ΔS_{univ} expression yields

$$\Delta S_{\text{univ}} = -\frac{q}{T_1} + \frac{q}{T_2} = q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

ΔS_{univ} can be positive only if $T_1 > T_2$. Thus, heat flows spontaneously from hot to cold as a consequence of the second law of thermodynamics.



9.7 FREE ENERGY AND REACTION SPONTANEITY

The second law allows us to predict the spontaneity of a reaction from the sign of ΔS_{univ} , but in order to use this predictive power, we need an expression for ΔS_{univ} that contains only system quantities. We begin by dividing the entropy change in the universe into its system and surroundings components: $\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}}$. ΔS is already a system quantity, so we need only obtain an expression for ΔS_{sur} in terms of system quantities. We do so by realizing that the entropy of the surroundings changes because the surroundings exchange heat with the system, $q_{\text{sur}} = -q$.^{*} At constant temperature and pressure, $q = \Delta H$, so $q_{\text{sur}} = -\Delta H$, which can be substituted into Equation 9.5 to yield $\Delta S_{\text{sur}} = -(\Delta H/T)$. Further substitution of this form of ΔS_{sur} into $\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}}$ yields

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides by $-T$ and rearranging, we obtain $-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$. $T\Delta S_{\text{univ}}$ is a function of system quantities alone, so it too is a system quantity, which is called the **Gibbs free energy change (ΔG)**. Setting $\Delta G = -T\Delta S_{\text{univ}}$, we obtain Equation 9.6.

$$\Delta G = \Delta H - T\Delta S$$

$$\text{Eq. 9.6}$$

ΔG is negative when ΔS_{univ} is positive, so we conclude that spontaneous processes at constant temperature and pressure are those that decrease the free energy of the system; *i.e.*, those for which $\Delta G < 0$. Thus, we must modify our initial hypothesis that spontaneous reactions are those that go downhill in energy to spontaneous reactions at constant temperature and pressure are those that go downhill in Gibbs free energy. Equation 9.6 indicates that there are two components to the free energy change.

1. ΔH is the energy absorbed ($-\Delta H$ is the energy released) when the potential energy of the reactants is changed to that of the products. In Figure 9.4a, the products are at higher potential energy than the reactants, so the reaction is endothermic ($\Delta H > 0$). If this process is to occur spontaneously, energy must be supplied by the $T\Delta S$ term; *i.e.*, $\Delta S > 0$ for spontaneous processes in which $\Delta H > 0$. The process in Figure 9.3b is exothermic ($\Delta H < 0$). The released energy can be used to decrease the entropy of the system if $\Delta S < 0$, but any released energy that is not used to decrease entropy can be used to do work.
2. $-T\Delta S$ is the energy required to decrease the entropy ($+T\Delta S$ is the energy released when the entropy increases). In the reaction shown in Figure 9.4a, $\Delta S < 0$, so $-T\Delta S$ joules of energy must be supplied from ΔH to decrease the entropy if the process is to be spontaneous ($\Delta G < 0$). $\Delta S > 0$ for the reaction shown in Figure 9.4b, so $T\Delta S$ joules of energy are released. The released energy can be used to increase the potential energy of the system if the process is endothermic, but any released $T\Delta S$ energy that is not used to do so can be used to do work.

* For example, the heat that is given off in an exothermic reaction is absorbed by the surroundings, which causes the entropy of the surroundings to increase by q/T .

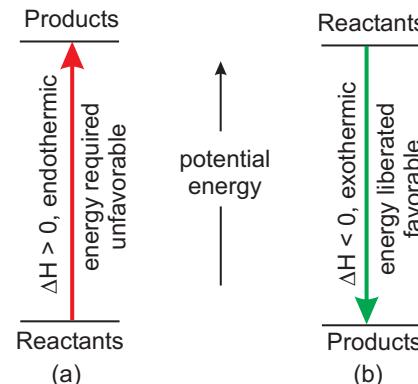


Figure 9.3 Enthalpy change

- (a) Energy is required in an endothermic reaction because the potential energy of the products is greater than that of the reactants.
 (b) Energy is released in an exothermic reaction because the potential energy of the reactants is greater than that of the products.

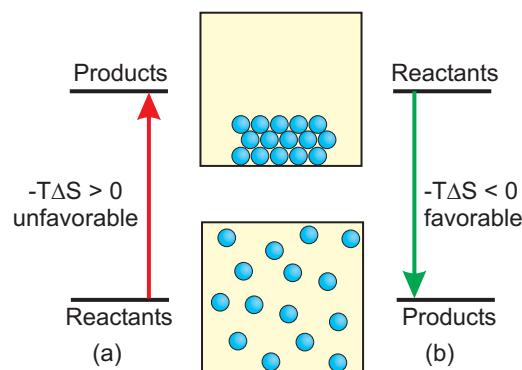


Figure 9.4 $T\Delta S$ energy

- (a) Reactions that increase constraints require $-T\Delta S$ J of energy.
 (b) Reactions that remove constraints release $T\Delta S$ J.

The free energy that is released during a reaction ($-\Delta G$) is free to do work, so work can be extracted from spontaneous processes. In fact, **$-\Delta G$ is the maximum amount of work that can be obtained from a process at constant T and P.**

There are driving forces in both the forward and reverse directions of most reactions, so double arrows are often used in chemical equations. $A \rightleftharpoons B$ shows that there are driving forces for both $A \rightarrow B$ and $A \leftarrow B$. ΔG is the difference between these forces. If $\Delta G < 0$, the forward driving force is greater, so there is a net force in the forward direction and the reaction consumes A to produce B. When $\Delta G > 0$, the reverse driving force is greater, so there is a net force in the reverse direction, and the reaction produces A by consuming B. If $\Delta G = 0$, the two forces are equal, and there is no net driving force or change in concentrations as the reaction has reached equilibrium. Indeed, **$\Delta G = 0$ is the thermodynamic definition of equilibrium at constant temperature and pressure.** We conclude that **ΔG gives us the spontaneous direction of reaction:**

- $\Delta G < 0$: The forward reaction is spontaneous (\rightarrow).
- $\Delta G > 0$: The reverse reaction is spontaneous (\leftarrow).
- $\Delta G = 0$: The reaction is at equilibrium (\rightleftharpoons).

The value of ΔG varies with the concentrations of the reactants and products, so it changes as the process continues. Consider the evaporation of water: $H_2O(l) \rightleftharpoons H_2O(g)$.

Initially, only liquid is present, so there is no driving force in the reverse direction (no condensation). Consequently, $\Delta G < 0$ and the liquid begins to evaporate. However, as the pressure of the vapor increases, so does the driving force in the reverse direction, so ΔG gets less negative. Eventually, the pressure of the vapor is such that the driving force in the reverse direction equals that in the forward direction, $\Delta G = 0$, and the process has reached equilibrium.

9.8 STANDARD FREE ENERGY AND THE EXTENT OF REACTION

ΔG° is the value of ΔG when all reactants and products are in their standard states. Consider the process: $A(g) \rightleftharpoons B(g)$. If $\Delta G^\circ < 0$, the reaction is spontaneous in the forward direction *when both pressures are 1 atm*, so equilibrium is attained by consuming A, which reduces P_A to less than 1 atm, and producing B, which increases P_B to more than 1 atm. If $P_B > P_A$ at equilibrium, the reaction is said to be **extensive** because the amount of product at equilibrium is much greater than the amount of reactant.* If $\Delta G^\circ > 0$, the

* An extensive reaction is one in which the equilibrium amount of product is much greater than that of reactant. A reaction in which there is only slightly more product than reactant at equilibrium is not considered extensive. Thus, the criteria for an extensive reaction are $P_B \gg P_A$ and $\Delta G^\circ \ll 0$, but for simplicity, we will classify as extensive any reaction in which $\Delta G^\circ < 0$.

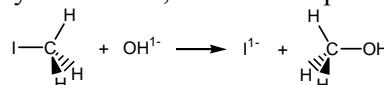
process is spontaneous in the reverse direction at standard conditions. Equilibrium in this case is attained when $P_A > P_B$, so there is more reactant than product at equilibrium and the reaction $A \rightarrow B$ is not extensive. We conclude that ΔG° gives us the extent of the reaction.

- $\Delta G^\circ \ll 0$: Extensive as much more product than reactant is present at equilibrium.
- $\Delta G^\circ \gg 0$: Not extensive as much more reactant than product is present at equilibrium.
- $\Delta G^\circ \sim 0$: The amounts of reactant and product at equilibrium are comparable.

The temperature dependence of the standard free energy and, therefore, the extent of reaction can be determined with Equation 9.6 ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$), which shows that a plot of free energy versus temperature is a straight line with an intercept of ΔH° and a slope of $-\Delta S^\circ$. At low temperatures, the $T\Delta S^\circ$ term is negligible, so ΔG° has the same sign as ΔH° at low T, but, at high temperatures, the $T\Delta S^\circ$ term can dominate if ΔS° is not negligible, so ΔG° can have the same sign as $-\Delta S^\circ$ at high T. Figure 9.5 treats five representative reactions, and Table 9.3 summarizes the conclusions.

9.9 ACTIVATION ENERGY

Thermodynamics considers only the reactants and products, while *kinetics* is concerned with the path used by the reactants to achieve the products. The energetics of a reaction are followed along a **reaction coordinate**, which is a combination of intermolecular distances, bond angles, and bond lengths that represents the molecular course of the reaction. Most reactions occur as a series of simple steps, which taken together comprise what is known as the **reaction mechanism**. However, we examine the following displacement of iodide by hydroxide ion, which takes place by a simple, one-step mechanism.



The reaction involves breaking one C-I bond and forming one C-O bond, so we can estimate the enthalpy of reaction from tabulated bond energies to be $\Delta H^\circ \sim D_{(\text{C-I})} - D_{(\text{C-O})} = 234 - 358$ or about -120 kJ/mol . The reaction takes place in solution, while bond energies apply to gas phase reactions only, so our number is not expected to be accurate. However, the fact that the estimated ΔH° is large and negative is important. There are no gases involved, so ΔS° is expected to be small, and we make the approximation that $\Delta G^\circ \sim \Delta H^\circ < 0$, so the reaction is expected to be extensive.

The hydroxide ion attacks the carbon by inserting itself into the center of the plane

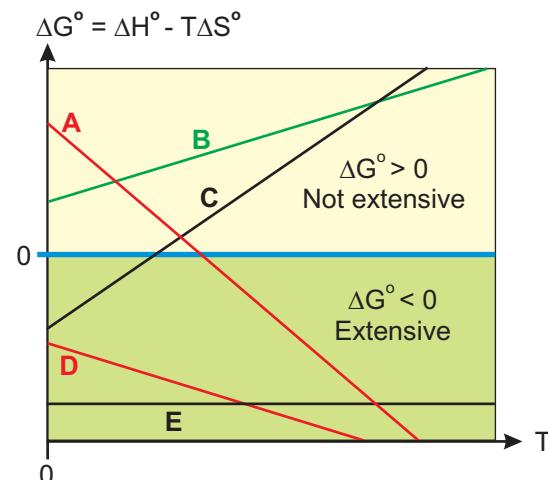


Figure 9.5 Standard free energy and temperature

Reactions in the yellow region are not extensive, but those in the green region are.

- $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$. At low T the unfavorable ΔH° term dominates, so $\Delta G^\circ > 0$ and the reaction is not extensive. At high T, the favorable entropy terms dominates, so $\Delta G^\circ < 0$ and the reaction is extensive.
- $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$. Both terms are unfavorable, so the reaction is never extensive.
- $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$. At low T, the favorable ΔH° term dominates and $\Delta G^\circ < 0$ and the reaction is extensive. At high T, the unfavorable ΔS° term dominates, so $\Delta G^\circ > 0$ and the reaction is not extensive.
- $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$. Both terms are favorable, so the reaction is extensive at all T.
- $\Delta H^\circ < 0$ and $\Delta S^\circ \sim 0$. ΔG° has the same sign as ΔH° at all T.

Table 9.3 Extent of Reaction

	ΔH°	ΔS°	$\Delta G^\circ < 0$, extensive reaction
A)	+	+	high T, where $ T\Delta S > \Delta H $
B)	+	-	no T
C)	-	-	low T, where $ \Delta H > T\Delta S $
D)	-	+	all T
E)	-	~ 0	all T

defined by the three hydrogen atoms. In order for the hydroxide ion to reach the carbon atom, the hydrogen atoms must be pushed apart; that is, the H-C-H bond angles must open up from their tetrahedral values. Figure 9.6 shows the potential energy of the system along the reaction coordinate, which is some combination of C-I and C-O distances and H-C-H bond angles. Initially, the OH^{1-} ion is far from the CH_3I molecule, and the bonds of the two reactants dictate the energy. As the OH^{1-} ion enters the plane of the three H atoms, it forces them apart, the C-I bond begins to lengthen and weaken, and the C-O bond begins to form. As a result of all of these changes, the energy rises sharply. When the H-C-H bond angles reach 120° and the CH_3 unit is planar, the energy is at a maximum, and a very unstable species, $[\text{ICH}_3(\text{OH})]^{1-}$, has formed.

The species present at the energy maximum is called the **transition state** for the reaction because it is the species through which the reactants make the transition to the products. The energy required to form the transition state from the reactants is known as the **activation energy** for the forward reaction, $E_a(f)$, and the energy required to reach the transition state from the products is the activation energy for the reverse reaction, $E_a(r)$. Once formed, the transition state immediately proceeds to lower energy by either continuing to form products or by returning to reactants. Either direction is equally probable. Thus, we can represent the reaction as



The double arrows (\rightleftharpoons) indicate that the process can proceed through the transition state from either direction; *i.e.*, $[\text{ICH}_3(\text{OH})]^{1-}$ can be produced by collisions between ICH_3 and OH^{1-} or by collisions between I^{1-} + H_3COH .

In order for a reaction to take place, the collision between reactants must be sufficiently energetic to form the transition state. Although the reaction we are discussing is exothermic, it will not occur if the energy of the collision between OH^{1-} and CH_3I is less than the activation energy for the reaction. Remember that thermal energy ($\sim RT$) is only ~ 3 kJ/mol at room temperature. Consequently, many reactions must be heated to get them started even if they are exothermic. For example, gasoline reacts spontaneously with oxygen in a very exothermic reaction. Yet the reaction does not occur in the absence of a flame or spark to provide the energy required to overcome the activation energy for the reaction. Thus, the activation energy is a barrier that must be overcome if reaction is to take place. Consequently, the activation energy is often referred to as an **energy barrier**.

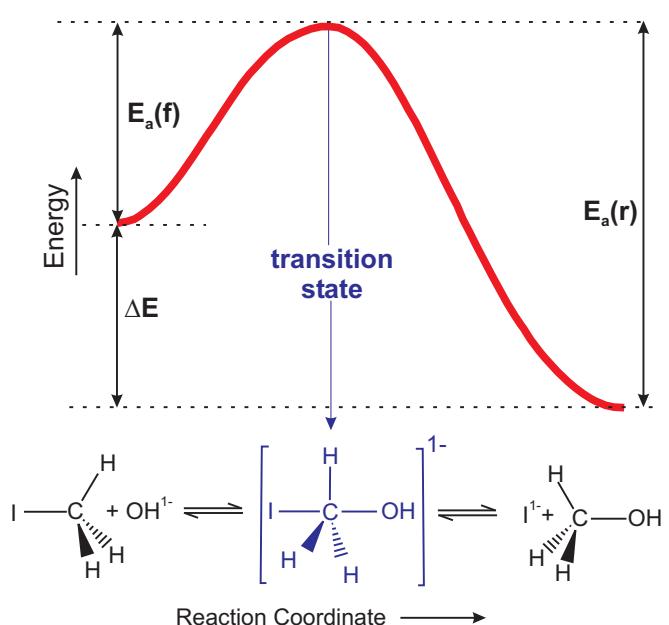


Figure 9.6 Reaction energy diagram for $\text{CH}_3\text{I} + \text{OH}^{1-}$

There are no gases involved in the reaction, so $\Delta H = \Delta E$.

9.10 RATES OF REACTION AND THE RATE LAW

The **rate of a reaction (R)** is the rate at which a reactant is consumed or the rate at which a product is produced. Reaction rates frequently have units of molarity per unit time. The rate of reaction depends on the rate at which the transition state is reached, which in turn depends on the following two factors:

1. The **collision frequency** is the number of collisions between reactant particles per second in a liter of solution. It is proportional to the product of their *molar concentrations*. Thus, the frequency of collisions between CH_3I molecules and OH^{1-} ions is proportional to $[\text{CH}_3\text{I}][\text{OH}^{1-}]$.
2. The **fraction of collisions leading to the transition state** depends upon the orientation of the molecules at collision, their kinetic energies, and the activation energy for the reaction. As shown in Figure 9.7, the reactants have the correct orientation to achieve the transition state in only a fraction of their collisions. In addition to having the correct orientation, the molecules must have sufficient thermal energy to overcome the activation energy for the reaction.

The collision frequency and the fraction of collisions that result in the transition state are combined into a **rate law** for the reaction, which is a mathematical expression that describes the rate of the reaction. For a one-step process,* the rate law is the product of the concentrations of the reactants (the collision frequency) times a **rate constant** (the fraction of collisions leading to the transition state). Thus, the rate law for $\text{CH}_3\text{I} + \text{OH}^{1-} \rightarrow \text{CH}_3\text{OH} + \text{I}^{1-}$ is $R = k[\text{CH}_3\text{I}][\text{OH}^{1-}]$ where k is the rate constant for the forward reaction. The *rate constant is a function of the activation energy and the thermal energy (temperature); it always increases with temperature*. For two reactions with comparable orientation requirements, the one with the larger rate constant has the smaller activation energy.

Example 9.8

What is the ratio of collision frequencies for $\text{CH}_3\text{OH} + \text{I}^{1-}$ collisions to $\text{CH}_3\text{I} + \text{OH}^{1-}$ collisions in a solution that is 1.0 M in CH_3OH , 3.0 M in I^{1-} , 0.1 M in CH_3I and 0.2 M in OH^{1-} ?

Each collision frequency is proportional to the product of the concentrations of the colliding particles, so the ratio is obtained as follows:

$$\frac{\text{frequency of } \text{CH}_3\text{OH} + \text{I}^{1-} \text{ collisions}}{\text{frequency of } \text{CH}_3\text{I} + \text{OH}^{1-} \text{ collisions}} = \frac{[\text{CH}_3\text{OH}][\text{I}^{1-}]}{[\text{CH}_3\text{I}][\text{OH}^{1-}]} = \frac{(1.0)(3.0)}{(0.1)(0.2)} = 150$$

At these concentrations, CH_3OH and I^{1-} collisions occur 150 times more frequently than those between CH_3I and OH^{1-} .

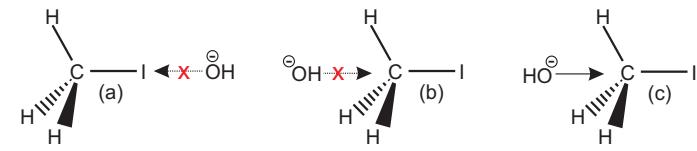


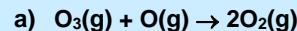
Figure 9.7 Not all collisions lead to the transition state

Collisions (a) and (b) do not lead to the transition state because the reactants are not aligned correctly. Only collision (c) can lead to a C-O bond and the transition state.

* The processes discussed in this section are all simple, one-step reactions that can be treated in the manner discussed here. However, most chemical reactions occur in more than one step, and the rate law of such reactions must be determined experimentally.

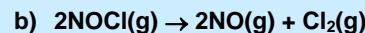
Example 9.8

Express the rate law for each of the following one-step processes:



The rate law is simply the rate constant (the fraction of collisions resulting in the transition state) times the product of the concentrations of all reactants (the number of collisions).

$$\text{Rate} = k[O_3][O]$$

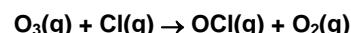


Two NOCl particles ($2NOCl = NOCl + NOCl$) collide in this reaction.

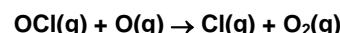
$$\text{Rate} = k[NOCl][NOCl] = k[NOCl]^2$$

The rate of a reaction can be increased by increasing the concentrations of the reactants or by increasing the temperature. Increasing the concentrations increases the frequency of collisions, while increasing the temperature increases both the rate of collisions (the molecules are moving faster) and the fraction of collisions with sufficient energy to attain the transition state. However, the rate of a reaction can also be increased by reducing the activation energy by altering the mechanism and the transition state of the reaction. This is done with the addition of a **catalyst**, which is a material that speeds the rate of reaction without being changed by the reaction.

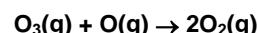
Biochemical reactions occur at the low temperatures and concentrations found in the human body due to the presence of catalysts called *enzymes*. The *catalytic converter* in an automobile aids the conversion of unwanted pollutants into CO_2 , H_2O and N_2 . As an example of unwanted catalysis, consider the situation of the industrially important class of compounds known as chlorofluorocarbons or CFC's. These compounds were used in aerosol sprays and refrigeration units and were once produced at levels exceeding one billion kilograms a year. Then it was discovered that they absorbed high energy light in the upper atmosphere to create chlorine atoms, which react with ozone molecules as follows:



OCl molecules then react with oxygen atoms and regenerate chlorine atoms.



Summing the two reactions yields the net reaction for the depletion of the ozone layer.



The Cl atoms do not appear in the net reaction because they are formed in the second reaction after being consumed in the first; that is, there is no *net* change in the chlorine

atoms. A similar argument holds for the OCl molecules, but OCl molecules are formed by the reaction and then consumed, so they are called **intermediates**. *Catalysts appear first as reactants and must be added to the reaction only to be released later, while intermediates are formed in the reaction but consumed later.*

Figure 9.8 shows the reaction energy diagram for the reaction in the absence and presence of Cl atoms. In the absence of Cl, the transition state of the final reaction involves an O₄ species, and the activation energy of the reaction is 17 kJ/mol. Such a high activation energy means that this reaction occurs very rarely in the atmosphere. However, the activation energies for the two reactions involving chlorine are both very small (~2 kJ/mol), so the overall reaction occurs much more readily in the presence of chlorine atoms. Thus, the chlorine atoms catalyze the reaction because they increase the rate of the reaction, but they are unchanged by it. A worldwide ban on the production of CFC's has resulted as a consequence of the discovery of these reactions in the atmosphere.

In summary, there are three ways to increase the rate of a reaction:

1. increase the concentrations of the reactants to increase the frequency of collisions;
2. increase the temperature to increase the collision frequency and the fraction of collisions with sufficient energy to form the transition state; and
3. add a catalyst to decrease the activation energy.

9.11 EQUILIBRIUM AND THE EQUILIBRIUM CONSTANT

In Section 9.8, we discussed the thermodynamic definition of equilibrium ($\Delta G = 0$), and we now turn to the kinetic definition. Consider the reaction $\text{CH}_3\text{I} + \text{OH}^{1-} \rightarrow \text{CH}_3\text{OH} + \text{I}^{1-}$. Once some product molecules have formed, they can also collide to produce the reverse reaction, $\text{CH}_3\text{OH} + \text{I}^{1-} \rightarrow \text{CH}_3\text{I} + \text{OH}^{1-}$, and as the forward reaction proceeds, the concentrations of I^{1-} and CH_3OH increase causing the rate of the reverse reaction ($R_r = k_r[\text{CH}_3\text{OH}][\text{I}^{1-}]$) to increase. Simultaneously, the concentrations of OH^{1-} and CH_3I decrease, reducing the rate of the forward reaction. Eventually, the two rates become equal; that is, the transition state is reached at the same rate from both sides. At this point, all species are being formed and consumed at the same rate, and there is no longer any change in concentration; the system has reached equilibrium.* The reaction continues at equilibrium, but it does so in both directions with equal rates. Equilibria in which competing processes continue at equal rates are called dynamic equilibria, which is quite different from a static equilibrium in which the competing processes stop. Double arrows are used to represent an equilibrium in order to show that the reaction continues in both

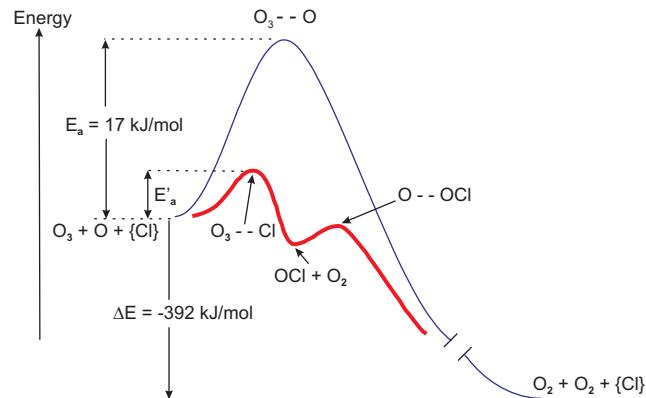


Figure 9.8 Energy diagram for $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$

Diagrams are in the absence (blue) and in the presence (red) of catalytic chlorine atoms. The activation energy E'_a is 2.1 kJ/mol. Note that OCl lies in a shallow well between the reactants and the products, which is typical of intermediates, while the transition states $\text{O}_3\text{-O}$, $\text{O}_3\text{-Cl}$, and $\text{O}\text{-OCl}$ all lie at peak maxima.

* The thermodynamic view is that the reaction causes concentration changes, which change the driving forces for the forward and reverse reactions. At equilibrium the driving forces are equal. In kinetics, the concentration changes cause rate changes, and equilibrium occurs when the rates equal.

directions. Writing the reaction as $\text{CH}_3\text{I} + \text{OH}^{1-} \rightleftharpoons \text{CH}_3\text{OH} + \text{I}^{1-}$ shows that it is an equilibrium process that consists of a forward reaction ($\text{CH}_3\text{I} + \text{OH}^{1-} \rightarrow$) and a reverse reaction ($\leftarrow \text{CH}_3\text{OH} + \text{I}^{1-}$) occurring simultaneously.

As a result of the back reaction, there will always be at least some of the reactants (substances on the left side of the chemical equation) present at equilibrium; *i.e.*, the limiting reactant does not disappear completely. How far the reaction proceeds before reaching equilibrium is established by the **equilibrium constant, K**, for the reaction. The equilibrium constant expression can be derived from the thermodynamic definition of equilibrium, but we use the kinetic definition in the following.

At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, so $R_f = R_r$. Substitution of the rate laws for the forward and reverse reactions, produces the following for an equilibrium system:

$$k_f[\text{CH}_3\text{I}][\text{OH}^{1-}] = k_r[\text{CH}_3\text{OH}][\text{I}^{1-}]$$

where the concentrations are the equilibrium concentrations. Next, we divide both sides of the equation by k_r and then by $[\text{CH}_3\text{I}][\text{OH}^{1-}]$ to get the constants (k_f and k_r) on one side and the equilibrium concentrations on the other. The ratio of two constants is a constant, so the ratio k_f/k_r is set equal to K , the equilibrium constant.

$$\frac{k_f}{k_r} = \frac{[\text{CH}_3\text{OH}][\text{I}^{1-}]}{[\text{CH}_3\text{I}][\text{OH}^{1-}]} = K, \text{ the equilibrium constant} \quad \text{Eq. 9.7}$$

The equilibrium mixture must satisfy the equilibrium constant regardless of how it is formed. Thus, the same concentrations are produced by the reaction of one mole each of CH_3OH and I^{1-} or one mole each of $\text{CH}_3\text{I} + \text{OH}^{1-}$.

The equilibrium constant expression for a reaction in which all of the reactants and products are in aqueous solution is the product of the concentrations of the substances on the right side of the reaction (products) divided by the product of the concentrations of the substances on the left side of the reaction (reactants). The concentration of each substance is raised to an exponent equal to its coefficient in the balanced equation. In the reaction between CH_3I and OH^{1-} , all of the coefficients are one, so the exponents do not appear explicitly. Most of the reactions studied in the remainder of the text take place in aqueous solutions, so consider the following generic equilibrium in water* and its equilibrium constant expression.

* Recall that the abbreviation 'aq' is used to show that a substance is in an aqueous solution.

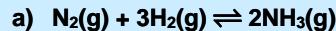
$$aA(aq) + bB(aq) \rightleftharpoons cC(aq) + dD(aq) \quad K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Thus far, we have expressed the equilibrium constant in terms of the concentrations of reactants and products, but that is because we have considered only reactions in which all reactants and products are in solution. However, that is not always the case, and the manner in which a reactant or product enters the equilibrium constant expression depends upon the state of the substance as follows:

- Substances in aqueous solution enter K as their molar concentrations.
- Substances that are gases enter K as their partial pressures in atmospheres.
- Substances that are liquids or solids enter K as one (1) because their concentrations do not change during the reaction.[†]

Example 9.10

Write the equilibrium constant expression for each of the following reactions.



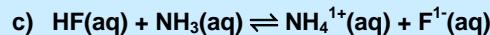
The reactants and products are all gases, so the equilibrium constant expression consists of their equilibrium pressures in atmospheres. The pressure of each substance is raised to a power equal to its coefficient in the balanced equation.

$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$



The solid reactant enters the expression as a one (1) in the denominator. The (aq) after Ag^{1+} and S^{2-} indicates that these ions are dissolved in water, so these products enter the expression as their molar concentrations in the numerator. The two in front of the Ag^{1+} means that we must square the Ag^{1+} ion concentration. Reactions like this are discussed in more detail in Chapter 10.

$$K = \frac{[Ag^{1+}]^2[S^{2-}]}{1} = [Ag^{1+}]^2[S^{2-}]$$



As indicated by (aq), all reactants and products are dissolved in water, so they enter as their molar concentrations. This is an acid-base reaction, the topic of Chapter 12.

$$K = \frac{[NH_4^{1+}][F^{1-}]}{[HF][NH_3]}$$

[†] The amount of a pure solid or liquid changes during the reaction but not its concentration. For example, the concentration of pure water is 1 g/mL = 56 M (its density), which is unchanged during any reaction.

Example 9.11

The following equilibrium pressures were observed at some temperature:

$$[\text{HI}] = 0.200 \text{ atm}; [\text{I}_2] = 0.500 \text{ atm}; \text{ and } [\text{H}_2] = 0.100 \text{ atm}$$

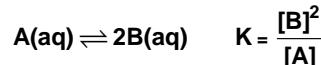
What is the value of K for the following reaction? $2\text{HI}(g) \rightleftharpoons \text{I}_2(g) + \text{H}_2(g)$

Recall that gases enter the equilibrium expression as their pressures expressed in atmospheres. The coefficient of HI is two, so its pressure must be squared. We determine K as follows:

$$K = \frac{P_{\text{I}_2} P_{\text{H}_2}}{P_{\text{HI}}^2} = \frac{(0.500)(0.100)}{(0.200)^2} = 1.25$$

THE MEANING OF K

The amount of product that forms in a reaction can be determined from the amount of reactant that *reacts* (not just present) and the stoichiometry (mole ratios) of the balanced chemical equation. However, the amount of reactant that reacts is determined by the equilibrium constant for the reaction. Calculations based solely on the initial amounts of reactant assume that at least one of the reactants, the **limiting reactant**, is completely consumed in the reaction. That is, they assume that the reaction is extensive. In reactions that are not extensive, only a fraction of each reactant is consumed. In these cases, the equilibrium constant must be used along with stoichiometry to determine the amount of product. For example, consider the following reaction:



Stoichiometry predicts that two moles of B are produced for each mole of A that reacts. However, as shown in Table 9.4 that does not mean that two moles of B form simply because 1 mole of A was present initially. The amount of B that is produced depends upon both the amount of A and the value of K. For example, consider the equilibrium concentrations that result when the initial concentration of A is 1.0 M. When $K \gg 1$, the forward reaction ($\text{A} \rightarrow 2\text{B}$) dominates, so there is very little A remaining at equilibrium, and the stoichiometric amount of B forms and the final concentration of B is 2.0 M. However, when the reaction is not extensive, the back reaction ($2\text{B} \rightarrow \text{A}$) cannot be ignored. Thus, when $K \sim 1$, the forward and back reactions are comparable, so the equilibrium concentrations are comparable. When $K \ll 1$, the back reaction dominates, so very little A reacts and almost no B forms.

Table 9.4 Equilibrium concentrations of A and B resulting in a solution that is initially 1.0 M in A as a function of the equilibrium constant for the reaction $\text{A} \rightleftharpoons 2\text{B}$.

K	[A]	[B]
1.0×10^{-6}	4.0×10^{-6} M	2.0 M
10^a	0.23	1.53
1.0	0.61 M	0.78 M
1.0×10^{-6}	1.0 M	1.0×10^{-3} M

^a $K > 1$, but the equilibrium concentration of A is still appreciable, so the reaction is not extensive. This is why we use $K \gg 1$ for extensive reactions.

Reactions that are expected to have appreciable amounts of the reactants present at equilibrium are often distinguished from those that are extensive with the use of double or single arrows, respectively. Thus, the reaction is often written $A \rightarrow 2B$ when $K \gg 1$ (the reaction is extensive). However, it should be written $A \rightleftharpoons 2B$ when K is not very large (the reaction is not extensive). The amount of product formed can be determined strictly from stoichiometry without the use of K for extensive reactions, but K must be used to determine the amount of product formed in a reaction that is not extensive.* Note that reactions written with single arrows also achieve equilibrium; the single arrow simply implies that the back reaction occurs to such a small extent that it can be ignored when determining the amount of product that is formed.

THERMODYNAMIC DEFINITION OF K

In Section 9.8, we showed that $\Delta G = 0$ is the thermodynamic definition of equilibrium, and that $\Delta G^\circ < 0$ for an extensive reaction. As shown in Equation 9.8, the standard free energy of a reaction is related to its temperature and the natural logarithm of its equilibrium constant.

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad K = \exp\{-\Delta G^\circ/RT\}^*$$
 Eq. 9.8

Consider Table 9.5, which shows some values of ΔG° and K as determined with Equation 9.8. When ΔG° is very large and negative, K is very large, which can occur only when the denominator (amounts of reactants remaining) is exceedingly small. Thus, such reactions go nearly to completion and are said to be extensive. At low negative values of ΔG° , $K > 1$ and the reaction is still said to be extensive because the equilibrium amounts of products are higher than those of the reactants. However, substantial amounts of reactant can be present at equilibrium. When $\Delta G^\circ = 0$, $K = 1$, so the product and reactant amounts are comparable. As ΔG° becomes positive, the reactants begin to dominate the equilibrium mixture.

As mentioned earlier, ΔG° can be determined from tables, and the equilibrium constant can be determined from the value of ΔG° . In our treatment, we will *assume* that ΔG° is dominated by the value of ΔH° in reactions that do not involve a change in the number of moles of gas because the $T\Delta S^\circ$ term for these reactions is normally negligible compared to the much larger ΔH° term. Consequently, *we assume that K is large for exothermic reactions and small for endothermic reactions that do not involve a change in the number of moles of gas.*

* Such calculations are beyond the scope of this text but are covered extensively in *Chemistry – A Quantitative Science*.

Table 9.5 ΔG° and K at 298K

ΔG° (kJ/mol)	K	Comments
-75	1.4×10^{13}	extensive reaction that goes to completion
-10	57	extensive reaction but measurable amounts of reactants remain
0	1	equilibrium amounts of reactants and products are comparable
+10	0.018	not an extensive reaction but measurable amounts of product form
+75	7.1×10^{-13}	essentially no reaction

TEMPERATURE DEPENDENCE OF K

Increasing the temperature increases thermal energy, which increases the fraction of molecules at higher energy. The reactants are at higher energy in an exothermic reaction (Figure 9.9a), but the products are at higher energy in an endothermic reaction (Figure 9.9b). Thus, increasing the temperature of an endothermic reaction increases the concentration of the products and decreases that of the reactants. Increasing the temperature of an exothermic reaction increases the concentration of the reactants and decreases that of the products. Products are in the numerator and reactants in the denominator of K, so we conclude that *reducing the temperature increases K for an exothermic reaction, but decreases K for an endothermic reaction*. Note that the activation energy dictates the speed with which equilibrium is attained (kinetics), while the enthalpy change dictates the extent of reaction when ΔS is negligible (thermodynamics).

9.12 LE CHÂTELIER'S PRINCIPLE

Reactions are usually run so as to maximize the ratio of the product concentration to the concentrations of one of the reactants (usually the most expensive). For example, in the synthesis of methanol (CH_3OH) from methyl iodide (CH_3I) with the following reaction, $\text{CH}_3\text{I} + \text{OH}^{1-} \rightleftharpoons \text{CH}_3\text{OH} + \text{I}^{1-}$, the conditions would be adjusted to maximize the $[\text{CH}_3\text{OH}]/[\text{CH}_3\text{I}]$ ratio in the final mixture. The equilibrium constant expression is

$$K = \frac{[\text{CH}_3\text{OH}][\text{I}^{1-}]}{[\text{CH}_3\text{I}][\text{OH}^{1-}]}$$

which can be solved for the $[\text{CH}_3\text{OH}]/[\text{CH}_3\text{I}]$ ratio as follows:

$$\frac{[\text{CH}_3\text{OH}]}{[\text{CH}_3\text{I}]} = \frac{K[\text{OH}^{1-}]}{[\text{I}^{1-}]}$$

Thus, one way to increase the ratio is to increase K. The reaction is exothermic, so K can be increased by decreasing the temperature, but decreasing the temperature also decreases the rate of reaction. Consequently, the ratio is usually changed by either adding more hydroxide ion (increasing the numerator) or removing iodide ion (decreasing the denominator) as it is formed. Additional hydroxide ion reacts with more of the CH_3I to produce CH_3OH . Adding a cation, such as Tl^{1+} , that precipitates iodide but not hydroxide ion, would remove iodide ion from solution. In the absence of iodide ion, more CH_3I and OH^{1-} would have to react to produce more products and re-establish K. These considerations are generalized for any equilibrium by Le Châtelier's principle:

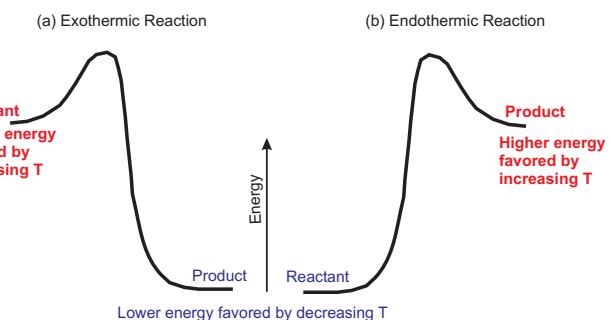


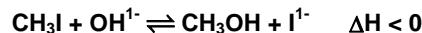
Figure 9.9 Reaction diagrams for an exothermic (a) and an endothermic reaction (b)

Le Châtelier's Principle: Systems at equilibrium respond to stress in such a way as to minimize the effect of the stress.

We conclude the following based on Le Châtelier's principle:

- The addition of a substance to an equilibrium mixture causes the reaction to proceed so as to reduce the amount of the added substance.
- The removal of a substance from an equilibrium mixture causes the reaction to proceed so as to replace some of the removed substance.

To drive reactions more to completion, products are often removed from the reaction as they are formed, or a large excess of one reactant is used. The following applies Le Châtelier's principle to the exothermic reaction that we have been studying:



- Removing CH_3I results in the reaction of more $\text{CH}_3\text{OH} + \text{I}^{1-}$ to replace some of the removed CH_3I thus producing more OH^{1-} .
- Adding CH_3OH also results in more reaction with I^{1-} to produce more $\text{CH}_3\text{I} + \text{OH}^{1-}$ in order to remove some of the additional CH_3OH .
- Removing CH_3OH causes further reaction between CH_3I and OH^{1-} to replace the removed CH_3OH . Additional I^{1-} and heat are also produced.
- Because the reaction is exothermic, heat is a product and we can write,



Heat is a product of the reaction, so cooling (removing heat from) the system reacts so as to replace some of the heat, which also produces $\text{CH}_3\text{OH} + \text{I}^{1-}$ and consumes $\text{CH}_3\text{I} + \text{OH}^{1-}$.

In summary, *the amount of product in an exothermic reaction can be increased by reducing temperature, adding more reactant, or by removing other products.*

Example 9.12

Use the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H^\circ = -90 \text{ kJ}$ to predict the effect of each of the following on the equilibrium concentration of hydrogen:

a) **Increasing the temperature**

The reaction is exothermic, so heat is a product (reactants are at higher energy in the reaction diagram). Therefore, increasing the temperature drives the reaction back to the left by decreasing the value of K. Thus, $[\text{H}_2]$ increases.

b) **Removing N_2**

The reaction must replace some of the N_2 , so NH_3 reacts, which increases $[\text{H}_2]$.

c) **Adding NH_3**

Some of the added NH_3 reacts to produce more H_2 and N_2 , so $[\text{H}_2]$ increases.

Example 9.13

The two reaction energy diagrams in the margin can be used to describe four reactions: A \rightarrow B; B \rightarrow A; C \rightarrow D; and D \rightarrow C. Assume that the energy scales are the same for the two curves and that ΔS is very small for each process.

- a) Which process would have the greatest rate constant and which the smallest?

The reaction with the greatest rate constant is the one with the lowest activation energy, D \rightarrow C. The smallest rate constant would be observed in the reaction with the greatest activation energy, C \rightarrow D.

- b) Which process would be most extensive? Which would be the least extensive?

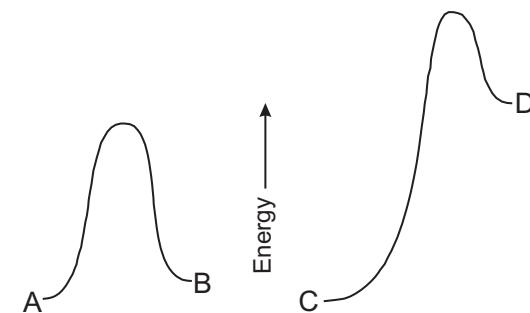
Because ΔS is small, the extent of the reaction is dictated by ΔH . Thus, the most exothermic reaction is the most extensive, so D \rightarrow C is the most extensive. The least extensive process would be the most endothermic process, C \rightarrow D.

- c) Increasing the temperature would increase the rates of which processes?

Increasing the temperature increases the rates of all processes.

- d) Increasing the temperature would increase the extent of which processes?

Increasing the temperature increases the fraction of molecules on the higher energy side of the reaction energy diagram, so the formation of B and D are favored by an increase in temperature. Consequently, the processes A \rightarrow B and C \rightarrow D are favored by an increase in temperature. However, the A \rightarrow B process would be affected much less than the C \rightarrow D process because the energy difference in the A \rightarrow B process is small.

**Example 9.13**

In the previous examples, we considered adding and removing gases or ions and molecules in solution. The change in concentration changes the ratio of concentrations given in the equilibrium constant expression so that it no longer equals K. The equilibrium must then shift to change the concentrations to values that re-establish the value of K. However, changing the amount of a pure solid or liquid does not change its concentration, which depends only upon its density. If no change in concentration results, the equilibrium does not shift. We conclude that ***the addition or removal of a pure solid or liquid component of the equilibrium does not affect the equilibrium concentrations.***

Example 9.14

What affect would each of the following have on the equilibrium concentration of Ag⁺ ions in the following equilibrium: $\text{AgCN(s)} \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{CN}^{-}(\text{aq})$?

- a) adding an acid (H⁺) to react with CN⁻ ions and produce HCN molecules.

Removal of CN⁻ ions from the equilibrium would result in more AgCN dissolving to produce Ag⁺ ions. The Ag⁺ ion concentration would increase.

b) adding solid KCN to increase the CN^{1-} ion concentration

The increased concentration of CN^{1-} ions would shift the equilibrium back toward AgCN by reacting with some of the Ag^{1+} ions in solution. The Ag^{1+} ion concentration would decrease. Note that the addition of a solid can shift the equilibrium if it dissolves to increase the concentrations of at least one ion involved in the equilibrium.

c) adding more solid AgCN

Adding more AgCN has no effect on the Ag^{1+} concentration because it does not change the concentration of AgCN . Recall that solids and liquids enter the equilibrium expression as one (1), so the equilibrium constant expression for this equilibrium is $K = [\text{Ag}^{1+}][\text{CN}^{1-}]$. Thus, only changing $[\text{Ag}^{1+}]$ or $[\text{CN}^{1-}]$ can shift the equilibrium.

9.13 CHAPTER SUMMARY AND OBJECTIVES

This chapter explored the kinetic and thermodynamic factors that dictate the feasibility, rate, and equilibrium position of a reaction. The enthalpy of reaction, ΔH , is the heat absorbed at constant pressure. When $\Delta H > 0$, heat is absorbed and the reaction is said to be endothermic, but when $\Delta H < 0$, heat is given off and the reaction is said to be exothermic. ΔH of a gas phase reaction can be approximated as the difference between the energy required to break the bonds in the reactants and to form them in the products. Entropy is a thermodynamic quantity that measures the ability of a system to disburse its energy; systems with more ways to disburse their energy have higher entropies. The number of ways the energy of a system can be disbursed decreases whenever constraints are placed on the system. Thus, the entropy of a substance in the gas is much greater than its entropy in the much more constrained liquid or solid state. Constraints in nature impose order on systems, so systems that are ordered (solid) have lower entropies than systems that are disordered (gas). The second law of thermodynamics states that $\Delta S_{\text{univ}} > 0$ for spontaneous processes. The Gibbs free energy is $\Delta G = -T\Delta S_{\text{univ}}$ at constant T and P, so $\Delta G < 0$ for a spontaneous process at constant T and P. $\Delta G = \Delta H - T\Delta S$, so both the enthalpy and entropy of reaction help establish spontaneity. ΔG indicates the spontaneous direction of a reaction; $\Delta G < 0$ indicates that the reaction is spontaneous in the direction written, $\Delta G < 0$ indicates that it is spontaneous in the reverse direction, and $\Delta G = 0$ indicates that the reaction is at equilibrium. ΔG° indicates the extent of reaction; $\Delta G^\circ \gg 0$ means the reaction is extensive and essentially all of the limiting reactant is consumed.

Kinetics deals with the rates of reactions. Rates are governed by the frequency of collisions between the reactants and the fraction of those collisions that result in the

formation of the transition state of the reaction. The frequency of collisions between two particles is expressed in terms of the product of their molar concentrations. The fraction of these collisions that yield the transition state depends upon the activation energy of the reaction, the thermal energy of the reacting molecules, and the orientation of the reacting molecules when they collide.

Equilibrium is established when the products and reactants reach the transition state at the same rate. Solute concentrations and gas pressures in an equilibrium mixture are dictated by the equilibrium constant for the reaction, K. The effect of adding or removing reactants, products, or heat on the equilibrium concentrations can be predicted by Le Châtelier's principle.

After studying the material presented in this chapter, you should be able to:

1. define the thermodynamic system, surroundings, and universe (Section 9.1);
2. state the first law of thermodynamics (Section 9.1);
3. determine ΔE from q and w (Section 9.1);
4. define enthalpy (Section 9.2);
5. define combustion and explain the importance of combustion reactions (Section 9.3);
6. use bond dissociation energies to approximate enthalpies of reaction (Section 9.4);
7. define entropy (Section 9.5);
8. predict the importance and the sign of ΔS for a chemical reaction (Section 9.5);
9. state the second law of thermodynamics (Section 9.6);
10. define Gibbs free energy (Section 9.7);
11. determine spontaneity from the sign of ΔG (Section 9.7);
12. determine the extent of reaction from the sign of ΔG° (Section 9.8);
13. discuss how the extent of reaction varies with T (Section 9.8);
14. sketch a reaction energy diagram showing the activation energies for the forward and reverse reactions (Section 9.9);
15. write the rate law for a simple collision process (Section 9.10);
16. describe and define chemical equilibrium from the viewpoint of kinetics (Section 9.11);
17. predict relative rate constants and extents of reaction from reaction energy diagrams (Section 9.11);
18. explain the meaning of single versus double arrows in a chemical equation (Section 9.11);
19. write the equilibrium constant expression for a chemical equation (Sections 9.11);
20. predict the temperature dependence of ΔG° and K (Sections 9.8 and 9.11); and
21. predict the impact of a stress on an equilibrium (Section 9.12).

9.14 EXERCISES

1. What are the signs of ΔH° and ΔS° for the evaporation of water?
2. What are the signs of ΔH° and ΔS° for cooling liquid water?
3. A system gives off 600 J of heat while 200 J of work are done on it. What are ΔE , ΔE_{sur} , and ΔE_{univ} ?
4. A system does 400 J of work and absorbs 150 J of heat. What are ΔE , ΔE_{sur} and ΔE_{univ} ?
5. What is the difference between ΔH and ΔE ? Why is ΔH used more frequently by chemists than ΔE ?
6. What are the standard states of a gas and a solute?
7. When is the entropy change of a reaction expected to be significant?
8. Indicate whether each of the following is true, false, or cannot be determined for a non-extensive reaction at constant pressure and temperature that is proceeding spontaneously to consume gas molecules.
 - a) $\Delta G < 0$
 - b) $\Delta S^\circ \sim 0$
 - c) $\Delta G^\circ < 0$
 - d) $\Delta E_{\text{univ}} = 0$
 - e) $\Delta H^\circ < 0$
 - f) the extent of reaction increases with T
9. Indicate whether each of the following is true, false, or cannot be determined for an extensive endothermic reaction that is at equilibrium at constant pressure and temperature.
 - a) $\Delta G < 0$
 - b) $\Delta H^\circ < 0$
 - c) $\Delta G^\circ < 0$
 - d) $\Delta S_{\text{univ}} > 0$
 - e) $\Delta S^\circ > 0$
 - f) the extent of reaction increases with T
10. The enthalpy of combustion of propane gas, $C_3H_8(g)$, is -2,220 kJ/mol.
 - a) Write the balanced equation for the combustion reaction.
 - b) Propane is often used for gas grills, which usually have a propane tank with 20 pounds of propane. How much heat can be obtained by burning all of the propane in a 20 lb tank? (1 lb = 454 g)
 - c) What is the enthalpy change for $6CO_2(g) + 8H_2O(l) \rightarrow 2C_3H_8(g) + 10O_2(g)$?

11. Combustion of 0.150 g of $C_2H_5OH(l)$ (grain alcohol) releases 4.47 kJ of heat.
 - a) What is the enthalpy of combustion of $C_2H_5OH(l)$?
 - b) Write the chemical equation for the combustion reaction.
 - c) What is ΔH° for $4CO_2(g) + 6H_2O(l) \rightarrow 2C_2H_5OH(l) + 6O_2(g)$?
12. Use the data in Table 9.2 to estimate the enthalpies of the following reactions:
 - a) $H_2CBr_2(g) + F_2(g) \rightarrow H_2CF_2(g) + Br_2(g)$
 - b) $H_3Cl(g) + H_2O(g) \rightarrow H_3COH(g) + HI(g)$
 - c) $HC\equiv CH(g) + 2H_2(g) \rightarrow H_3C-CH_3(g)$
 - d) $CH_4(g) \rightarrow C(g) + 2H_2(g)$
13. Use Table 9.2 to estimate the enthalpies of the following reactions:
 - a) $H_2C=CH_2(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
 - b) $4CH_3NH_2(g) + 9O_2(g) \rightarrow 4CO_2(g) + 10H_2O(g) + 2N_2(g)$
 - c) $CCl_4(g) + O_2(g) \rightarrow CO_2(g) + 2Cl_2(g)$
 - d) $4HC\equiv N(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g) + 2N_2(g)$
14. Indicate $\Delta S^\circ > 0$, $\Delta S^\circ \sim 0$, or $\Delta S^\circ < 0$ for each of the following reactions:
 - a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
 - b) $HF(aq) + NO_2^{1-}(aq) \rightarrow F^{1-}(aq) + HNO_2(aq)$
 - c) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
 - d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
15. Indicate $\Delta S^\circ > 0$, $\Delta S^\circ \sim 0$, or $\Delta S^\circ < 0$ for each of the following reactions:
 - a) $H_3Cl(aq) + OH^{1-}(aq) \rightarrow H_3COH(aq) + I^{1-}(aq)$
 - b) $CCl_4(l) \rightarrow CCl_4(g)$
 - c) $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$
 - d) $H_2(g) + CO_2(g) \rightarrow H_2O(g) + CO(g)$
16. Indicate the sign of ΔG° at low and high temperatures for each of the following processes:
 - a) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ $\Delta H^\circ < 0$
 - b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta H^\circ > 0$
 - c) $CH_3OH(l) \rightarrow CH_3OH(g)$ $\Delta H^\circ > 0$
 - d) $2Cl_2(g) + 7O_2(g) \rightarrow 2Cl_2O_7(l)$ $\Delta H^\circ > 0$

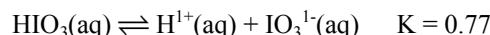
17. Indicate the sign of ΔG° at low and high temperatures for each of the reactions in Exercise 12.
18. Consider the reaction, $2\text{NH}_3(\text{g}) \rightarrow 3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$.
- Use bond energies to estimate the value of ΔH° at 298 K.
 - Is $\Delta S^\circ > 0$, $\Delta S^\circ \sim 0$, or $\Delta S^\circ < 0$?
 - Indicate the sign of ΔG° at high and at low temperatures.
 - Write the equilibrium expression for the reaction.
19. Consider the reaction, $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- Use bond energies to estimate the value of ΔH° at 298 K.
 - Is $\Delta S^\circ > 0$, $\Delta S^\circ \sim 0$, or $\Delta S^\circ < 0$?
 - Indicate the sign of ΔG° at high and at low temperatures.
 - Write the equilibrium expression for the reaction.
20. Consider the reaction, $\text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g})$
- Use bond energies to estimate the value of ΔH° at 298 K.
 - Is $\Delta S^\circ > 0$, $\Delta S^\circ \sim 0$, or $\Delta S^\circ < 0$?
 - Indicate the sign of ΔG° at high and at low temperatures.
 - Write the equilibrium expression for the reaction.
21. A reaction has a very high activation energy, is very exothermic, and involves almost no entropy change.
- Is the equilibrium constant expected to be large or small?
 - Will the value of the equilibrium constant increase, decrease, or remain unchanged when the temperature is increased?
 - Will the value of the equilibrium constant increase, decrease, or remain unchanged when more reactant is added?
 - Will the value of the equilibrium constant increase, decrease or remain unchanged when a catalyst is added?
 - Is the rate constant of the forward reaction larger or smaller than the rate constant for the reverse reaction?
22. Indicate the effect of each of the following on the equilibrium concentration of iodine: $\text{I}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \quad \Delta H^\circ < 0$
- add H_2
 - add HI
 - remove H_2
 - increase the temperature
23. Indicate the effect of each of the following on the equilibrium amount of CO : $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \quad \Delta H^\circ = 41 \text{ kJ/mol}$
- increasing the concentration of H_2
 - decreasing the concentration of CO_2
 - increasing the concentration of H_2O
 - increasing the temperature
24. Explain why the rate of a reaction increases as the concentrations of the reactants increase. What happens to the rate of the reaction when the concentrations of the products increase? Why?
25. Explain why the rate of a reaction increases as the temperature increases.
26. Express the rate law for each of the following *one-step processes*:
- $2\text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$
 - $\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$
 - $\text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl}$
27. Express the rate law for each of the following *one-step processes*:
- $\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I}$
 - $2\text{H}_2 \rightarrow 4\text{H}$
 - $\text{HO} + \text{H} \rightarrow \text{H}_2\text{O}$
28. Write the equilibrium constant expression in terms of the concentrations of the reactants and products for each of the following reactions:
- $2\text{HNO}_2(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightleftharpoons 2\text{NO}_2^{-}(\text{aq}) + \text{H}_2\text{PO}_4^{-}(\text{aq})$
 - $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
 - $\text{NO}(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightleftharpoons \text{NOCl}(\text{g})$
29. Write the equilibrium constant expression in terms of the concentrations of the reactants and products for each of the following reactions:
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$
 - $\text{H}_2\text{SO}_3(\text{aq}) + 2\text{CN}^{-}(\text{aq}) \rightleftharpoons 2\text{HCN}(\text{aq}) + \text{SO}_3^{2-}(\text{aq})$
 - $\text{NH}_3(\text{aq}) + \text{HF}(\text{aq}) \rightleftharpoons \text{NH}_4^{1+}(\text{aq}) + \text{F}^{-}(\text{aq})$

30. A solution is made 0.1 M each in A and B. A and B then react by the following equation: $A + B \rightleftharpoons C + D$. Indicate the approximate concentrations of A and C at equilibrium (use ~ 0 M to indicate a very small concentration) when K has the following values:

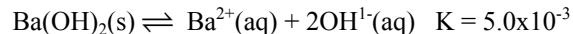
a) $K = 1 \times 10^8$ b) $K = 1$ c) $K = 1 \times 10^{-8}$

31. Consider the following equilibrium: $2\text{NO(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2\text{NOBr}$ $K = 2.0$. What is the equilibrium pressure of NOBr if the equilibrium pressures of NO and Br_2 are 1.6 and 3.6 atm, respectively?

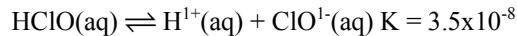
32. What is the concentration of IO_3^{1-} ion in an equilibrium solution that is 0.10 M in HIO_3 and 0.00026 M in H^{1+} ?



33. What is the concentration of Ba^{2+} ions in an equilibrium mixture that contains 0.12 mol Ba(OH)_2 and is 0.086 M in hydroxide ion?



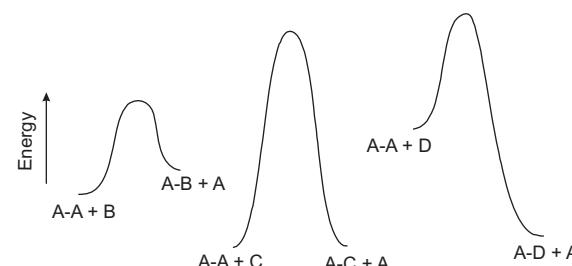
34. What is the concentration of H^{1+} ions in an equilibrium solution of HClO in which the $\text{HClO}/\text{ClO}^{1-}$ mole ratio is 0.66?



35. Consider the following energy diagram for the process $\text{X(g)} \rightleftharpoons \text{Y(g)}$.

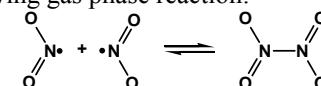
- a) What is ΔE of the reaction $\text{X} \rightarrow \text{Y}$? Is it an endothermic or an exothermic reaction?
 - b) What is the activation energy for the forward reaction ($\text{X} \rightarrow \text{Y}$)?
 - c) What is the activation energy for the reverse reaction ($\text{Y} \rightarrow \text{X}$)?
 - d) Which reaction has the greater rate constant, $\text{X} \rightarrow \text{Y}$ or $\text{Y} \rightarrow \text{X}$?
 - e) Does the pressure of X in the equilibrium mixture increase or decrease as the temperature rises?
 - f) Which point(s) would change in the presence of a catalyst.
-

36. Compare the reaction energy diagrams for the three gas phase reactions shown below.



- a) Assume that the steric factors are all comparable and predict which of the following reactions would most likely have the largest rate constant? Explain your choice.
 $\text{A}_2 + \text{B} \rightarrow \text{AB} + \text{A}$ $\text{A}_2 + \text{C} \rightarrow \text{AC} + \text{A}$ $\text{A}_2 + \text{D} \rightarrow \text{AD} + \text{A}$
- b) Which of the following reactions would have the largest equilibrium constant? Why?
 $\text{A}_2 + \text{B} \rightleftharpoons \text{AB} + \text{A}$ $\text{A}_2 + \text{C} \rightleftharpoons \text{AC} + \text{A}$ $\text{A}_2 + \text{D} \rightleftharpoons \text{AD} + \text{A}$
- c) The equilibrium constant of which of the following would increase the most with an increase in temperature? Explain your choice.
 $\text{A}_2 + \text{B} \rightleftharpoons \text{AB} + \text{A}$ $\text{A}_2 + \text{C} \rightleftharpoons \text{AC} + \text{A}$ $\text{A}_2 + \text{D} \rightleftharpoons \text{AD} + \text{A}$
- d) Rank the following bonds in order of increasing bond strength?
 A-A A-B A-C A-D

37. Consider the following gas phase reaction:



Indicate which statement is true in each set of a - d.

- a) $\Delta S^\circ > 0$ $\Delta S^\circ \sim 0$; $\Delta S^\circ < 0$
- b) $\Delta H^\circ > 0$ $\Delta H^\circ \sim 0$ $\Delta H^\circ < 0$
- c) at high temperatures
 $\Delta G^\circ > 0$ $\Delta G^\circ \sim 0$ $\Delta G^\circ < 0$
- d) at low temperatures
 $\Delta G^\circ > 0$ $\Delta G^\circ \sim 0$ $\Delta G^\circ < 0$
- e) Write the equilibrium constant expression for this reaction.
- f) What would be the effect on the equilibrium concentration of NO_2 of
 - i) removing N_2O_4
 - ii) increasing the temperature
 - iii) adding a catalyst

38. Draw a reaction diagram for a reaction in which the activation energies of the forward and reverse reactions are 20 and 40 kJ/mol, respectively. What is ΔH for the reaction? Draw the reaction diagram for the same reaction in the presence of a catalyst.
39. Write the equilibrium constant expression for each of the following reactions:
- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 - $HF(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + F^{1-}(aq)$
 - $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
 - $2NO_3^{1-}(aq) + 8H^{1+}(aq) + 6Br^{1-}(aq) \rightleftharpoons 2NO(g) + 4H_2O(l) + 3Br_2(aq)$
40. Write the equilibrium constant expression for each of the following reactions:
- $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$
 - $H_2SO_3(aq) + 2NH_3(aq) \rightleftharpoons SO_3^{2-}(aq) + 2NH_4^{1+}(aq)$
 - $2Ag^{1+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons Ag_2CrO_4(s)$
 - $3Fe(s) + 2Au^{3+}(aq) \rightleftharpoons 2Au(s) + 3Fe^{2+}(aq)$
41. The following pressures were measured in an equilibrium mixture at some temperature: $P_{NH_3} = 0.20$ atm; $P_{H_2} = 0.080$ atm and $P_{N_2} = 0.16$ atm. What is the value of the equilibrium constant for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ at this temperature?
42. An equilibrium mixture at 25 °C consists of an aqueous solution that is 0.010 M in Pb^{2+} ions and 0.041 M in Cl^{1-} ions above 0.010 mol of solid $PbCl_2$. What is the value of the equilibrium constant for the following reaction: $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{1-}(aq)$?
43. What is the pressure of I_2 in equilibrium with 0.065 atm of H_2 and 0.021 atm of HI at a temperature where $K = 6.7$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$?
44. Given that $K = 7.2 \times 10^{-4}$ for $HF(aq) + H_2O(l) \rightleftharpoons F^{1-}(aq) + H_3O^{1+}(aq)$, determine the molar concentration of F^{1-} ion in equilibrium with $[HF] = 0.10$ M and $[H_3O^{1+}] = 5.0 \times 10^{-4}$ M.
45. Consider the following thermochemical reaction,
- $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\circ = -91.8 \text{ kJ/mol}$$
- How much heat is released when 1.0 g of NH_3 is formed?
 - How much heat is released when 1.0 mol of H_2 reacts?
 - How much heat must be absorbed to form 2.0 g of N_2 ?
 - How many moles of ammonia are formed in a reaction that produces 200 kJ of heat?
46. Consider the combustion of methane,
- $$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l) \quad \Delta H^\circ = -882 \text{ kJ/mol}$$
- How many grams of methane must burn to produce 1,000 kJ of heat?
 - How much heat is released when 4.0 g of O_2 react?
 - How much heat is released when 1.5 mol of CO_2 is formed?

Chapter 10

Solutions

-
- 10.0 Introduction
 - 10.1 Concentration
 - 10.2 The Solution Process
 - 10.3 Organic Compounds
 - 10.4 Detergents and Micelles
 - 10.5 Electrolytes
 - 10.6 Electrolyte Solutions
 - 10.7 Dissolution of Ionic Compounds
 - 10.8 Precipitation of Ionic Compounds
 - 10.9 Solubility Equilibria
 - 10.10 Chapter Summary and Objectives
 - 10.11 Exercises
-

10.0 INTRODUCTION

Thus far, our study of chemistry has focused on pure substances (elements and compounds). However, most chemical reactions occur in mixtures, which can be classified as either *heterogeneous* or *homogeneous*. The properties of a **heterogeneous** mixture vary within the mixture. If you were to sample a heterogeneous mixture of oil in water, you would find its properties to be those of either oil or water, depending on where the mixture was sampled. A **homogeneous** mixture is characterized by uniform properties throughout; for example, the sweetness of a homogeneous mixture of sugar dissolved in water is the same everywhere in the mixture. Homogeneous mixtures are called **solutions**, the topic of this chapter.

Solutions are all around us. The atmosphere is a solution of gases in gases (mainly oxygen and nitrogen). Vinegar is a solution of a liquid in a liquid (acetic acid in water). A carbonated beverage is a solution of a gas in a liquid (carbon dioxide in water). Sweetened water is a solution of a solid in a liquid (sugar dissolved in water). Solder is a solution of a solid in a solid (tin in lead). These are but a few examples of the types of solutions we deal with every day.

Each of the components of a solution is characterized as either the **solvent** or a **solute**. There is only one solvent in a solution, but there can be several solutes. If there is only one liquid present, it is the solvent and any gases or solids that are dissolved in it are solutes. If more than one liquid is present, the liquid in the greater amount is usually considered to be the solvent. For example, a carbonated, non-diet soft drink is a solution made with *solid* sugar, *liquid* water, and *gaseous* carbon dioxide. Water is the only liquid, so it is the solvent, while the sugar and the carbon dioxide are solutes.

THE OBJECTIVES OF CHAPTER 10 ARE TO:

- define and describe solutions;
- define various units of concentration;
- define solubility and describe the solution process;
- present simple principles for predicting solubilities;
- describe the function of detergents;
- define electrolytes and the nature of their aqueous solutions;
- introduce net equations; and
- describe solubility equilibria and define the solubility product constant.

10.1 CONCENTRATION

The relative amounts of solute and solvent in a solution are important characteristics of the solution. They are usually given in terms of the **concentration** of the solute in the solvent or solution. There are many concentration units, but we will consider only three.

%(m/m)	percent by mass	grams of solute/100 g of solution
%(V/V)	percent by volume	mL of solute/100 mL of solution
M	molarity	moles of solute/L of solution

Percent by mass is most commonly used in solid solutions. A 60/40 solder is a solution of lead and tin that is 60% lead and 40% tin by mass. **Percent by volume** is used for solutions of liquids in liquids. Ethylene glycol ($C_2H_6O_2$) is a common antifreeze, which gives a maximum freezing protection in a 50% mixture by volume. Thus, your car is best protected from freezing when half of the *volume* of the solution in the cooling system is ethylene glycol and half is water. The grain alcohol or ethanol (C_2H_5OH) content in alcoholic beverages is given in terms of *proof*, which is simply twice the percent by volume of the alcohol in the solution. Thus, 100 mL of 90 proof rum contains 45 mL of C_2H_5OH .

The mole is the most useful measure of amount in a chemistry laboratory because it is easily related to the number of molecules or ions, so **molarity** is a very common unit of concentration in the laboratory. A solution of sugar that is composed of 0.10 mole of sugar ($C_{12}H_{22}O_{11}$) in a liter of solution is said to have a concentration of 0.10 M (read as 0.10 molar). The molarity of a solute is represented by enclosing its formula in square brackets; thus, the above sugar solution is one in which $[C_{12}H_{22}O_{11}] = 0.10\text{ M}$.

Example 10.1

A solution is prepared by dissolving a teaspoon (4.8 g) of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$; $M_m = 342 \text{ g/mol}$) in enough water to make 100 mL of solution.

- a) What is the concentration of sugar in g/mL?

$$\frac{4.8 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{100 \text{ mL solution}} = 0.048 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}/\text{mL solution}$$

- b) What is the concentration of the sugar in mol/L?

$$4.8 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{342 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}} = 0.014 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}$$
$$[\text{C}_{12}\text{H}_{22}\text{O}_{11}] = \frac{0.014 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{0.100 \text{ L solution}} = 0.14 \text{ M}$$

- c) How many moles of sugar are in 35 mL of the solution?

$$35 \text{ mL solution} \times \frac{1 \text{ L solution}}{1000 \text{ mL solution}} \times \frac{0.14 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ L solution}} = 0.0049 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}$$

The density of solids was discussed in Chapter 8, but density is also an important characteristic of pure liquids and solutions. Density (**d**) is mass per unit volume,

$$\text{density} = \frac{\text{mass of sample}}{\text{volume of sample}}$$

The density of water is 1.0 g/cm^3 , which means that 1 cubic centimeter of water has a mass of 1.0 g. The density of lead is 11.3 g/cm^3 . Thus, lead is much denser than water, which is the reason that lead does not float on water.

Example 10.2

What is the molarity of pure water?

The question essentially asks for the number of moles of water that are present in one liter of pure water. The problem can be solved by finding the mass of a liter of water and determining the number of moles it contains. The density of water is 1.0 g/mL , and its molar mass is 18.0 g/mol .

$$1000 \text{ mL H}_2\text{O} \times \frac{1.0 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} = 56 \text{ mol H}_2\text{O}$$

There are 56 moles of water molecules in a liter. Thus, liquid water is 56 M.

One liter of a 0.1 M sugar solution contains 0.1 mol of sugar and 56 mol of water. This means that there are ~560 water molecules for every sugar molecule in the solution!

10.2 THE SOLUTION PROCESS

There is usually a limit to how much solute can dissolve in a given amount of solvent at a given temperature. This limit is called the **solubility** of the solute in that solvent at that temperature. Solutions in which the concentration of the solute has reached this level are said to be **saturated**. Substances are often classified as soluble or insoluble in a solvent, but solubilities vary continuously. In this text, substances with solubilities of 0.1 M or greater are considered to be **soluble**; those with solubilities between 0.1 and 0.01 M are referred to as **moderately soluble**, and those with solubilities below 0.01 M are called **insoluble**. Thus, a saturated solution of NaCl in water is about 7 M, so NaCl is soluble in water; a saturated solution of MgSO₄ is 0.015 M, so MgSO₄ is moderately soluble in water; a saturated solution of silver chloride is only about 10⁻⁵ M, so AgCl is considered to be insoluble in water. Two substances, such as water and ethanol that are soluble in one another in all proportions are said to be **miscible**.

Example 10.3

Given the following solubilities of some fluorides in 100 mL of water at 25 °C, classify each as soluble, moderately soluble, or insoluble.

- a) 2.56 g NiF₂ ($M_m = 96.7 \text{ g/mol}$)

Molarity is moles of solute per liter of solution, using the factor-label method we obtain

$$\frac{2.56 \text{ g NiF}_2}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol NiF}_2}{96.7 \text{ g NiF}_2} = \frac{0.265 \text{ mol NiF}_2}{1 \text{ L}} = 0.265 \text{ M}$$

The solubility in water is greater than 0.1 M. We conclude that NiF₂ is soluble in water.

- b) 0.075 g CuF₂ ($M_m = 102 \text{ g/mol}$)

Proceed as in Part A.

$$\frac{0.075 \text{ g CuF}_2}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol CuF}_2}{102 \text{ g CuF}_2} = \frac{7.4 \times 10^{-3} \text{ mol CuF}_2}{1 \text{ L water}} = 7.4 \times 10^{-3} \text{ M}$$

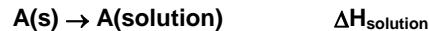
The solubility of CuF₂ is less than 0.01 M, so we conclude that CuF₂ is insoluble in water.

- c) 0.417 g S₂F₂ ($M_m = 102 \text{ g/mol}$)

$$\frac{0.417 \text{ g S}_2\text{F}_2}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol S}_2\text{F}_2}{102 \text{ g S}_2\text{F}_2} = \frac{0.0409 \text{ mol S}_2\text{F}_2}{1 \text{ L water}} = 0.0409 \text{ M}$$

The solubility of S₂F₂ is between 0.01 M and 0.1 M, so it is moderately soluble in water.

Consider the solution process in which substance **A** dissolves in a solvent to make a solution. If **A** is a solid, we can represent the process as



$\Delta H_{\text{solution}}$ is the **enthalpy (or heat) of solution**. Recall from Section 9.8 that the extent of a reaction depends upon the value of ΔG° . Thus, **A** is considered soluble if $\Delta G^\circ_{\text{solution}}$ is not large and positive.* We can apply Equation 9.6 to the solution process to obtain $\Delta G^\circ_{\text{solution}} = \Delta H^\circ_{\text{solution}} - T\Delta S^\circ_{\text{solution}}$, where $\Delta S^\circ_{\text{solution}}$ is the standard entropy of solution. There are competing factors that tend to keep $\Delta S^\circ_{\text{solution}}$ small, so $\Delta H^\circ_{\text{solution}}$ usually dominates the solution process. We use the approximation that a substance is soluble if its heat of solution is negative or only slightly positive.

In Section 9.4, the enthalpy of a reaction was approximated in terms of the energy required to break reactant bonds and form product bonds. Dissolving a molecular solute can be viewed in the same manner; that is, existing interactions must be broken and new interactions must be formed. The difference is that, in the solution process, the interactions are *intermolecular* rather than *intramolecular*.

As discussed in Chapter 7, molecular substances are held in the liquid and solid states by a combination of three intermolecular forces: dispersion, dipole-dipole, and hydrogen bonding. If the solute is an ionic compound, it is maintained in the solid state by ionic bonds. In order for the solute to dissolve, it must disperse itself uniformly into the solvent. Consequently, the solution process can be understood in terms of three steps, each with its own contribution to the enthalpy of solution:

1. ΔH_{solute} is the enthalpy required to separate solute particles. $\Delta H_{\text{solute}} > 0$.
2. $\Delta H_{\text{solvent}}$ is the energy required to create the “cavities” in the solvent that will be occupied by the solute particles. $\Delta H_{\text{solvent}} > 0$.
3. ΔH_{mixing} is the enthalpy change that occurs when the solute and the solvent particles interact. $\Delta H_{\text{mixing}} < 0$.

As shown in Equation 10.1, the enthalpy of solution is the sum of three enthalpy terms,

$$\Delta H_{\text{solution}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mixing}} \quad \text{Eq. 10.1}$$

A substance is soluble in a solvent so long as the energy required to break the solute-solute and solvent-solvent interactions is not much greater than the energy released when the solute-solvent interactions are established. However, solute-solvent interactions are comparable to solvent-solvent and solute-solute interactions only if all of the interactions are of the same type, which is summarized by the rule that *like dissolves like*.

* $\Delta G^\circ > 0$ implies only that the equilibrium concentration of A is less than 1 M (the standard state). Thus, it is slightly positive when $[A] = 0.1$ M, our definition of soluble.

Ionic substances and polar molecules are more soluble in polar solvents, while nonpolar molecules are more soluble in nonpolar solvents.

Figure 10.1 demonstrates the solution process for dissolving a polar solute in water. $\Delta H_{\text{solute}} > 0$ for a solid or liquid composed of polar molecules because energy is required to overcome the dipolar and dispersion forces. $\Delta H_{\text{solvent}} > 0$ because dipolar and H-bonding forces must be overcome to separate water molecules and create cavities for the solute molecules. Energy is released ($\Delta H_{\text{mixing}} < 0$) when regions of opposite charge on solute and solvent interact. If the solute is not polar, $\Delta H_{\text{mixing}} \sim 0$, the entire process is endothermic, and the solute is insoluble.

The combined process of creating a cavity in the solvent and placing the solute into the cavity (steps 2 and 3 above) is known as **solvation**. Thus, we can write

$$\Delta H_{\text{solvation}} = \Delta H_{\text{solvent}} + \Delta H_{\text{mixing}} \quad \text{Eq. 10.2}$$

The solute is said to be **solvated**, because it is surrounded by and interacting with solvent molecules. In the special case where the solvent is water, the process is called **hydration** and the solute is said to be **hydrated**.

Example 10.4

a) Which has the greater solubility in water, HBr or Br₂?

HBr is a polar molecule, and Br₂ is a nonpolar molecule, so HBr is more soluble in polar substances such as water.

b) Which is the better solvent for I₂, CS₂(l) or H₂O(l)?

Iodine is a nonpolar molecule and dissolves best in nonpolar solvents. Because water is polar, it is a poor solvent for nonpolar molecules such as I₂. Carbon disulfide, on the other hand, is nonpolar (CS₂ is linear, and both electron regions around the carbon are identical), and is a much better solvent for nonpolar molecules such as I₂. (In fact, I₂ is almost 1,000 times more soluble in CS₂ than in H₂O.)

c) In which solvent would KCl be more soluble, CCl₄ or water?

KCl is ionic, and ionic substances are most soluble in polar solvents. Thus, KCl is more soluble in water than in a nonpolar solvent such as CCl₄.

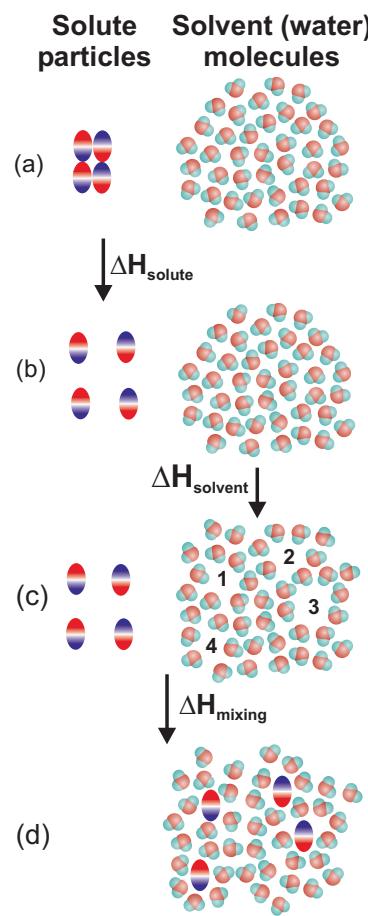


Figure 10.1 The Solution Process

- A polar solid solute (blue end is positive and red end is negative) and a liquid solvent (H₂O in the figure).
- The solute particles are separated.
- Solvent molecules are separated to produce cavities (labeled 1 through 4).
- The solute particles enter the cavities and interact with the solvent to produce a solution.

10.3 ORGANIC COMPOUNDS

Many of the compounds encountered outside the chemistry laboratory, such as vitamins, carbohydrates, grease, oils, gasoline, paint removers, plastics, and dyes, are *organic compounds*. **Organic compounds** are based on carbon, and their number is limitless because of the manner in which carbon atoms can bond to one another (Chapter 13). We now examine the solubility of this important class of compounds in water.

Gasoline and water ‘don’t mix’, and, based on the discussion in Section 10.2, we conclude that the reason they do not mix is that they do not interact with one another very well. Gasoline is a solution of many organic compounds, most of which are hydrocarbons like octane (Figure 10.2a). **Hydrocarbons** are compounds that contain only carbon and hydrogen atoms. The C and H atoms in octane form CH₃ and CH₂ groups connected by C-C single bonds. CH₃ groups and CH₂ groups are not polar, so octane molecules interact with each other only through dispersion forces. Consequently, octane molecules do not interact well with the polar and strongly hydrogen-bonded water molecules. Thus, when a hydrocarbon enters water, the water molecules position themselves so as to form highly ordered, ice-like cages* around each of the hydrocarbon molecules. These cages form to optimize the hydrogen bonding between the water molecules in the vicinity of the hydrocarbon because they cannot hydrogen bond to the hydrocarbon. Formation of a highly ordered cage results in a large negative entropy of solution, which assures that the free energy of solution is large and positive and the hydrocarbon is not water soluble. This effect is called the **hydrophobic effect**. The hydrophobic effect is especially important in biochemistry where it leads to membrane formation. Compounds with many CH₂ groups, which interact very poorly with water, are said to be **hydrophobic**, while polar molecules and ions, which interact strongly with water, are **hydrophilic**.[†] Octane is hydrophobic, but not all organic molecules are. For example, sucrose (table sugar) is a hydrophilic substance because it contains many O-H groups (Figure 10.2b) that hydrogen bond with water.

Alcohols are organic molecules that contain one or more hydroxyl (OH) groups. Our discussion and Table 10.1 center around alcohols with the generic formula ROH, where R is CH₃(CH₂)_n (n = 0 to 6). Each alcohol contains a hydrophilic (OH) and a hydrophobic (R) region, and its solubility in water depends upon n, number of CH₂ groups in the hydrophobic chain. When n is small (0, 1, or 2), the OH group dominates and the alcohol is hydrophilic. Thus, CH₃OH (methanol or wood alcohol), CH₃CH₂OH (ethanol or grain

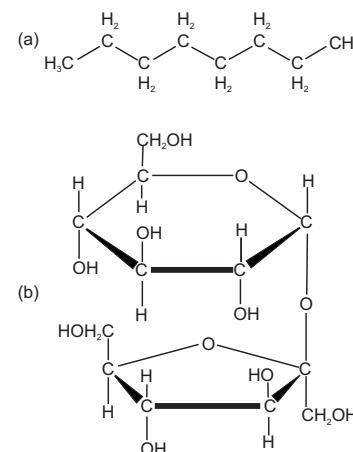


Figure 10.2 Hydrophobic and hydrophilic molecules

(a) Octane, C₈H₁₈, is hydrophobic due to CH₂ and CH₃ groups and is not soluble in water. (b) Sucrose (or table sugar, C₁₂H₂₂O₁₁) is hydrophilic because the O-H groups allow it to hydrogen bond to water. Consequently, sucrose is soluble in water.

* See Figure 7.10 for the ice structure. The ice-like cage around a hydrocarbon solute shares the hexagonal structure of ice, but it lacks the long range order of ice.

† The term hydrophobic comes from the Greek for ‘water fearing’, and hydrophilic comes from the Greek for ‘water loving’.

Table 10.1 Solubilities of some alcohols in Water

Alcohol	Solubility in H ₂ O
CH ₃ OH	miscible
CH ₃ CH ₂ OH	miscible
CH ₃ (CH ₂) ₂ OH	miscible
CH ₃ (CH ₂) ₃ OH	0.91 M
CH ₃ (CH ₂) ₄ OH	0.31 M
CH ₃ (CH ₂) ₅ OH	0.059 M
CH ₃ (CH ₂) ₆ OH	0.015 M

alcohol) and $\text{CH}_3(\text{CH}_2)_2\text{OH}$ (rubbing alcohol) are all miscible with water. However, as the hydrophobic chain gets longer, the alcohol becomes more hydrophobic, and its solubility in water drops. By the time n is six, the solubility has dropped down to 0.015 M. Similarly, increasing the number of hydroxyl groups increases the hydrophilic nature of the alcohol and its solubility in water. For example, the solubility of $\text{CH}_3(\text{CH}_2)_5\text{OH}$ in water is only 0.059 M, but $\text{HO}(\text{CH}_2)_5\text{OH}$, which differs only by the substitution of a hydrophilic OH for a hydrophobic CH_3 , is miscible with water.

Acetone, $(\text{CH}_3)_2\text{C=O}$ (Figure 10.3), is a common laboratory solvent because many organic substances are soluble in it, and it is miscible with water. Acetone contains CH_3 groups that interact with other organic compounds through dispersion forces, so many organic substances dissolve in acetone. However, it also contains a polar C=O group, which makes the molecule hydrophilic. As with alcohols, the water solubility of compounds like this depends upon the lengths of the carbon chains; as the hydrophobic portion of the molecule increases, its solubility in water decreases. For example, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{C=O}$ is only slightly soluble in water.

Example 10.5

Indicate whether each of the following substances is more soluble in water or in ether, $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$, a solvent with nonpolar components similar to those in acetone. See the margin for structures.

a) **Decane**

Decane is a hydrophobic molecule with no hydrophilic (polar) regions. Consequently, it is soluble in ether but not in water.

b) **Dodecanedioic acid**

Dodecanedioic acid has two hydrophilic regions, the COOH groups at either end, and it also has a large hydrophobic region (ten CH_2 groups) in the center. In this case, the hydrophobic region dominates, and the acid is soluble in ether but not in water.

c) **Ethanedioic (oxalic) acid**

Oxalic acid has two hydrophilic groups but no hydrophobic region. It is soluble in water but not in ether.

d) **Sodium propanoate**

Ionic substances are always more soluble in water than in ether.

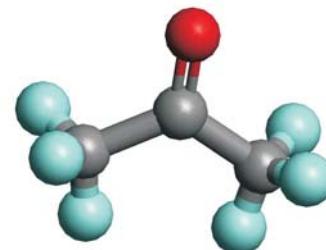
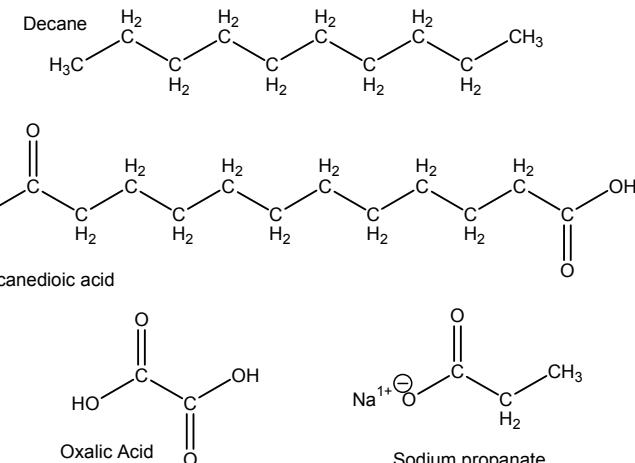


Figure 10.3 Ball-and-stick model of acetone



Example 10.4

10.4 DETERGENTS AND MICELLES

Water is the most common household solvent because it is plentiful and easily handled. While ionic substances, such as table salt, or those substances with which it can hydrogen bond, such as sugar (Figure 10.2b), are water soluble, grease, oil, and most dirt are hydrophobic and do not dissolve in water. These hydrophobic substances are frequently soluble in common laboratory solvents, such as acetone or ether, but these solvents are too costly and dangerous for general use. If water is to be used as a solvent for removing hydrophobic materials from clothing and dishes, some other substance, one that is both hydrophilic so it will be soluble in water and hydrophobic so it can dissolve dirt, must be added to the water. Such substances are called detergents.

A **detergent** is a substance that has a hydrophobic region consisting of a long carbon chain (referred to as the ‘tail’) and a hydrophilic region in the form of an ionic or polar group (referred to as the ‘head’) at one end. Figure 10.4 shows four representations of sodium dodecyl sulfate (SDS), $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, a common synthetic detergent found in shampoos and toothpastes. SDS readily dissolves in water to yield Na^{+} and $\text{C}_{12}\text{H}_{25}\text{SO}_4^{-}$ ions. The ionic sulfate ‘head’ makes it water soluble, while the hydrophobic $\text{C}_{12}\text{H}_{25}$ ‘tail’ interacts with the nonpolar grease through dispersion forces. The 12-carbon tail of SDS is quite short for a detergent as most detergents have tails containing 15 to 19 carbon atoms, which makes them more hydrophobic and better at dissolving grease. **Soaps** are detergents that are derived from fatty acids (Section 13.4) and have the general formula RCOONa , where R is a hydrophobic tail and the COO^{-} group is the polar head.

When a small amount of SDS is placed in water, the hydrophobic effect is so strong that the hydrophobic tails stick out of the water, while the polar heads remain in the water. The result is a **monolayer** (a layer that is only one molecule thick) lying on the surface of the water (Figure 10.5). If the hydrophobic tails are forced into the water by an increase in concentration coupled with agitation to accelerate the process, they interact with one another to form spherical aggregates called **micelles** (pronounced ‘my-cells’). Figure 10.6 shows a cross-sectional view of a micelle sphere. The polar heads are pointed toward the water and form the surface of the sphere making the sphere water soluble. The interior of the sphere is a *liquid hydrocarbon* composed of the hydrophobic tails interacting through dispersion forces. A small micelle contains 80 - 100 detergent molecules. Grease and oil molecules are hydrophobic and interact well with the hydrocarbon interior of the micelle. As a result, the grease and oil dissolve in the hydrocarbon liquid. We wash our clothes and

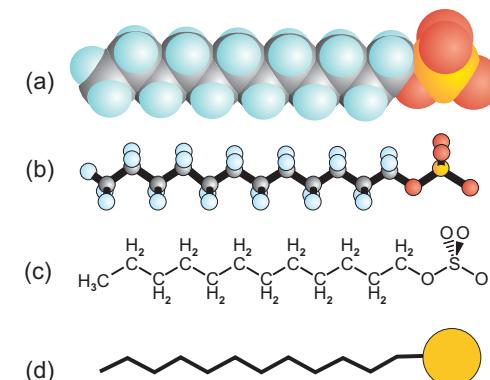


Figure 10.4 SDS ($\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-$), a synthetic detergent

Space-filling (a) and ball-and-stick (b) models, condensed structure (c), and the common abbreviation (d). The -1 charge is centered on the OSO_3^- ionic head. Na^{+} counterion is not shown.

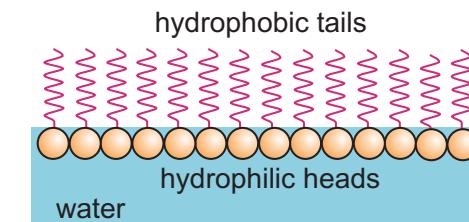


Figure 10.5 SDS monolayer

At small concentrations, SDS forms a monolayer on the surface of the water, with the hydrophobic tails sticking out of the water.

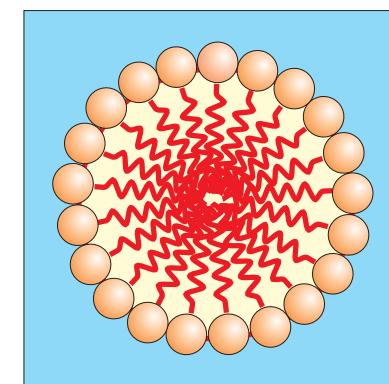


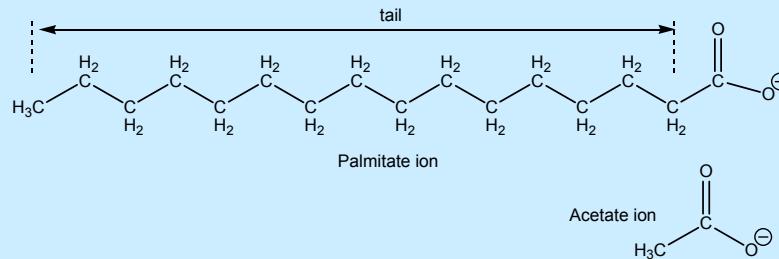
Figure 10.6 A micelle

Cross-sectional view of the spherical shell around the hydrophobic interior. The polar heads are in direct contact with the aqueous environment (blue background) and form the outer shell.

dishes by adding a detergent, agitating it to accelerate the formation of micelles that dissolve the hydrophobic dirt, and then rinsing the micelles and the captured oil and grease down the drain.

Example 10.6

Which would form a better micelle, sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) or sodium palmitate ($\text{NaC}_{16}\text{H}_{31}\text{O}_2$)? Explain.



The CH_3 group of the acetate ion is not hydrophobic enough for acetate to form micelles. Sodium acetate is soluble in water. The $\text{CH}_3(\text{CH}_2)_{14}$ chain of the palmitate ion is very hydrophobic, so the ion makes an excellent micelle.

10.5 ELECTROLYTES

In Chapter 8, we saw that ionic substances form extended solids in which there are no clearly defined ‘ionic molecules.’ Rather, each ion is surrounded by some number (the coordination number) of ions of opposite charge. In this section, we consider the nature of solutions composed of ionic substances dissolved in water by examining their ability to conduct electricity. Consider the apparatus shown in Figure 10.7. How brightly the light bulb glows depends upon how well charge flows from one electrode to the other, *i.e.*, how well charge flows through the solution. The movement of charge through the solution is due to the migration of ions, not free electrons. The light bulb does not glow when the electrodes are immersed in pure water or in a 0.1 M sugar solution because there are no ions in these solutions. The bulb glows very brightly when the solution is 0.1 M NaCl, but it does not glow at if solid sodium chloride is used. Thus, an aqueous solution of NaCl is a good conductor of electricity, but the solid is not. The difference between the solution and the solid is that the ions in solution are mobile, while those in the solid are not. Conduction in the solution results from a migration of ions as Na^{1+} ions migrate toward the negative

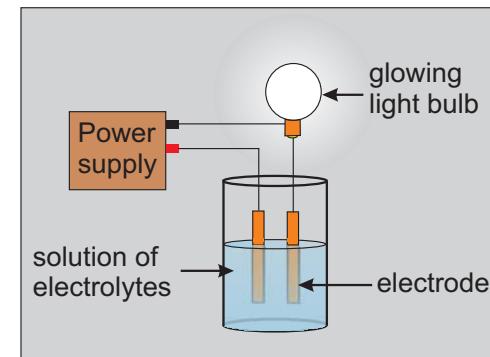
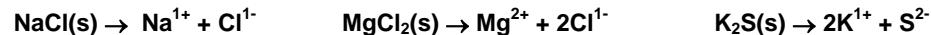


Figure 10.7 Solutions of electrolytes conduct electricity

The light bulb glows if there are ions present in the solution. Cations migrate to the negative electrode and anions to the positive electrode. The migration of ions results in current passing through the solution from one electrode to the other in a process called *electrolytic conduction*.

electrode and Cl^{1-} ions migrate toward the positive electrode. Substances that dissociate completely into ions when they dissolve in water are said to be **strong electrolytes**, substances that dissociate only partially in water are **weak electrolytes**, and substances that do not dissociate in water are called **nonelectrolytes**. Table 10.2 summarizes the results of several other solutions.

Ionic compounds are strong electrolytes, so when a solid ionic compound is dissolved in water, it goes into solution completely as ions.* For example,



A solution of NaCl contains only Na^{1+} and Cl^{1-} ions; there are no NaCl molecules. Note that the chemical equation for the dissociation must have the same stoichiometry as the substance. Thus, the formula MgCl_2 indicates that there are 2Cl^{1-} ions for every one Mg^{2+} ion, so the dissociation must express the same stoichiometry. Many ionic compounds contain polyatomic ions,[†] but *the bonds that hold the atoms in polyatomic ions are covalent and do not dissociate in water*, so polyatomic ions enter solution in tact.

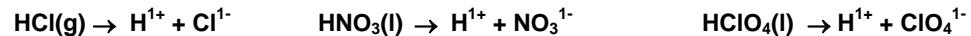


Ionic compounds are not the only class of compounds that are electrolytes; acids and bases are electrolytes as well. The first chemical definition of acids and bases was made by Svante Arrhenius.

Arrhenius acids are substances that produce H^{1+} ions when dissolved in water.

Arrhenius bases are compounds that produce OH^{1-} ions when dissolved in water.

Acids can be identified because the acidic protons are usually written first in their chemical formulas. For example, H_2S is an acid, so the protons appear first in its formula, but NH_3 is not, so the protons do not appear first in its formula. In Arrhenius theory, acids *ionize* in water in a manner similar to ionic substances, but only **strong acids** ionize completely. The common strong acids are HCl, HBr, HI, HNO_3 , HClO_4 , and H_2SO_4 . For example, the following chemical equations represent the Arrhenius view of dissolving HCl, HNO_3 , and HClO_4 in water:



Most acids dissociate only partially in water, so they are **weak acids**. Weak acids are weak electrolytes because they produce only small amounts of H^{1+} and the anion in water. HF, HNO_2 , and HClO_2 are examples of weak acids. The light bulb glows only dimly in a 0.1 M solution of a weak electrolyte because there are far fewer ions to conduct the electricity.

Table 10.2 Conduction in some 0.1 M aqueous solutions

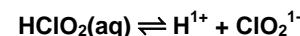
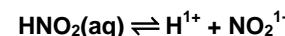
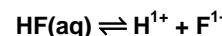
Solution	Glow ^a	Type of Solution	Particles in Solution
pure water	none	nonelectrolyte	H_2O molecules
NaCl	bright	strong electrolyte	$\text{Na}^{1+} + \text{Cl}^{1-}$ ions
HCl	bright	strong electrolyte	$\text{H}^{1+} + \text{Cl}^{1-}$ ions
HF	dim	weak electrolyte	mostly HF molecules
sugar	none	nonelectrolyte	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ molecules
NaNO_3	bright	strong electrolyte	$\text{Na}^{1+} + \text{NO}_3^{1-}$ ions
NaOH	bright	strong electrolyte	$\text{Na}^{1+} + \text{OH}^{1-}$ ions
CH_3OH	none	nonelectrolyte	CH_3OH molecules
NH ₃	dim	weak electrolyte	mostly NH ₃ molecules

^a “Glow” refers to the light bulb in Figure 10.7.

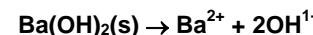
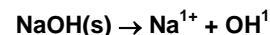
* Unless stated otherwise, it is understood that an isolated ion is in aqueous solution, so we drop the (aq) for clarity when writing ions.

[†] A list of some common polyatomic ions can be found in Table 4.1, which is reproduced on the last page facing the back cover.

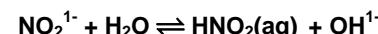
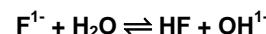
Hydrofluoric acid is a weak acid as less than 10% of the HF molecules in a typical solution dissociate into their ions. To emphasize the fact that there are many more molecules than ions in a solution of a weak acid, the solution process is written with equilibrium arrows:



Metal hydroxides are the most common **strong bases**:



Most weak bases are also ionic and produce OH¹⁻ ions as the result of the reaction of the anion with water. For example, F¹⁻ and NO₂¹⁻ ions are weak bases:



Ammonia is the most common example of a molecular substance that is a **weak base**:



Sugar is a **nonelectrolyte** because it retains its molecular identity when it dissolves. The chemical equation for dissolving sugar in water is



ION CONCENTRATIONS IN SOLUTIONS OF STRONG ELECTROLYTES

Ionic compounds, such as NaCl, are strong electrolytes, because *all* of the solid NaCl that dissolves *dissociates* into ions. Thus, a solution labeled 0.10 M NaCl contains Na¹⁺ and Cl¹⁻ ions, but no NaCl molecules. The ions react independently of one another; a chloride ion in a solution of NaCl is the same as one in a solution of KCl or MgCl₂. Thus, it is the concentration of the ion, not the parent compound that is important in solution chemistry. To convert from the concentration of the parent compound to that of any ion requires the stoichiometry of the chemical equation for the dissociation, which is given by the stoichiometry of the compound. For example, to determine the concentration of chloride ions in a 0.10 M MgCl₂ solution, we recognize that there are two moles of chloride ions for every one mole of MgCl₂ and write the following:

$$[\text{Cl}^{1-}] = \frac{0.10 \text{ mol MgCl}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol Cl}^{1-}}{1 \text{ mol MgCl}_2} = \frac{0.20 \text{ mol Cl}^{1-}}{1 \text{ L solution}} = 0.20 \text{ M}$$

An aqueous solution that is labeled 0.10 M MgCl₂, is 0.10 M in Mg²⁺ ions and 0.20 M in Cl¹⁻ ions, but it contains no MgCl₂!

Example 10.7

What are the concentrations of the ions in the following solutions?

a) 0.0364 M BaCl₂

Barium chloride is an ionic compound and a strong electrolyte, so it dissociates into its component ions when it dissolves: BaCl₂ → Ba²⁺ + 2Cl¹⁻. Use stoichiometry to determine the concentrations of the ions

$$[\text{Ba}^{2+}] = \frac{0.0364 \text{ mol BaCl}_2}{1 \text{ L solution}} \times \frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaCl}_2} = \frac{0.0364 \text{ mol Ba}^{2+}}{1 \text{ L solution}} = 0.0364 \text{ M}$$

$$[\text{Cl}^{1-}] = \frac{0.0364 \text{ mol BaCl}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol Cl}^{1-}}{1 \text{ mol BaCl}_2} = \frac{0.0728 \text{ mol Cl}^{1-}}{1 \text{ L solution}} = 0.0728 \text{ M}$$

b) 0.108 M K₃PO₄

PO₄³⁻ is the phosphate ion, so the dissociation is K₃PO₄ → 3K¹⁺ + PO₄³⁻, and the ion concentrations are determined as follows:

$$[\text{K}^{1+}] = \frac{0.108 \text{ mol K}_3\text{PO}_4}{1 \text{ L solution}} \times \frac{3 \text{ mol K}^{1+}}{1 \text{ mol K}_3\text{PO}_4} = \frac{0.324 \text{ mol K}^{1+}}{1 \text{ L solution}} = 0.324 \text{ M}$$

$$[\text{PO}_4^{3-}] = \frac{0.108 \text{ mol K}_3\text{PO}_4}{1 \text{ L solution}} \times \frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol K}_3\text{PO}_4} = \frac{0.108 \text{ mol PO}_4^{3-}}{1 \text{ L solution}} = 0.108 \text{ M}$$

10.6 ELECTROLYTE SOLUTIONS

Ionic bonds must be broken when an ionic substance dissolves, but ionic bonds are strong interactions, so ΔH_{solute} is large and positive. Thus, $\Delta H_{\text{solvation}}$, the enthalpy of solvation (hydration in this case because the solvent is water), must be large and negative for an ionic substance to dissolve in water. In other words, the interaction between the water molecules and the ions must be very strong. This strong interaction arises because water has a strong dipole (Section 7.2), which points from the center of the hydrogen atoms toward the electronegative oxygen atom (Figure 10.8).

When a crystal of sodium chloride is placed in water, H₂O molecules approach it with their dipoles aligned to interact with the ions at the surface (Figure 10.9). Consequently, the negative end of the water dipole points toward the positive Na¹⁺ ions, and the positive end of the dipole points toward the negative Cl¹⁻ ions (Figure 10.9a). As the ions are pulled into solution by the water molecules, more and more water molecules surround them. The ions become solvated or hydrated in this case because water is the solvent. Keep in mind that pure water is ~56 M (Section 10.1), so a 0.1 M solution of sodium chloride contains

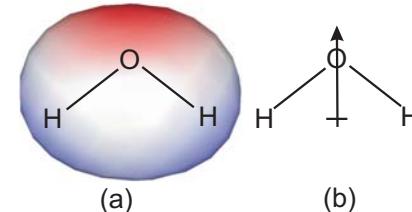


Figure 10.8 The water dipole

- The region in red carries negative charge, while the one in blue is positively charged.
- The dipole, which is represented by the arrow, points from the center of positive charge toward the center of negative charge.

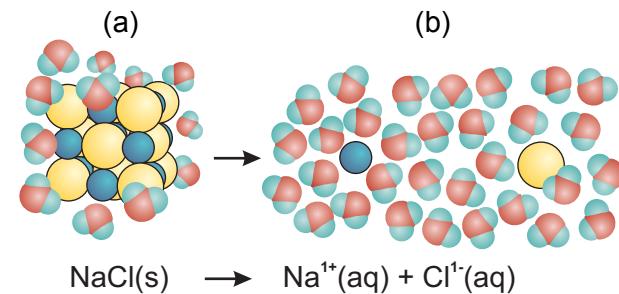


Figure 10.9 Dissolving NaCl in water

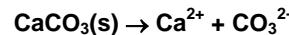
- Water molecules approach the crystal such that the positive ends of the water dipoles align with chloride ions and the negative ends align with sodium ions.
- The ions are pulled into solution and are surrounded by water molecules. We say that the ions are solvated or, in this case, hydrated.

~560 H₂O molecules for each NaCl unit or ~280 H₂O molecules for each Na¹⁺ ion and ~280 H₂O molecules for each Cl¹⁻ ion. In Figure 10.9, there are about only ~10 H₂O molecules for each ion, but there are actually hundreds in a typical solution.

Figure 10.9 demonstrates the difference between the environments of the ions in solid and aqueous NaCl. In the solid (Figure 10.9a), all interactions are between Na¹⁺ and Cl¹⁻ ions, so the solid is represented as NaCl. In aqueous NaCl (Figure 10.9b), each ion is hydrated, so its interactions are with water; interactions with other ions are very weak due to the high dielectric (ϵ) of water. Consequently, an aqueous solution of a salt is usually represented as the separated ions: Na¹⁺ + Cl¹⁻.

10.7 DISSOLUTION OF IONIC SUBSTANCES

The process whereby an ionic substance dissolves in water is called **dissolution***. The chemical equation for the dissolution of calcium carbonate is



As an approximation, we assume that an ionic substance is soluble when the force of attraction between its ions in solution is small enough that the ions can exist separately in solution; *i.e.*, the force is not great enough that the separated ions attract one another to reverse the dissolution process. The force of attraction is described by Coulomb's law, $F = kq_1q_2/\epsilon^2$ (Equation 1.3). We conclude that an ionic substance is soluble when

- r is very large. r is a property of the solution because it is the distance between the ions in the solution. r depends only upon concentration; ions in concentrated solutions are closer than ions in dilute solutions. If a substance is soluble, then the force of attraction cannot be great even at moderate concentration, so r cannot be very large.
- ϵ is large. ϵ is the dielectric constant of the solvent and measures how well the solvent screens the charges in solution. The dielectric constants for some common solvents are given in Table 10.3. The dielectric constant of water is about 40 times greater than that of a nonpolar solvent such as hexane (C₆H₁₄). This means that the force of attraction of two oppositely charged ions separated by the same distance is 40 times greater in C₆H₁₄ than in water, which is another reason that ionic substances are more soluble in water.
- q_1q_2 is small. The product of the charges on the ions is the only factor that is a property of the ionic solute. Recall that the charges on ions typically fall in the range of -3 to +3, thus $1 \leq |q_1q_2| \leq 9$. If the magnitude of the charge on either ion is one, $|q_1q_2|$ cannot exceed 3, but if neither charge is 1, then $|q_1q_2|$ cannot be less than 4. Consequently, we expect that ionic compounds containing highly charged ions will not be as soluble in water as those containing +1 and -1 ions because the force of attraction between highly charged ions is too strong.

* Dissolution means a decomposition of a whole into its parts. Here, it refers to the breaking apart of an ionic solid into its constituent ions in solution.

Table 10.3 Dielectric constants of selected solvents at 20 °C

Solvent Name	Formula	ϵ
acetic acid	CH ₃ COOH	6.20
acetone	(CH ₃) ₂ C=O	21.0
benzene	C ₆ H ₆	2.28
carbon disulfide	CS ₂	2.63
carbon tetrachloride	CCl ₄	2.24
dimethyl sulfoxide	(CH ₃) ₂ S=O	47.2
ether	(C ₂ H ₅) ₂ O	4.27
ethanol	C ₂ H ₅ OH	25.3
hexane	C ₆ H ₁₄	1.89
methanol	CH ₃ OH	33.0
water	H ₂ O	80.10

The effect of the $q_1 q_2$ product on the solubility of ionic compounds is summarized by the **Solubility Rules** shown in Table 10.4. The rules should be considered to be *rules of thumb* only; they summarize many, but not *all* cases. Rules 1 and 2 indicate that if either ion is +1 or -1 then the salt is *likely* to be soluble. Rule 3 continues with this theme but indicates what appear to be some exceptions to the +1/-1 rule. However, recall from Section 5.2 that late metals, such as those in Rule 3 are highly electronegative, so their bonds to halides have substantial covalent character and are not very ionic. Thus, Coulomb's Law is not applicable to those halides. Rule 4 indicates that sulfate is the only ion having a charge different from +1 or -1 that forms compounds that are usually soluble in water. Rule 5 states that *any compound that is not listed as soluble in Rules 1 through 4 should be assumed to be insoluble.*

Example 10.8

- a) Which of the following compounds can be used to make a solution that is 0.1 M in Pb^{2+} ions? PbSO_4 , $\text{Pb}(\text{NO}_3)_2$, PbI_2 , and Pb(OH)_2

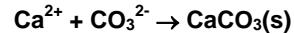
To make a 0.1 M solution, you must use a substance that is soluble. PbSO_4 is not soluble (Rule 4), $\text{Pb}(\text{NO}_3)_2$ is soluble (Rule 2), PbI_2 is not soluble (Rule 3), and Pb(OH)_2 is not soluble (Rule 5). Thus, only $\text{Pb}(\text{NO}_3)_2$ is soluble and can be used to make the solution.

- b) Which of the following compounds can be used to make a solution that is 0.1 M in CrO_4^{2-} ions? K_2CrO_4 , BaCrO_4 , $(\text{NH}_4)_2\text{CrO}_4$, FeCrO_4 , and Ag_2CrO_4

CrO_4^{2-} ions are not listed in the solubility rules, so we assume that all of its compounds are insoluble unless the cation is the ammonium ion or a Group 1A metal (Rule 1). Therefore, K_2CrO_4 and $(\text{NH}_4)_2\text{CrO}_4$ could be used, but none of the others are soluble enough to make the solution.

10.8 PRECIPITATION OF IONIC SUBSTANCES

The ions in solution are mobile, so when two solutions are mixed the ions in one solution encounter those from the other solution. If their interaction is strong enough, they precipitate from solution as an insoluble solid. **Precipitation** is the reverse of dissolution. The chemical equation for the precipitation of Ca^{2+} and CO_3^{2-} ions from solution is

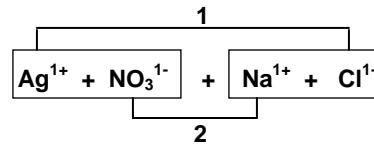


Two ions precipitate from an aqueous solution if the compound they form is insoluble; *i.e.*, when r is small (the solution is too concentrated) and/or $q_1 q_2$ is large. To determine if a precipitate forms when two solutions are mixed, we use the solubility rules to see if the

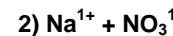
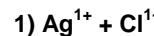
Table 10.4 Solubility Rules for Ionic Compounds in water

-
- | | |
|---------------|--|
| Rule 1 | Compounds of NH_4^{1+} and group 1A metal ions are soluble. |
| Rule 2 | Compounds of NO_3^{1-} , ClO_4^{1-} , ClO_3^{1-} and $\text{C}_2\text{H}_3\text{O}_2^{1-}$ are soluble. |
| Rule 3 | Compounds of Cl^{1-} , Br^{1-} , and I^{1-} are soluble <i>except</i> those of Ag^{1+} , Cu^{1+} , Tl^{1+} , Hg_2^{2+} and Pb^{2+} . |
| Rule 4 | Compounds of SO_4^{2-} are soluble <i>except</i> those of Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{2+} . |
| Rule 5 | Most other ionic compounds are insoluble; <i>i.e.</i> , most other combinations of ions form precipitates in water. |

combination of the cation in one compound with the anion in the other results in a compound that is insoluble. For example, consider mixing solutions of AgNO_3 and NaCl . Both substances are strong electrolytes, so they are found as their separated ions in aqueous solution. Thus, we represent the two solutions in different boxes as follows:



We then designate the two new cation-anion combinations that are possible in the mixed solution by the lines labeled 1 and 2. The possibilities for opposite charge interaction are therefore



Rule 3 states that AgCl is insoluble, so it precipitates from solution, while NaNO_3 is soluble (Rules 1 and 2) and does not precipitate.

Example 10.9

Write the formula of the precipitate that forms when the following aqueous solutions are mixed or write none if no precipitate is expected.

a) **Solutions of FeSO_4 and KOH**

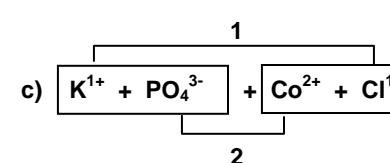
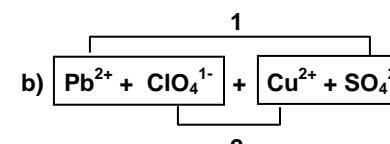
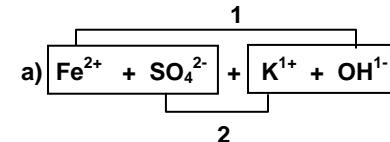
Express the solutions as the separated ions as shown in the margin and determine the new cation-anion combinations. (1) $\text{Fe}^{2+} + \text{OH}^{1-}$ and (2) $\text{K}^{1+} + \text{SO}_4^{2-}$. No precipitate results from the $\text{K}^{1+} + \text{SO}_4^{2-}$ combination (Rules 1 and 4), but neither Fe^{2+} nor OH^{1-} are listed in the solubility rules, so combination (1) produces an insoluble compound (Rule 5). The +2 charge on Fe^{2+} requires 2OH^{1-} , so the formula of the precipitate is $\text{Fe}(\text{OH})_2$.

b) **Solutions of $\text{Pb}(\text{ClO}_4)_2$ and CuSO_4**

As shown in the margin, the new cation-anion combinations that are possible upon mixing are (1) $\text{Pb}^{2+} + \text{SO}_4^{2-}$ and (2) $\text{Cu}^{2+} + \text{ClO}_4^{1-}$. No precipitate results from $\text{Cu}^{2+} + \text{ClO}_4^{1-}$ (Rule 2), but the combination of $\text{Pb}^{2+} + \text{SO}_4^{2-}$ is insoluble (Rule 4). The formula of the precipitate is PbSO_4 .

c) **Solutions of K_3PO_4 and CoCl_2**

Mixing introduces the following interactions: 1) $\text{K}^{1+} + \text{Cl}^{1-}$ and 2) $\text{Co}^{2+} + \text{PO}_4^{3-}$. Combination (1) results in KCl , which is soluble (Rules 1 and 3). Neither Co^{2+} nor PO_4^{3-} is listed in the solubility rules, so combination (2) produces a precipitate. The lowest common multiple of the +2 and -3 charges is 6, so three cations and two anions are required in the formula. The precipitate is cobalt(II) phosphate: $\text{Co}_3(\text{PO}_4)_2$.



Example 10.9

Example 10.10

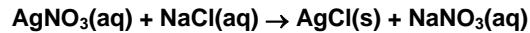
- a) A solution is known to contain Ba^{2+} and/or Ag^{1+} ions. Which ion is present if the addition of Cl^{1-} ions does not cause a precipitate, but the addition of SO_4^{2-} does?

BaCl_2 is soluble, but AgCl is not (Rule 3), so the solution cannot contain Ag^{1+} ions because AgCl does not precipitate. Ag_2SO_4 is soluble, but BaSO_4 is not (Rule 4), so the precipitate must be BaSO_4 . We conclude that the solution contains Ba^{2+} but not Ag^{1+} ions.

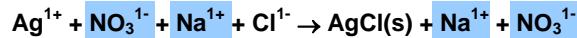
- b) A solution is known to contain Br^{1-} and/or OH^{1-} ions. Which ion is present if the addition of Pb^{2+} ions causes a precipitate, but the addition of Fe^{2+} does not?

Neither PbBr_2 (Rule 3) and $\text{Pb}(\text{OH})_2$ (Rule 5) are soluble, so the precipitate could be due to either anion. However, FeBr_2 is soluble (Rule 3), while $\text{Fe}(\text{OH})_2$ is not, so the lack of precipitate with the addition of Fe^{2+} rules out the presence of OH^{1-} ions. We conclude that the solution contains Br^{1-} , but not OH^{1-} ions.

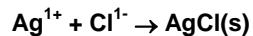
The reaction that occurs when solutions of silver nitrate and sodium chloride are mixed could be represented by the following chemical equation:



The fact that silver chloride precipitated is indicated by showing that it is a solid, while all others are aqueous (in solution). However, strong electrolytes are typically represented by their ions in aqueous solutions, so the reaction mixture could also be represented as



As indicated by the blue rectangles, the sodium and nitrate ions are unchanged during the reaction; each ion is surrounded by hundreds of water molecules before and after the reaction. Ions that do not participate in the reaction but are present throughout are called **spectator ions**. Both Na^{1+} and NO_3^{1-} are spectator ions in the above. Because these ions do not participate in the reaction, they are not included in the **net equation**, which shows only those species that change. The net equation for the precipitation of silver chloride, regardless of the source of the ions, is written as follows:



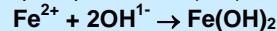
Net equations indicate only the *changes* that occur during a chemical reaction. They are most important when dealing with aqueous reactions of ionic substances. We will use them extensively in the next two chapters when we discuss redox (reduction-oxidation) reactions and acid-base reactions. In balancing a net reaction containing ions, it is important to realize that *charge balance is as important as atom balance*.

Example 10.11

Write net equations for the precipitation reactions in example 10.9.

a) Solutions of FeSO_4 and KOH

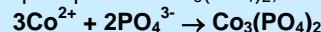
The precipitate is Fe(OH)_2 , so 2OH^{1-} ions are required for each Fe^{2+} ion.

**b) Solutions of $\text{Pb(ClO}_4)_2$ and CuSO_4**

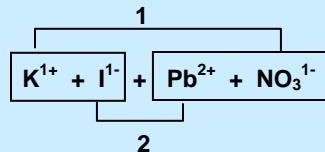
The precipitate is PbSO_4 . There is 1:1 ratio of ions, so the net equation is

**c) Solutions of K_3PO_4 and CoCl_2**

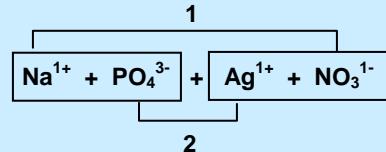
The precipitate is $\text{Co}_3(\text{PO}_4)_2$, so 3Co^{2+} and 2PO_4^{3-} are required.

**Example 10.12**

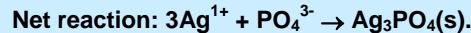
Write net equations for the reactions occurring when solutions of the following substances are mixed. Indicate ‘no reaction’ if no precipitate is expected to form.

a) Potassium iodide + lead nitrate

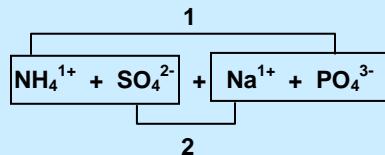
1. No reaction because KNO_3 is soluble by Rules 1 and 2.
2. PbI_2 precipitates by Rule 3.

**b) Sodium phosphate + silver nitrate**

1. No reaction because NaNO_3 is soluble by Rules 1 and 2.
2. Ag_3PO_4 precipitates by Rule 5.



c) Ammonium sulfate + sodium phosphate



1. No reaction because (NH₄)₃PO₄ is soluble by Rule 1.
2. No reaction because Na₂SO₄ is soluble by Rules 1 and 4.

No reaction occurs when these solutions are mixed.

The following are left as student activities. The answers are on the following page.

d) Lead nitrate + potassium chromate

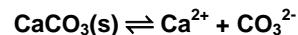
e) Barium acetate + ammonium sulfate

f) Cobalt(II) chloride + sodium phosphate

g) Ammonium sulfate + silver nitrate

10.9 SOLUBILITY EQUILIBRIA

The precipitation and dissolution processes are in dynamic equilibrium in a saturated solution; *i.e.*, the rate at which the solid dissolves equals the rate at which the ions precipitate. For CaCO₃(s), the chemical equation that represents this equilibrium is



The concentrations of the ions in the saturated solution can be used to determine the equilibrium constant for the reaction, or they can be determined from the equilibrium constant, if it is known. As discussed in Section 9.11, solutes enter the equilibrium

constant expression as their molar concentrations raised to an exponent equal to their coefficient in the balanced equation, while solids enter the expression as 1. Substances on the right (products) are in the numerator, and substances on the left (reactants) are in the denominator. Thus, the equilibrium constant expression for the dissolution of CaCO_3 is

$$K_{\text{sp}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{1} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.8 \times 10^{-9} \quad \text{Eq. 10.3}$$

The equilibrium constant, which involves only a product of concentrations (there is no denominator), is called the **solubility product constant** and given the symbol K_{sp} .[†] A small value for K_{sp} means that the product of the concentrations of the ions present at equilibrium is very small, which indicates that the substance is not very soluble. The K_{sp} of CaCO_3 is 4.8×10^{-9} at 298K, $K_{\text{sp}} \ll 1$, so it is an insoluble compound. Table 10.5 shows the solubility product constants of a few other insoluble salts. In a saturated solution of AgCl ($K_{\text{sp}} = 1.8 \times 10^{-10}$), $[\text{Ag}^{1+}] \sim 10^{-5}$ M, while in a saturated solution of Ag_2S ($K_{\text{sp}} = 8 \times 10^{-48}$), $[\text{Ag}^{1+}] \sim 10^{-17}$ M. Thus, silver chloride may be fairly insoluble, but Ag_2S is even more insoluble.

Example 10.13

The K_{sp} of zinc carbonate is 1.0×10^{-10} . Write the process and the expression that correspond to that value.

The process is the dissolution of ZnCO_3 in water. In this process, the ionic bonds between the Zn^{2+} ions and the CO_3^{2-} ions are broken, but the covalent C-O bonds within the carbonate ion remain intact. The chemical process and K_{sp} expression are



Example 10.14

The K_{sp} of iron(III) hydroxide is 1.6×10^{-39} . Write the process and the expression that correspond to that value.

Three OH^{1-} ions are required for each Fe^{3+} ion, so the chemical formula is $\text{Fe}(\text{OH})_3$. In addition, three hydroxide ions must be produced in the dissolution, so the hydroxide ion concentration must be cubed in the K_{sp} expression.



[†] Do not think that this equilibrium constant is somehow different because it has its own name. The 'K' in K_{sp} signifies an equilibrium constant, and the 'sp' subscript simply indicates that the equilibrium process is the dissolution of an ionic solid.

Table 10.5 Some solubility products (K_{sp}) in water at 25 °C

Compound	K_{sp}	Compound	K_{sp}
AgCl	1.8×10^{-10}	Ag_2S	6.3×10^{-50}
Ag_2CrO_4	1.1×10^{-12}	CaSO_4	2.4×10^{-5}
Agl	8.3×10^{-17}	BaSO_4	1.1×10^{-10}

Answers to student exercises in Example 10.12

- d) $\text{Pb}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{PbCrO}_4$
- e) $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$
- f) $3\text{Co}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Co}_3(\text{PO}_4)_2$
- g) No reaction

Example 10.15

The hydroxide ion concentration in pure water is 1.0×10^{-7} M. What is the maximum concentration of Fe^{3+} that can exist at that hydroxide ion concentration?

From Example 10.14,

$$K_{\text{sp}} = 1.6 \times 10^{-39} = [\text{Fe}^{3+}][\text{OH}^1]^3$$

Solving for the Fe^{3+} ion concentration, we obtain

$$[\text{Fe}^{3+}] = \frac{K_{\text{sp}}}{[\text{OH}^{1-}]^3}$$

Substitution of the given K_{sp} and the fact that $[\text{OH}^1] = 1.0 \times 10^{-7}$ M in pure water yields

$$[\text{Fe}^{3+}] = \frac{1.6 \times 10^{-39}}{(1.0 \times 10^{-7})^3} = 1.6 \times 10^{-18} \text{ M}$$

Thus, it is not possible to obtain high concentrations of iron(III) in water due to the precipitation of iron(III) hydroxide!

10.10 CHAPTER SUMMARY AND OBJECTIVES

Solutions are homogeneous mixtures characterized by the concentration of a solute in a solvent. The most useful and common unit of concentration in the chemistry laboratory is molarity, the number of moles of solute present in a liter of solution. The maximum concentration of solute that can be obtained in solution is called the solubility of the solute in that solvent at that temperature. The enthalpy of solution involves three terms: 1) the enthalpy required to loosen the solute particles from their interactions with one another; 2) the enthalpy required to create cavities in the solvent to accommodate the particles, and 3) the enthalpy released when the solute-solvent interactions are established. The first two terms are endothermic, while the third term is exothermic. Because ΔS is usually positive, the free energy of solution will be negative when the exothermic term is not much less than the sum of the two endothermic terms. This consideration is summarized in the rule *like dissolves like*: compounds with similar types of intermolecular forces are soluble in one another.

Compounds with many CH_2 groups interact so poorly with water that they are said to be hydrophobic. Consequently, many organic compounds are insoluble in water. However, there are a number of hydrophilic organic compounds that readily dissolve in water due to the presence of polar groups such as $-\text{OH}$, or ionic groups such as $-\text{OSO}_3^{1-}$, that interact

well with water. Organic compounds are soluble in water as long as they contain hydrophilic regions and their hydrophobic regions are not very large. Substances with both large hydrophobic regions and ionic regions can form spherical *micelles* when they are agitated in water. Detergents form micelles that function by dissolving the grease and oils into the hydrophobic micelle interior. The grease-and-oil containing micelles can be rinsed away because the hydrophilic ionic heads of the micelles are water soluble.

Electrolytes are substances whose aqueous solutions conduct electricity. The conduction of electricity is the result of the mobility of ions in solution. Ionic substances are strong electrolytes, while covalent substances are nonelectrolytes. Ions in aqueous solution are hydrated, which means they are surrounded by many water molecules that screen the ions from one another. In a saturated aqueous solution of an ionic solid, the dissolution and precipitation processes occur at the same rate, and the equilibrium constant for dissolution is called the solubility product constant, K_{sp} .

After studying the material presented in this chapter, you should be able to:

1. calculate the molarity of a solution from the mass of solute and the volume of the solution or the number of moles of solute in a given volume of solution of known molarity (Section 10.1);
2. describe the solution process, including the factors that contribute to the enthalpy of solution (Section 10.2);
3. explain and use the rule “like dissolves like” (Section 10.2);
4. classify compounds as hydrophilic or hydrophobic (Section 10.3);
5. explain the action of micelles and detergents (Section 10.4);
6. classify substances as strong, weak, or nonelectrolytes (Section 10.5);
7. determine the concentrations of all ions in a solution from the concentration of the parent compound (Section 10.6);
8. explain how ionic compounds dissolve in water (Section 10.7);
9. write the chemical equation for the dissolution of an ionic substance (Section 10.7);
10. use the solubility rules to predict whether a precipitate should form when aqueous solutions of ionic compounds are mixed (Section 10.8);
11. differentiate between spectator ions and reacting ions and write net equations for precipitation reactions (Section 10.8);
12. write the expression that relates the concentrations of the ions in a saturated solution to the solubility product of a substance (Section 10.9) and
13. calculate the concentration of an ion in a saturated solution given the K_{sp} and the concentrations of the other ions (Section 10.9).

10.11 EXERCISES

- Distinguish between the terms ‘solute’ and ‘solvent.’ Give an example of a solution and identify each component.
- Distinguish between ‘homogenous’ and ‘heterogeneous’ mixtures. Give an example of each.

Review Appendix C (Molarity) if you need help on Exercises 3-8.

- What is the concentration of nitrate ion in each of the following solutions?
a) 0.25 M KNO_3 b) 0.10 M $\text{Al}(\text{NO}_3)_3$ c) 0.20 M $\text{Ca}(\text{NO}_3)_2$
- What is the concentration of all ions in each of the following solutions?
a) 0.16 M CaCl_2 b) 0.080 M Na_2SO_4 c) 0.060 M KBr
- A solution is prepared by dissolving 25.0 g of sodium sulfate in enough water to prepare 250 mL of solution.
 - What is the molarity of sodium sulfate in the solution?
 - What are the molarities of the sodium and sulfate ions in the solution?
 - How many moles of sodium ions are present in 17 mL of the solution?
- A solution is labeled 0.0650 M K_3PO_4 .
 - How many moles of K^{1+} ions are present in 500 mL of this solution?
 - How many moles of PO_4^{3-} ions are present in 500 mL of this solution?
 - How many grams of K_3PO_4 are present in 50 mL of this solution?
- A solution of K_2SO_4 , which has a volume of 75.0 mL, contains 0.0048 moles of potassium ions. What is the molarity of the K_2SO_4 solution?
- What mass of KCl is required to make 45 mL of a 0.13 M KCl solution? How many moles of chloride ion are present in the solution?
- What are the two steps involved in solvation?
- Explain the meaning of *like dissolves like*.
- Explain the hydrophobic effect.
- Indicate whether each of the following substances are more soluble in H_2O or C_6H_{14} :
a) KI b) C_8H_{18} c) grease d) $\text{CH}_3(\text{CH}_2)_{12}\text{OH}$
- Indicate whether each of the following substances are more soluble in H_2O or C_6H_{14} :
a) HF b) CH_3OH c) $\text{NaC}_2\text{H}_3\text{O}_2$ d) CH_4

- What are the characteristics of a good detergent?
- Differentiate between a monolayer and a micelle. Under what conditions is a detergent expected to form in each?
- Represent $\text{CH}_3(\text{CH}_2)_{15}\text{COONa}$ with symbol shown in Figure 10.4d.
- Identify each of the following as a weak, strong, or nonelectrolyte:
a) CCl_4 b) NH_4NO_3 c) H_2CO_3 d) HNO_3 e) CH_3OH
- Identify each of the following as a weak, strong, or nonelectrolyte:
a) KF b) CH_3Cl c) HF d) NH_3 e) CH_3COONa
- What are the predominant solute species in aqueous solutions of the following? Write the molecule or the separated ions as appropriate.
a) CO_2 b) CaCl_2 c) PF_3 d) $\text{K}_2\text{Cr}_2\text{O}_7$ e) KOH
- What are the predominant solute species in aqueous solutions of the following? Write the molecule or the separated ions as appropriate.
a) CoCl_3 b) $\text{Pb}(\text{NO}_3)_2$ c) NH_4F d) $\text{C}_2\text{H}_5\text{OH}$ e) BrF_3
- What is the ratio of the force of attraction experienced by Ca^{2+} and SO_4^{2-} to that experienced by Al^{3+} and Cl^{1-} ? Assume that the ions are the same distance apart and in the same medium.
- What is the ratio of the force of attraction experienced by Na^{1+} and Cl^{1-} to that experienced by Al^{3+} and P^{3-} ? Assume that the ions are the same distance apart and in the same medium.
- What property of water makes it a good solvent for ionic compounds? How is this property expressed in Coulomb’s Law?
- Which solid(s) can be used to make a solution that is 0.1 M in Pb^{2+} ions?
a) $\text{Pb}(\text{ClO}_4)_2$ b) PbCl_2 c) PbCrO_4 d) PbCO_3 e) PbS
- Which solid(s) can be used to make a solution that is 0.1 M in Zn^{2+} ions?
a) $\text{Zn}(\text{ClO}_4)_2$ b) ZnCl_2 c) ZnCrO_4 d) ZnCO_3 e) ZnS
- Which solid(s) can be used to make a solution that is 0.1 M in SO_4^{2-} ions?
a) PbSO_4 b) K_2SO_4 c) CuSO_4 d) BaSO_4 e) FeSO_4
- Which solid(s) can be used to make a solution that is 0.1 M in CrO_4^{2-} ions?
a) ZnCrO_4 b) K_2CrO_4 c) CuCrO_4 d) BaCrO_4 e) FeCrO_4

28. A student finds two unlabelled jars, one is BaSO_4 and the other is Na_2SO_4 . Suggest an easy way to determine which jar contains Na_2SO_4 .
29. A solution is known to contain one of the following cations: Na^{1+} , Ag^{1+} , or Fe^{2+} . The addition of chloride ion to part of the solution had no apparent effect, but addition of CrO_4^{2-} ion resulted in a precipitate. What is the identity of the cation in the original solution?
30. A solution is known to contain one of the following anions: Cl^{-} , SO_4^{2-} , or NO_3^{-} . What is the identity of the anion if a precipitate was observed with the addition of Pb^{2+} , but no precipitate formed with the addition of Ag^{1+} ?
31. Write net equations for any precipitation reactions that occur when the following 0.1 M solutions are mixed or write ‘no reaction’ if appropriate.
- manganese(II) chloride + sodium sulfide
 - iron(III) chloride + sodium carbonate
 - potassium sulfide + zinc nitrate
 - silver sulfate + barium iodide
 - lead acetate + lithium hydroxide
 - ammonium phosphate + copper(II) sulfate
32. Write net equations for any precipitation reactions that occur when the following 0.1 M solutions are mixed or write ‘no reaction’ if appropriate.
- potassium chromate + nickel(II) chloride
 - cadmium nitrate + ammonium carbonate
 - manganese(II) acetate + zinc sulfate
 - lithium perchlorate + silver acetate
 - barium nitrate + silver sulfate
 - cesium hydroxide + iron(III) acetate
33. Write the chemical equation of the dissolution of the following salts in water and give the K_{sp} expression.
- FeS
 - PbCl_2
 - $\text{Ca}_3(\text{PO}_4)_2$
34. Write the chemical equation of the dissolution of the following salts in water and give the K_{sp} expression.:
- $\text{Al}(\text{OH})_3$
 - Fe_2S_3
 - CoPO_4
35. What is the maximum concentration of Fe^{2+} ions that can exist in a solution in which $[\text{OH}^{-}] = 1.0 \times 10^{-7} \text{ M}$? $K_{sp}(\text{Fe(OH)}_2) = 8.0 \times 10^{-16}$
36. What is the maximum concentration of Pb^{2+} ions that can exist in a solution which is 0.10 M in chloride ion? $K_{sp}(\text{PbCl}_2) = 1.7 \times 10^{-5}$.
37. What is the K_{sp} of AgCN if the concentrations of silver and cyanide ions in a saturated solution of silver cyanide are each $1.1 \times 10^{-8} \text{ M}$?
38. What is the K_{sp} of BaCO_3 if the concentrations of barium and carbonate ions in a saturated solution of barium carbonate are each $9.0 \times 10^{-5} \text{ M}$?
- Review Appendix D4 if you need help on Exercises 39 - 42.**
39. A student mixes 1.50 L of 0.20 M K_2CrO_4 and 1.20 L of 0.30 M AgNO_3 .
- Write the net reaction that occurs.
 - How many moles of CrO_4^{2-} ion were added?
 - How many moles of Ag^{1+} ion were added?
 - How many moles of Ag_2CrO_4 precipitate?
 - How many grams of Ag_2CrO_4 precipitate?
40. A student mixes 25.0 mL of 0.20 M KCl and 15.0 mL of 0.30 M $\text{Pb}(\text{NO}_3)_2$.
- Write the net reaction that occurs.
 - How many moles of Cl^{-} ion were added?
 - How many moles of Pb^{2+} ion were added?
 - How many moles of PbCl_2 precipitate?
 - How many grams of PbCl_2 precipitate?
41. A student mixes 0.36 L of 0.10 M $\text{Ba}(\text{ClO}_4)_2$ and 0.52 L of 0.10 M Na_2SO_4 .
- Write the net reaction that occurs.
 - How many moles of SO_4^{2-} ion were added?
 - How many moles of Ba^{2+} ion were added?
 - How many moles of BaSO_4 precipitate?
 - How many grams of BaSO_4 precipitate?
42. A student mixes 78 mL of 0.17 M $\text{Fe}(\text{NO}_3)_3$ and 85 mL of 0.20 M Na_2CO_3 .
- Write the net reaction that occurs.
 - How many moles of CO_3^{2-} ion were added?
 - How many moles of Fe^{3+} ion were added?
 - How many moles of $\text{Fe}_2(\text{CO}_3)_3$ precipitate?
 - How many grams of $\text{Fe}_2(\text{CO}_3)_3$ precipitate?

Chapter 11

Electron Transfer And Electrochemistry

- 11.0 Introduction*
- 11.1 Electron Transfer or Redox Reactions*
- 11.2 Half-Reactions*
- 11.3 Galvanic Cells*
- 11.4 Standard Reduction Potentials*
- 11.5 Writing Redox Reactions*

- 11.6 Common Batteries*
- 11.7 Corrosion*
- 11.8 Electrolytic Cells*
- 11.9 Chapter Summary and Objectives*
- 11.10 Exercises*

11.0 INTRODUCTION

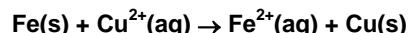
Electron transfer reactions, reactions in which electrons are transferred from one reactant to another, constitute one of the broadest and most important classes of reactions in chemistry. This should not be too surprising when we consider the central role of the electron in chemistry. All reactions that involve oxygen, such as combustion and corrosion of metals, are electron transfer reactions. Biological processes, such as photosynthesis, respiration, and the breakdown of food molecules, are connected sequences of complex, electron transfer reactions that serve to transport and utilize energy received from the sun. Batteries extract the free energy from electron transfer reactions. In this chapter, we introduce this important field of study.

THE OBJECTIVES OF CHAPTER 11 ARE TO:

- explain the electron transfer process and define the terms associated with redox reactions;
- describe galvanic cells;
- explain how balanced chemical equations are written for electron transfer reactions;
- show how to calculate standard cell potentials and how to use them to predict whether a redox process is extensive;
- describe some common batteries;
- explain the process of corrosion; and
- describe electrolytic cells.

11.1 ELECTRON TRANSFER OR REDOX REACTIONS

The solution of CuSO_4 in Figure 11.1a has a deep blue color due to the presence of aqueous Cu^{2+} ions. When steel wool, which is primarily iron, is immersed into such a solution and allowed to sit for a time, the color of the solution begins to pale, and iron atoms in the steel dissolve to be replaced with a red-brown coating of metallic copper (Figure 11.1b). Our conclusion is that the Cu^{2+} ions are converted into Cu atoms as the blue color fades and metallic copper forms. The steel wool dissolves as the Fe atoms in the steel wool enter the solution as Fe^{2+} ions. The chemical equation for the reaction is



In the reaction, an Fe atom donates two electrons to a Cu^{2+} ion, so Fe is an **electron donor** and Cu^{2+} is an **electron acceptor**. The loss of two electrons increases the oxidation state of Fe from 0 to +2, and the gain of two electrons by Cu^{2+} reduces its oxidation state from +2 to 0. The loss and gain of electrons are such important processes as are the substances involved in the electron transfer that they are given special names,

Oxidation is a loss of electrons. Oxidation increases the oxidation state of an atom.

Reduction is a gain of electrons.* Reduction reduces the oxidation state of an atom.

Oxidants or **oxidizing agents** are substances that oxidize other substances. They do so by accepting electrons from the other substance. The gain of electrons reduces them.

Reducants or **reducing agents** are substances that reduce other substances. They do so by donating electrons to the other substance. The loss of electrons oxidizes them.

Electron transfer reactions always involve both reduction and oxidation, so they are frequently referred to as **redox reactions**.

Electrons transfer from a set valence orbitals on the reductant, called the **donor orbitals**, into a set of unfilled orbitals on the oxidant called the **acceptor orbitals**. Thus, electron transfer usually empties the donor orbitals, but once emptied, these orbitals can accept electrons; *i.e.*, a redox reaction converts the reductant into an oxidant. Similarly, once the acceptor orbitals have accepted electrons, the orbitals have electrons they can donate; *i.e.*, the acceptor orbitals are converted into donor orbitals. The oxidant and reductant that are converted into one another form a **redox couple**. We represent redox couples as oxidant/reductant. Each redox reaction has two redox couples. The two couples in the reaction we are studying are the Fe^{2+}/Fe couple and the Cu^{2+}/Cu couple.

The abbreviations OX and RED, are used for oxidant and reductant, respectively. A

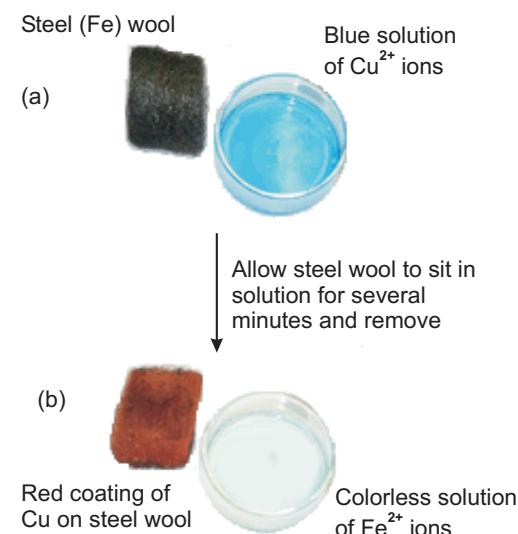
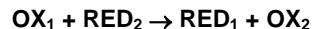


Figure 11.1 $\text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}$

(a) Steel wool (Fe) and a blue solution of Cu^{2+} . (b) Steel wool with a red-brown coating of metallic copper and a solution of Fe^{2+} . The slight blue tint of the solution is due to unreacted Cu^{2+} .

* There are several mnemonics that aid in remembering these terms. For example, “OIL RIG” stands for **Oxidation Is Loss of electrons**, and **Reduction Is Gain of electrons**.

subscript is then used to distinguish substances. For example, if we use 1 for Cu and 2 for Fe, then $\text{OX}_1 = \text{Cu}^{2+}$ ions (the oxidized form of Cu), and $\text{RED}_2 = \text{Fe}$ atoms (the reduced form of Fe). A gain of electrons by OX_1 converts it into the reducing agent RED_1 . Similarly, the loss of electrons by RED_2 converts it into an oxidizing agent OX_2 . Thus, as shown in the following, a redox reaction contains oxidants and reductants on both sides:



The various terms introduced to this point are summarized in the margin.

We saw in Section 9.7 that $\Delta G < 0$ for all spontaneous processes carried out at constant temperature and pressure. Thus, electrons transfer spontaneously from Fe to Cu^{2+} because their free energy is lower on Cu than on Fe. The following factors affect the value of ΔG :

1. the energy difference between the donor and acceptor orbitals;
2. the bond energies of any bonds that must be broken or formed; and
3. entropy effects.

The first factor usually dominates because orbital energy differences are usually large, bond energies often cancel in simple processes, and entropy is seldom important in reactions that do not involve gases. In general,

The acceptor (unfilled) orbitals on good oxidants are at relatively low energy, and the electrons on good reductants are at relatively high energy.

However, the other factors can dictate the spontaneous direction of electron transfer when the orbital energies are not very different.

Example 11.1

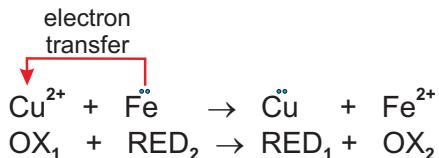
Use the diagrams for the valence orbitals of A and B in the margin to answer the following. Assume that orbital energy differences dominate ΔG .

a) Which is the better reductant and which is the better oxidant?

The highest energy electrons on A (green circle in margin figure) are much higher in energy than those on atom B (red circle), so A is the better reducing agent. The lowest-energy unfilled orbital on B (yellow ellipse) is lower in energy than the unfilled orbitals on A, which are too high in energy to be shown, so B is the better oxidizing agent.

b) Will B oxidize A to A^{4+} ; i.e., is $\text{A} + 2\text{B} \rightarrow \text{A}^{4+} + 2\text{B}^{2-}$ spontaneous?

For this reaction to occur, all four valence electrons on A would have to transfer to the empty orbital on B. While the high-energy electrons (green circle) are higher in energy and would transfer, the low-energy electrons (red circle) are at lower energy than the unfilled orbital on B and will not transfer. B is not a strong enough oxidant to oxidize A to A^{4+} .



OX_1

- Oxidizing agent or oxidant
- Substance that is reduced during reaction
- Electron acceptor
- That half of redox couple 1 in the higher oxidation state

RED_2

- Reducing agent or reductant
- Substance that is oxidized during the reaction
- Electron donor
- That half of redox couple 2 in the lower oxidation state

RED_1

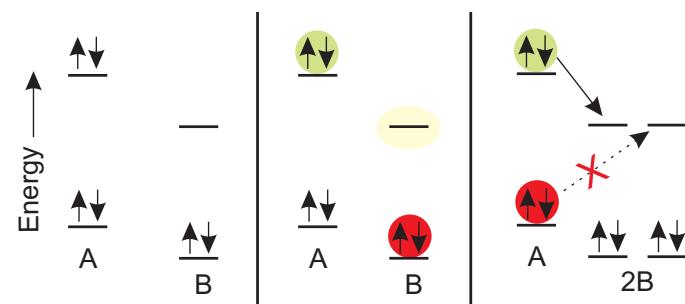
- Reduced form of OX_1

OX_2

- Oxidized form of RED_2

OX_1/RED_1 and OX_2/RED_2

- Redox couples involved in the reaction



Example 11.1

Example 11.1a

Example 11.1b

c) Will A reduce B to B^{2-} ; i.e., is $A + B \rightarrow A^{2+} + B^{2-}$ spontaneous?

The empty orbital on B is lower in energy than the high-energy electrons of A (green circle), so the electrons transfer spontaneously from A to B. B is a strong enough oxidant to oxidize A to A^{2+} . Alternatively, A is a strong enough reductant to reduce B to B^{2-} .

d) Will B^{2+} oxidize A to A^{4+} ; i.e., is $A + 2B^{2+} \rightarrow A^{4+} + 2B$ spontaneous?

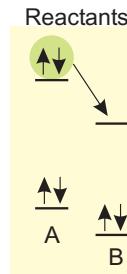
Both valence orbitals are empty in the B^{2+} ion, and they are lower in energy than all of the valence electrons on A, so all four electrons transfer spontaneously. One B^{2+} would accept the high-energy pair ($A + B^{2+} \rightarrow A^{2+} + B$), and a second B^{2+} would accept the low-energy pair ($A^{2+} + B^{2+} \rightarrow A^{4+} + B$). Thus, B^{2+} is a strong enough oxidizing agent to oxidize A to A^{4+} .

The number of electrons gained during the reduction, the number of electrons lost during the oxidation, and the number of electrons transferred during the redox reaction are all the same number, n. For example, the reaction between Cu^{2+} and Fe involves a gain of two electrons by Cu^{2+} , a loss of two electrons by Fe, and is a two-electron transfer from Fe to Cu^{2+} ; i.e., n = 2 electrons. To determine the number of electrons transferred,

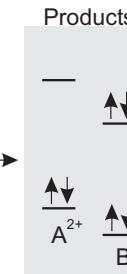
1. Identify the oxidant and reductant.
2. Determine the oxidation state changes of the atoms involved in the oxidation and reduction.
3. Multiply the oxidation state change of the atoms involved in the oxidation or reduction by the number of atoms involved in the process to obtain n, the number of electrons transferred.

Redox reactions often involve ions that are not involved in the electron transfer, and the species that are involved can be polyatomic ions or molecules with several elements, so the identities of the oxidant and reductant are not always obvious. Although, the change in oxidation number is attributed to a single atom in the molecule or ion, the entire ion or molecule is considered to be the oxidizing or reducing agent. The following guidelines can be helpful in identifying the atoms whose oxidation states* are changing:

- a. Atoms appearing in elements are always being oxidized or reduced.
- b. O and H often appear as H_2O , OH^{1-} , and/or H^{1+} , but they are not involved in the electron transfer unless they are elemental (O_2 or H_2), hydride (H^{1+}), or peroxide (O_2^{2-}).
- c. Most transition elements can exist in several oxidation states, so they are involved in many redox reactions.
- d. The central atoms of polyatomic ions frequently undergo oxidation or reduction.



Example 11.1c



Example 11.1d

* Oxidation states were discussed in Section 4.4. A review of that material would help your understanding here.

Example 11.2

Identify the oxidants and reductants in the following redox reactions.



O₂ is elemental and is the oxidant as the oxidation state of O changes from 0 in O₂ to -2 on the right. C₁₂H₂₂O₁₁ is the reducing agent. Assigning oxidation states of +1 to H and -2 to O allows us to determine that C is zero in C₁₂H₂₂O₁₁, while it is +4 in CO₂. Each of the 24 O atoms in 12O₂ undergoes a two-electron oxidation (0 to -2), so it is a 48-electron reduction. Similarly, each of the 12 C atoms undergoes a four-electron oxidation (0 to +4), so it is a 48-electron oxidation.* Thus, n = 48 electrons.



Elemental copper undergoes a two-electron oxidation from 0 to +2, so it is the reducing agent. Each of the three Cu atoms undergoes a two-electron oxidation, so this is a 3 x 2 = 6 electron oxidation. NO₃¹⁻ is then identified as the oxidant. The oxidation state of N changes from +5 in NO₃¹⁻ to +2 in NO. Each N undergoes a three-electron reduction so this is a 2 x 3 = 6 electron reduction. Consequently, n = 6.

* This is a redox reaction that does not involve an electron transfer because the transfer of 48 electrons requires the formation of C⁴⁺ and O²⁻ ions, while all of the product and reactant bonds are covalent, and all of the atoms have zero formal charge. The bonds become more polar but not ionic, so electrons move away from carbon atoms and toward oxygen atoms, but they are not transferred.

Example 11.3

How many electrons are required for the reduction of 0.15 mol of Cr₂O₇²⁻ to Cr³⁺?

First, balance the Cr atoms in the electron transfer: Cr₂O₇²⁻ → 2Cr³⁺

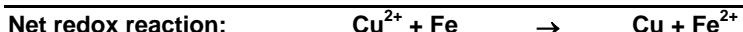
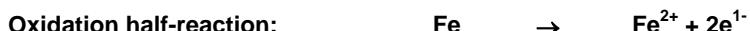
The oxidation state of chromium is +6 in Cr₂O₇²⁻ and +3 in Cr³⁺, so 3 mol electrons are required for each mole of Cr. Use the factor-label method to determine moles of electrons.

$$0.15 \text{ mol Cr}_2\text{O}_7^{2-} \times \frac{2 \text{ mol Cr}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} \times \frac{3 \text{ mol e}^1}{1 \text{ mol Cr}} = 0.90 \text{ mol e}^1$$

11.2 HALF-REACTIONS

A redox reaction can be written as the sum of two half-reactions: oxidation and reduction.

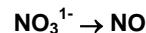
The two half-reactions for the reaction of iron and copper (II) are:



The two half-reactions indicate the changes that occur in each of the two redox couples. In this reaction, two electrons are given up in the oxidation half-reaction, and two electrons

are gained in the reduction half-reaction. Summing the two half-reactions yields the net reaction. Electrons are neither created nor destroyed in a redox process, so *the number of electrons lost in the oxidation half-reaction must equal the number gained in the reduction half-reaction*. Electrons appear in half-reactions, but they never appear in a net reaction!

Although we will use tabulated half-reactions to construct balanced redox reactions, it is informative to see why some half reactions contain atoms that are not involved in the electron transfer. Consider the half-reaction for the reduction of NO_3^{1-} to NO.



The nitrogen atom is being reduced from +5 in NO_3^{1-} to +2 in NO, so three electrons are required to reduce NO_3^{1-} to NO.



However, neither the charge nor the number of oxygen atoms is balanced in the above equation. Water serves as a source of oxygen atoms in aqueous solutions, so H_2O molecules must be added to the right side to balance the oxygen atoms. However, the addition of water also introduces hydrogen atoms. Recall from Section 10.5 that an Arrhenius acid is a substance that produces H^{1+} ions in water, so H^{1+} ions can be used to balance hydrogen atoms and charge in acidic solutions. The half-reaction for the reduction of NO_3^{1-} in acid is



Both the atoms and the charge are now balanced. Nitrate ion in the presence of H^{1+} is nitric acid, a strong acid and a strong oxidant. The above half-reaction would be used in any reaction involving nitric acid as an oxidant.

We have seen that Fe spontaneously reduces copper(II) ion. We know from experience that iron reacts with water to form rust, but the copper in water pipes does not corrode. How can we predict whether a redox reaction is spontaneous? To answer that question, we introduce an important field of chemistry known as electrochemistry and then use it to quantitatively rate the oxidizing and reducing powers of reactants.

11.3 GALVANIC CELLS

Recall that free energy is released in all spontaneous processes, and it is the energy that is free to do work. When steel wool is placed in a solution of Cu^{2+} , the released free energy of the spontaneous redox reaction simply warms the solution. However, the released free energy can be harnessed to extract work from the reaction by separating the two half-

reactions and forcing the transferred electrons to move through an external circuit. The marriage of electrical conduction through a circuit and redox chemistry is called **electrochemistry**. The apparatus used is called an **electrochemical cell** and each half-reaction usually takes place in its own **half-cell**. Thus, electrochemical cells contain two half-cells just as redox reactions contain two half-reactions.

Electrochemical cells allow us to gain control of the free energy of the electrons in a redox reaction. We can extract work from spontaneous redox reactions in electrochemical cells called **galvanic cells**, or we can use an external power supply to change the relative free energies of the reactants and force non-spontaneous reactions to proceed in electrochemical cells called **electrolytic cells**. When a battery is discharging, it is a galvanic cell, but when it is recharging, it is an electrolytic cell. Galvanic cells are the major focus of this chapter, but electrolytic cells are discussed briefly in Section 11.8.

The maximum work that can be obtained from the electrons in a redox reaction equals the free energy decrease in the reaction; *i.e.*,

$$\text{Work done by electrons} = -\Delta G$$

Eq. 11.1

Electrochemical cells were investigated about 60 years prior to the discovery of the electron, so the early electrochemists expressed the work done in terms of charge and electrical potential rather than electrons and energy change. The absolute value of the charge on a mole of electrons is called the **faraday** and given the symbol \mathcal{F} . A faraday is Avogadro's number times the absolute value of the charge on a single electron.

$$1\mathcal{F} = (6.022 \times 10^{23} \text{ electrons/mol})(1.602 \times 10^{-19} \text{ C/electron}) = 96,500 \text{ C/mol.}$$

The work done by n moles of electrons (a charge of $n\mathcal{F}$ coulombs) being transferred through an electrical potential \mathcal{E} is given in Equation 11.2.

$$\text{Work done by electrons} = n\mathcal{F}\mathcal{E}$$

Eq 11.2

$n\mathcal{F}$ is the magnitude of the charge in coulombs that is transferred, and \mathcal{E} is the electrical potential difference through which the electrons move expressed in volts. A **volt (V)** is a joule per coulomb ($1V = 1 \text{ J/C}$), so Equation 11.2 gives the work done by the electrons in joules. Rearranging Equation 11.2 shows that the electrical potential equals the work done by the electrons divided by the number of coulombs. In other words, \mathcal{E} is the work that can be done by each coulomb of charge. Combining Equations 11.1 and 11.2 gives us the following relationship between the free energy of the redox reaction and the voltage that would be measured in the corresponding electrochemical cell:

$$\Delta G = -nFE = -96,500n\mathcal{E}$$

Eq 11.3

Equation 11.3 indicates that the cell potential (\mathcal{E}) becomes more positive as the free energy change of the redox reaction becomes more negative, which means that the amount of work that can be done by *each* electron increases as the cell potential becomes more positive.

A galvanic cell converts chemical potential energy into electrical energy by physically separating the two half-reactions and incorporating them into an electrical circuit. Electrochemical reactions occur at the surfaces of metals, the **electrodes** that are placed into each half-cell. Electrons are injected into the external circuit in the oxidation half-cell (**anode**) as the donor is oxidized and withdrawn from the circuit in the reduction half-cell (**cathode**) as the acceptor is reduced. A typical galvanic cell consists of four components: *anode half-cell, cathode half-cell, liquid junction, and load*.

- The anode half-cell houses the oxidation couple (Fe^{2+}/Fe). The anode is always the half-cell in which oxidation occurs. Oxidation is the loss of electrons, so electrons leave the anode during reaction. In the cell shown in Figure 11.2, the anode half-cell consists of a piece of metal (Fe) immersed in 1 M FeSO_4 (Fe^{2+}). The metal serves as the anode (the electrode for the oxidation half-reaction). Iron atoms at the surface of the anode each give up two electrons, which leave the anode and enter the electrical circuit. The resulting Fe^{2+} ions enter the solution as the iron electrode *dissolves*. The iron anode is an *active electrode* because it participates in the reaction.
- The cathode half-cell houses the reduction couple (Cu^{2+}/Cu). The cathode is always the half-cell in which reduction occurs. Reduction is the gain of electrons, so electrons enter the cathode during reaction. In the cell shown in Figure 11.2, the cathode half-cell consists of a piece of metal (Cu) immersed in 1 M CuSO_4 (Cu^{2+}). The metal servers as the cathode (the electrode for the reduction half-reaction). Electrons move from the anode to the cathode, where they transfer to Cu^{2+} ions in solution at the electrode surface. The metallic copper that results from the reduction of the Cu^{2+} ions deposits on and becomes a part of the cathode, which is also an active electrode.
- The liquid junction serves as a barrier to prevent mixing of the two half-cell solutions while allowing free movement of ions between them. A common liquid junction is a porous polymeric or ceramic material that is crisscrossed by very small, open channels through which ions can freely migrate. A special type of liquid junction is the salt bridge, which typically contains a gelled saturated KCl solution held within an open glass tube. As with any liquid junction, the salt bridge electrically “connects” the two half-cell solutions to allow charge to flow, while keeping the solutions physically separate. Each electron that flows through the circuit carries one unit of negative charge out of the anode compartment and into the cathode compartment. However, electrical neutrality must be maintained in each of these compartments, and the salt bridge is a reservoir of ions that can be used to maintain electrical neutrality. An electron flowing into the cathode can be balanced by either an anion flowing out of the cathode and into the salt bridge or by a cation flowing out of the bridge and into the cathode. For example, when

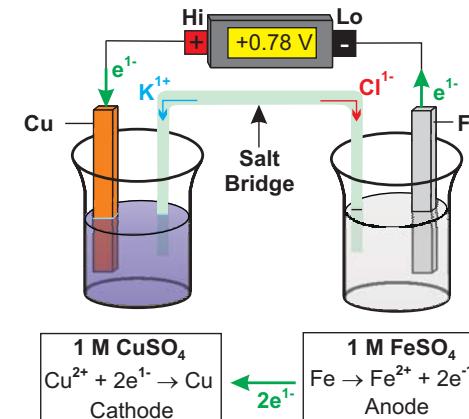


Figure 11.2 A galvanic cell

The galvanic cell using the Cu^{2+}/Cu and Fe^{2+}/Fe redox couples. Negative charge flows counterclockwise through the above cell with the electrons carrying the charge in the external circuit and the ions carrying it through the solution and the salt bridge.

two electrons flow into the cathode compartment shown in Figure 11.2, a Cu²⁺ ion is reduced to Cu metal. The reduction results in excess SO₄²⁻ ions in solution. The excess negative charge must then be neutralized either by two K⁺ ions flowing from the salt bridge into the cathode compartment or by a sulfate ion flowing into the salt bridge. The excess charge of the Fe²⁺ ion formed in the anode compartment can be balanced by two chloride ions flowing from the salt bridge or by the Fe²⁺ ion flowing into the bridge.

- The load is simply a device that uses the energy released by the transferred electrons; it can be anything operated with a battery. A voltmeter, which measures the electrical potential difference between the cathode and anode, is the load in Figure 11.2. One terminal is labeled ‘Hi’ or ‘+’ and one labeled ‘Lo’ or ‘-’ and the cell potential is determined as $\varepsilon = \varepsilon_{\text{Hi}} - \varepsilon_{\text{Lo}}$, which is +0.78 V in the cell shown in Figure 11.2.

Electrons are negatively charged, so their free energy depends upon the electrical potential they experience; the more positive the potential, the lower their free energy.* Thus, electrons flow spontaneously from lower (more negative) electrical potential to higher (more positive) electrical potential because doing so lowers their free energy.

The potential difference experienced by electrons flowing from point A with an electrical potential of ε_A to point B where the electrical potential is ε_B is defined as their final electrical potential (ε_B) minus their initial electrical potential (ε_A); *i.e.*, $\varepsilon = \varepsilon_B - \varepsilon_A$.† If ε_B is more positive than ε_A , then $\varepsilon > 0$ (the electrical potential increases) and the electrons flow spontaneously from A to B. The same considerations hold for electrochemical cells. Electrons flow from those species that are being oxidized at the anode to those species that are being reduced at the cathode, so the cell potential is $\varepsilon = \varepsilon_{\text{cathode}} - \varepsilon_{\text{anode}}$. The potential of the electron after it is transferred is related to the **cathode half-cell potential**, $\varepsilon_{\text{cathode}}$, while the potential of the electron before it is transferred is related to the **anode half-cell potential**, $\varepsilon_{\text{anode}}$. If $\varepsilon_{\text{cathode}} > \varepsilon_{\text{anode}}$, then the electrons experience an increase in their electrical potential ($\varepsilon > 0$), and they flow spontaneously from the anode to the cathode.

All reactants in the cell shown in Figure 11.2 are in their standard state, so the cell potential is the potential difference between the cathode and the anode under *standard* conditions. Consequently it is called the **standard cell potential**, $\varepsilon^{\circ}_{\text{cell}}$.

$$\varepsilon^{\circ}_{\text{cell}} = \varepsilon^{\circ}_{\text{cathode}} - \varepsilon^{\circ}_{\text{anode}} \quad \text{Eq. 11.4}$$

$\varepsilon^{\circ}_{\text{cathode}}$ and $\varepsilon^{\circ}_{\text{anode}}$ are the standard half-cell potentials. The extent of reaction depends upon ΔG° , which can be determined from Equation 11.3 to be

$$\Delta G^{\circ} = -nF\varepsilon^{\circ} \quad \text{Eq. 11.5}$$

$\Delta G^{\circ} < 0$ if $\varepsilon^{\circ}_{\text{cell}}$ is positive, so a reaction is extensive if the standard cathode half-cell potential ($\varepsilon^{\circ}_{\text{cathode}}$) is greater than the standard anode half-cell potential ($\varepsilon^{\circ}_{\text{anode}}$). Thus, we

* The effective nuclear charge (Section 3.2) represents the electrical potential experienced by the valence electrons. Recall that orbital energies decrease as Z_{eff} increases. This is equivalent to saying that orbital energies decrease as the electrical potential they experience becomes more positive.

† ε , not $\Delta\varepsilon$, is used even though it is the potential difference because ε is defined as the potential difference.

could predict the extent of a redox reaction if we knew the relative values of the standard half-cell potentials of the redox couples.

11.4 STANDARD REDUCTION POTENTIALS

Although we cannot measure a half-cell potential, we can measure the potential *difference* between two half-cells. *Relative* half-cell potentials can be obtained by defining one half-cell as a reference against which all other half-cells can be measured. Which half-reaction we choose for the reference half-cell and the value we assign its potential are arbitrary. The decision, made many decades ago, was to use the **standard hydrogen electrode (SHE)** as the reference and assign it a value of exactly 0 V. The SHE half-reaction is



By convention, the half-cell to be measured is connected to the ‘Hi’ terminal, so it is *assumed* to be the cathode or the reduction half-reaction. The SHE is then connected to the ‘Lo’ terminal, so it is *assumed* to be the anode or oxidation half-reaction. If both cells are in their standard states, then the resulting cell potential is the **standard reduction potential** of the half-cell. It is a ‘reduction potential’ because the half-cell is connected to the ‘Hi’ terminal. The standard reduction potentials for the Fe^{2+}/Fe and Cu^{2+}/Cu couples determined in this manner are -0.44 V and +0.34 V, respectively.*

The standard reduction potential of a couple is the potential at which the couple is at equilibrium with the cathode. The reduction half-reaction is written in the following form:



\mathcal{E}° , the standard reduction potential of the couple, is the electrical potential (relative to the SHE) at which OX and RED are in equilibrium. The standard reduction potential of the Cu^{2+}/Cu couple is +0.34 V, so metallic copper is in *equilibrium* with its +2 ion at a potential that is 0.34 V higher than the SHE.



The standard reduction potential of the Fe^{2+}/Fe couple is -0.44 V, so metallic iron is in equilibrium with its +2 ions at a potential that is 0.44 V lower than the SHE.



Equilibrium implies that both the forward and reverse reactions occur at the same rate. If a SHE half-cell is connected to another SHE, $\mathcal{E}^{\circ} = 0$ V (both cells are at the same potential), and *both* of the following processes occur at the same rate:



* The cell connected to the Hi terminal is assumed to be the cathode by convention, but it may well be acting as the anode in the spontaneous process. This will be the case whenever the cell potential is negative. A negative cell potential means that the reaction is spontaneous in the reverse direction. Thus, the negative potential observed for the Fe/Fe^{2+} half-cell means that it is actually the anode in the spontaneous redox process. If the SHE had been connected to the ‘Hi’ side and the Fe/Fe^{2+} couple to the ‘Lo’ side, then +0.44 V would be measured. Cell potentials measured with the SHE connected to the ‘Hi’ side are referred to as oxidation potentials. We consider only reduction potentials in this text.

However, if a SHE is connected to a different redox couple, one process will be favored over the other.

- **Process a** is favored when the SHE is paired with a redox couple with a more negative standard reduction potential. Thus, when the SHE is attached to Fe^{2+}/Fe at -0.44 V, electrons move to H^{1+} from Fe because H^{1+} is at the more positive potential. In this case, H^{1+} is reduced and Fe is oxidized.
- **Process b** is favored when the SHE is paired with a redox couple with a more positive standard reduction potential. Thus, when the SHE is attached to Cu^{2+}/Cu at +0.34 V, electrons flow from H_2 to Cu because Cu^{2+} is at the more positive potential. In this case, H_2 is oxidized and Cu^{2+} is reduced.

Electrons transfer from more negative to more positive electrical potential, so the reducing power of a reductant increases as its electrical potential decreases, and the oxidizing power of an oxidant increases as its electrical potential increases. That is,

Good oxidizing agents are those oxidants (OX) in redox couples with high (positive) standard reduction potentials, while good reducing agents are those reductants (RED) in redox couples with low (negative) standard reduction potentials.

The standard reduction potential of a Fe^{2+}/Fe couple (-0.44 V) is lower than that of a Cu^{2+}/Cu couple (+0.34 V), so Fe is a better reductant than Cu, and Cu^{2+} is a better oxidant than Fe^{2+} .

As shown in Figure 11.3, the standard cell potential is the difference between the standard reduction potentials of the two redox couples. The electrons start on an Fe atom (the better reducing agent) at -0.44 V and transfer to Cu^{2+} (the better oxidant) at +0.34 V. The change in electrical potential experienced by the electrons is equal to the difference between the two standard reduction potentials:

$$\mathcal{E}_{\text{cell}}^{\circ} = \mathcal{E}_{\text{cathode}}^{\circ} - \mathcal{E}_{\text{anode}}^{\circ} = +0.34 - (-0.44) = +0.78 \text{ V.}$$

The electrons increase their electrical potential by 0.78 V by transferring from Fe to Cu. The *standard reduction potential of a couple is proportional to the negative of the standard free energy of the electron in that couple*. Electron transfer to a couple at higher standard reduction potential is extensive because the free energy of the electron is lower in the couple at the higher potential.

Table 11.1 (following page) lists the standard reduction potentials for several common half-reactions. They are arranged so that the standard reduction potential increases (free energy decreases) going down the table. Thus, *electrons flow spontaneously when the reductant is situated above the oxidant in the table*.

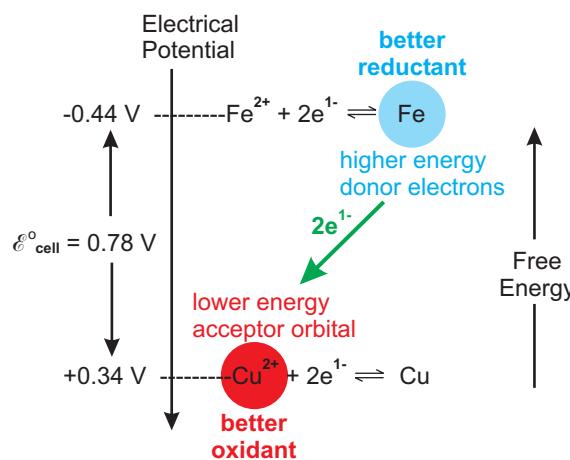


Figure 11.3 Standard reduction potentials of the Fe^{2+}/Fe and Cu^{2+}/Cu couples referenced to a SHE

The reduced form of the couple at more negative potential has the higher energy electrons and is the better reductant. The oxidized form of the couple at more positive potential has the lower energy orbital and is the better oxidant. The green arrow shows the direction of spontaneous electron transfer as the higher energy electrons on the donor flow into the empty orbital at lower energy on the acceptor.

Table 11.1 Standard Reduction Potentials at 25 °C.

Best Oxidants	$\text{OX} + ne^{1-}$	$\rightleftharpoons \text{RED}$	$E^\circ (\text{V})$
K ¹⁺ (aq) + e ¹⁻	$\rightleftharpoons \text{K(s)}$	-2.92	
Na ¹⁺ (aq) + e ¹⁻	$\rightleftharpoons \text{Na(s)}$	-2.71	
Mg ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Mg(s)}$	-2.36	
Al ³⁺ (aq) + 3e ¹⁻	$\rightleftharpoons \text{Al(s)}$	-1.66	
2H ₂ O + 2e ¹⁻	$\rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^{1-}(\text{aq})$	-0.83	
Zn ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Zn(s)}$	-0.76	
Fe ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Fe(s)}$	-0.44	
2H₂O + 2e¹⁻	$\rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^{1-}(\text{aq})$	-0.41^a	
PbSO ₄ (s) + 2e ¹⁻	$\rightleftharpoons \text{Pb(s)} + \text{SO}_4^{2-}(\text{aq})$	-0.36	
Ni ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Ni(s)}$	-0.23	
Sn ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Sn(s)}$	-0.14	
Pb ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Pb(s)}$	-0.13	
2H ¹⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{H}_2(\text{g})$	0.00	
Cu ²⁺ (aq) + 2e ¹⁻	$\rightleftharpoons \text{Cu(s)}$	+0.34	
O ₂ (g) + 2H ₂ O + 4e ¹⁻	$\rightleftharpoons 4\text{OH}^{1-}(\text{aq})$	+0.40	
I ₂ (s) + 2e ¹⁻	$\rightleftharpoons 2\text{I}^{1-}(\text{aq})$	+0.54	
Fe ³⁺ (aq) + e ¹⁻	$\rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77	
Ag ¹⁺ (aq) + e ¹⁻	$\rightleftharpoons \text{Ag(s)}$	+0.80	
O₂(g) + 4H¹⁺(aq) + 4e¹⁻	$\rightleftharpoons 2\text{H}_2\text{O}$	+0.88^a	
NO ₃ ¹⁻ (aq) + 4H ¹⁺ (aq) + 3e ¹⁻	$\rightleftharpoons \text{NO(g)} + 2\text{H}_2\text{O}$	+0.96	
Br ₂ (l) + 2e ¹⁻	$\rightleftharpoons 2\text{Br}^{1-}(\text{aq})$	+1.09	
O ₂ (g) + 4H ¹⁺ (aq) + 4e ¹⁻	$\rightleftharpoons 2\text{H}_2\text{O}$	+1.23	
Cr ₂ O ₇ ²⁻ (aq) + 14H ¹⁺ + 6e ¹⁻	$\rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33	
Cl ₂ (g) + 2e ¹⁻	$\rightleftharpoons 2\text{Cl}^{1-}(\text{aq})$	+1.36	
MnO ₄ ¹⁻ (aq) + 8H ¹⁺ + 5e ¹⁻	$\rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51	
PbO ₂ (s) + 4H ¹⁺ (aq) + SO ₄ ²⁻ (aq) + 2e ¹⁻	$\rightleftharpoons \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.69	
F ₂ (g) + 2e ¹⁻	$\rightleftharpoons 2\text{F}^{1-}(\text{aq})$	+2.87	

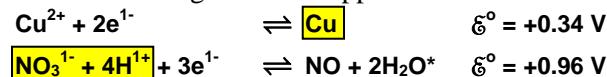
Best Reductants


Electron Free Energy

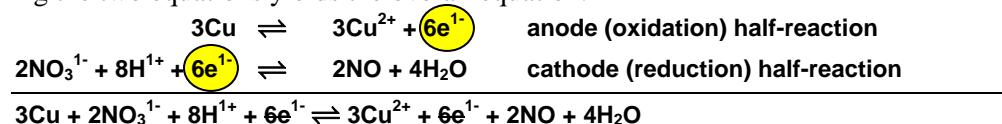
a. The O₂/H₂O and H₂O/H₂ half-cell potentials highlighted in yellow are for pure water. They are not the standard reduction potentials because [OH¹⁻] and [H¹⁺] are not 1.0 M.

11.5 WRITING REDOX REACTIONS

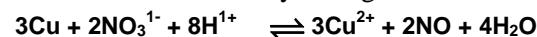
The number of electrons gained in the reduction half-reaction must equal the number lost in the oxidation half-reaction, so both the atoms and the number of electrons gained and lost must be balanced. The number of electrons transferred must be a multiple of the number shown for the half-reaction in Table 11.1. For example, consider the chemical equation for dissolving metallic copper in nitric acid. The two half-reactions are



The reactants, copper and nitric acid, are highlighted in yellow. All of the reactions in Table 11.1 are written as reductions, so one half-reaction must always be reversed to make it the oxidation. In this case, the Cu²⁺/Cu couple must be reversed because the half-reaction shows the metallic copper as a product, but it is a reactant in the reaction with nitric acid. In addition, both equations must be multiplied by an integer to make the number of electrons gained in the reduction of nitric acid equal to the number of electrons lost in the oxidation of copper. Each nitrate ion requires three electrons, but each copper atom gives up only two. The lowest common multiple (LCM)[†] of three and two is six, so the nitric acid half-reaction must be multiplied by two to obtain a six-electron gain, and the copper half-reaction must be reversed and multiplied by three to obtain a six-electron loss. Summing the two equations yields the overall equation.



The 6e⁻ on each side cancel, yielding the net balanced equation:



Electrons flow spontaneously from lower to higher potential, so redox reactions are extensive when the reducing agent is at a lower potential than the oxidizing agent. That is, *electron transfer is extensive when any half-reaction is coupled with the reverse of a half-reaction that is above it in Table 11.1*. This reactivity is summarized in Figure 11.4. The standard potential of the reaction would be the following if it were carried out in an electrochemical cell:

$$\mathcal{E}_{\text{rxn}}^{\circ} = \mathcal{E}_{\text{reduced}}^{\circ} - \mathcal{E}_{\text{oxidized}}^{\circ}$$

[†] The lowest common multiple (LCM) of two numbers is the smallest multiple that is exactly divisible by both numbers.

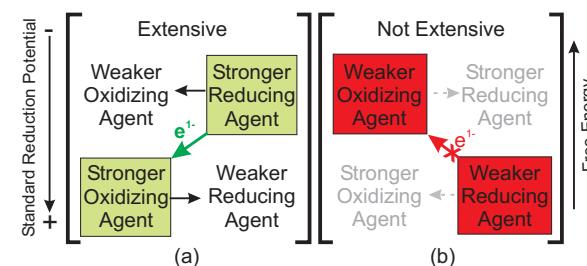


Figure 11.4 Relative position of reactants and products on a standard reduction potential chart

(a) The reaction of the stronger oxidizing and reducing agents to produce the weaker oxidizing and reducing agents is extensive. (b) The reaction of the weaker oxidizing and reducing agents to produce stronger oxidizing and reducing agents is not extensive. Electrons are transferred extensively downhill in Table 11.1 because that is the direction of more positive potential and lower free energy.

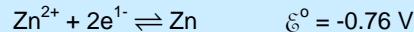
$\mathcal{E}_{\text{reduced}}^{\circ}$ is the standard reduction potential of the couple that is reduced, and $\mathcal{E}_{\text{oxidized}}^{\circ}$ is that of the couple that is oxidized during the reaction.

Example 11.4

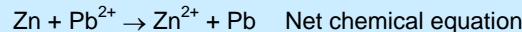
Write the anode and cathode half-reactions and the balanced chemical equation for the galvanic cells constructed from the following pairs of redox couples. Determine the standard cell potential for each cell.

a) Pb/Pb²⁺ and Zn/Zn²⁺

Get the reduction half-reactions and their standard reduction potentials from Table 11.1



The oxidation half-reaction is the one at more negative potential, so Zn is oxidized, and Pb²⁺ is reduced in the cell. Both half-reactions involve two electrons, so the balanced chemical equation is the sum of the following two reactions:

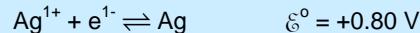


$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = -0.13 - (-0.76) = 0.63 \text{ V}$$

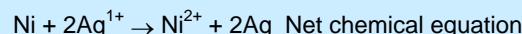
$\mathcal{E}^{\circ}_{\text{cell}}$ is positive, so the reaction is extensive.

b) Ni²⁺/Ni and Ag¹⁺/Ag

The two relevant half-reactions and their standard reduction potentials are



Reverse the half-reaction at more negative potential to obtain the oxidation and multiply the Ag¹⁺/Ag half-reaction by 2 to make the number of electrons gained by Ag¹⁺ equal to the number lost by the Ni. The balanced chemical equation for the cell is the sum of the two reactions.



Standard reduction potentials indicate the free energy of the electron(s), so multiplying a half-reaction by some number does not affect its standard reduction potential. Thus, multiplying the Ag¹⁺/Ag half-reaction by 2 does not change the potential at which the couple is at equilibrium. The cell potential is

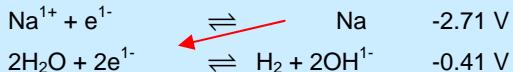
$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = +0.80 - (-0.23) = 1.03 \text{ V}$$

Example 11.5

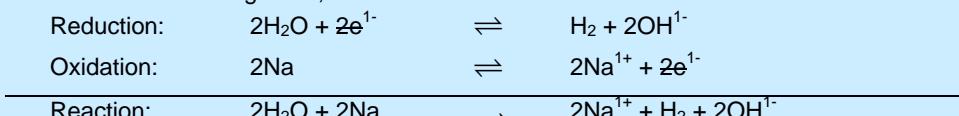
Write net equations or “no reaction” and determine $\mathcal{E}^{\circ}_{\text{rxn}}$ for each process.

a) Metallic sodium is added to water.

The two half-reactions and their standard reduction potentials are as follows:



The reductant (Na) is situated above the oxidant (H_2O) in Table 11.1, so the reaction is extensive.* Na is a reactant, not a product, so its half-reaction must be reversed. The half-reaction must also be multiplied by two in order to balance electrons lost and gained, but multiplying the reaction by a number does not *change the potential*. Rewriting the two half-reactions and summing them,



$$\mathcal{E}^{\circ}_{\text{rxn}} = \mathcal{E}^{\circ}_{\text{reduced}} - \mathcal{E}^{\circ}_{\text{oxidized}} = -0.41^{\$} - (-2.71) = +2.30 \text{ V}$$

The very high, positive value of $\mathcal{E}^{\circ}_{\text{rxn}}$ indicates that this is an extensive reaction.

b) Copper is placed in hydrochloric acid.

The SHE is used for strong acids other than nitric acid.



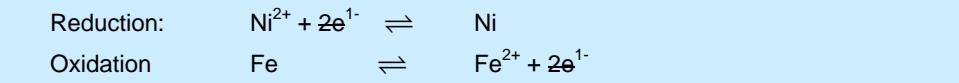
$$\text{No reaction. } \mathcal{E}^{\circ}_{\text{rxn}} = \mathcal{E}^{\circ}_{\text{reduced}} - \mathcal{E}^{\circ}_{\text{oxidized}} = 0.00 - 0.34 = -0.34 \text{ V}$$

The reductant is below the oxidant in Table 11.1, so electrons would have to flow to higher free energy, which is also indicated by the fact that $\mathcal{E}^{\circ}_{\text{rxn}}$ is negative. Thus, copper does not react with most strong acids.[†]

c) Iron is placed into a NiSO_4 solution.



The reductant is above the oxidant in Table 11.1, so electron transfer is extensive.



$$\mathcal{E}^{\circ}_{\text{rxn}} = \mathcal{E}^{\circ}_{\text{reduced}} - \mathcal{E}^{\circ}_{\text{oxidized}} = -0.23 - (-0.44) = +0.21 \text{ V}$$

* Note that red arrows are used in this example to emphasize the direction of the required electron flow. In Example 11.5a, the arrow shows that the electrons must flow from Na to H_2O , which is toward the couple at less negative potential and lower free energy.

[§] Note the reduction potential of pure water is used, not the standard reduction potential, which would require standard concentrations, i.e., $[\text{OH}^{1-}] = 1.0 \text{ M}$, which is a strongly basic solution.

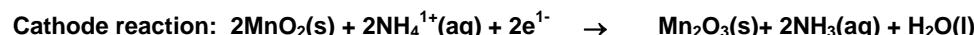
[†] The SHE is used for strong acids only when it is the H^{1+} that is the oxidant. However, some acids are much stronger oxidants due to their anion. Nitric acid ($\mathcal{E}^{\circ} = 0.96 \text{ V}$) is one example. Thus, copper does not react with most strong acids, but it does react with nitric acid because NO_3^{-} in acid is a stronger oxidant than H^{1+} .

11.6 COMMON BATTERIES

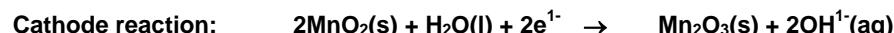
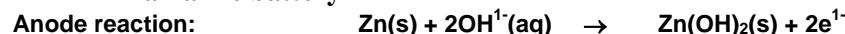
Batteries are self-contained, galvanic electrochemical cells (Section 11.3). There are many types of batteries, but we consider only three.

DRY CELL AND ALKALINE BATTERIES

Figure 11.5 shows either a dry cell or an alkaline battery, depending on the nature of electrolyte paste. This is the most commonly used battery in flashlights. The zinc base is an active anode (-). A graphite rod, which is immersed in an acidic electrolyte paste, serves as an inactive cathode (+). The paste is a moist combination of MnO_2 , NH_4Cl , ZnCl_2 , and water that is thickened with starch.



The cathode reaction is complicated and still not fully understood. It is known to involve the reduction of MnO_2 , but the reaction shown is but one possibility. The maximum cell voltage is 1.5 V. One of the major disadvantages of the dry cell is that it has a very short shelf life because the zinc container reacts with the acidic ammonium ions. To enhance the shelf life, the paste is made alkaline (basic) by replacing the NH_4Cl with KOH. The half-reactions for an **alkaline battery** are



MERCURY OXIDE AND SILVER OXIDE (BUTTON) BATTERIES

Button batteries are the small batteries used to power calculators, cameras, watches, hearing aids, *etc.* The mercury(II) oxide ($\xi = 1.3$ V) and silver oxide ($\xi = 1.6$ V) batteries are essentially the same as shown in Figure 11.6. The only difference is the cathode reaction, which is either the reduction of silver oxide or mercury(II) oxide. The porous separator serves as the liquid junction.

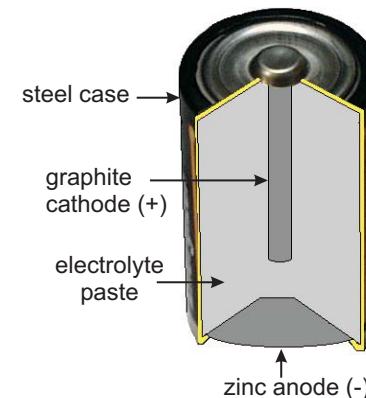
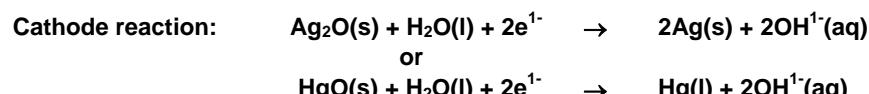
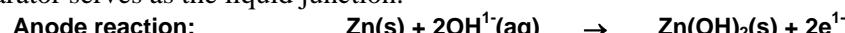


Figure 11.5 Dry cell battery

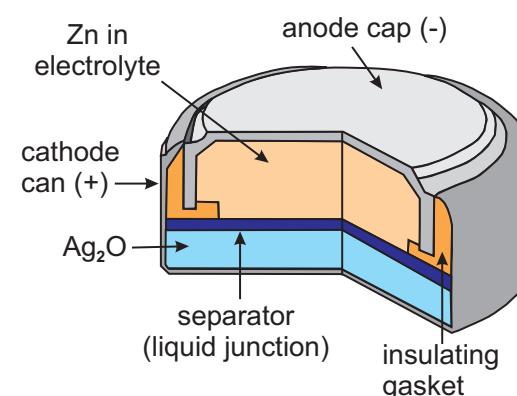
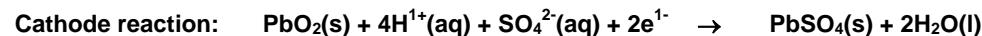
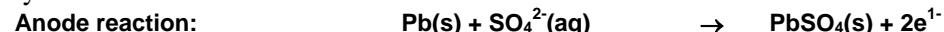


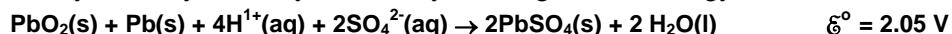
Figure 11.6 Silver oxide or button battery

LEAD-STORAGE BATTERY

Also known as the lead-acid battery, the lead-storage battery is the source of power for starting automobiles. A 12-V battery consists of six cells, each with a potential difference of 2V, connected in series. As shown in Figure 11.7, each cell consists of two lead grids, one packed with spongy Pb (anode) and the other with powdered PbO_2 (cathode). The cells are immersed in ~4.5 M sulfuric acid (H_2SO_4). The half-reactions for the lead storage battery are



Thus, when you start your car, you do so by utilizing the free energy of the reaction



Because the products are deposited on the electrodes, this reaction can be reversed by applying an external voltage across the battery. Thus, while your car is running, some of the energy of the combustion of gasoline is used to turn the generator (alternator), which generates the required voltage to reverse the battery reaction, thereby recharging the battery. Recharging the lead-storage battery is discussed in Section 11.8.

11.7 CORROSION

Many metals are good reducing agents, and those with reduction potentials more negative than -0.41 V (the non-standard reduction potential of pure water) react with water and oxygen. Such reactions can be very beneficial, but some can also be extremely costly. **Corrosion** is the *unwanted* oxidation of a metal. Approximately 20 to 25% of the steel produced in the United States is for the replacement of corroded steel! Although most metals corrode, we focus our discussion on the corrosion of iron, as it is the one most commonly encountered. We begin with the following observations:

1. A piece of corroded iron contains regions where rust (Fe_2O_3) has accumulated and regions where holes have formed in the iron. Due to the presence of holes in the corroded iron, it is often said to be 'pitted'. The two regions are often separated.
2. Iron will not rust in a dry climate; water is required.
3. Iron will not rust in water in the absence of O_2 .
4. Rusting is enhanced in the presence of acid.

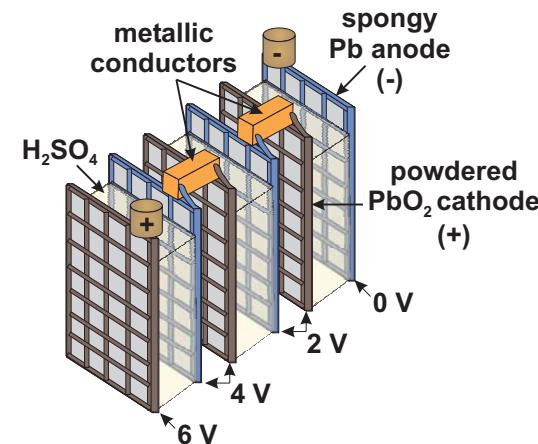
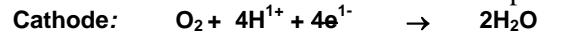


Figure 11.7 Lead-storage battery

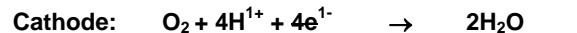
The potential of the cathode of each cell is 2 V higher than that of the anode. Metallic conductors keep the anode of each cell at the same potential as the cathode of the previous cell. For example, the anode of the first cell is at 0 V, so its cathode is at 2 V. The anode of the second cell is held at 2 V also, so the cathode potential is 4 V. The battery in the figure contains three cells and each cell increases the cell potential by 2 V, so the battery is a 6-V battery.

The mechanism shown in Figure 11.8 accounts for each of the preceding observations. The pits form at the anodic region as metallic iron is oxidized to iron(II), which passes into solution in the water drop. The electrons released by the iron oxidation are used to reduce O₂ at the cathode, where the importance of acid in the corrosion process can be seen. The two half-reactions and their standard reduction potentials are:



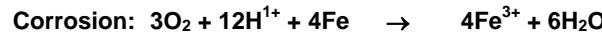
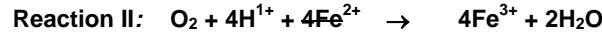
$$\mathcal{E}^\circ = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = 1.23 - (-0.44) = +1.67 \text{ V}^*$$

The Fe²⁺ ions in solution are further oxidized to Fe³⁺ by oxygen, either in solution or at the surface. The iron(III) precipitates as Fe₂O₃ (rust). Oxygen from the atmosphere is again the oxidizing agent. The following anode half-reaction has been multiplied by four to make the electrons released by Fe²⁺ equal to the number gained by O₂. The electrochemical reactions are



$$\mathcal{E}^\circ = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = 1.23 - 0.77 = +0.46 \text{ V}^*$$

The overall reaction for the corrosion of iron can be obtained by combining Reaction I and Reaction II. However, Reaction I must first be multiplied by two in order to deliver the four Fe²⁺ ions required in Reaction II. The Fe²⁺ ions then cancel in the summation:



The six H₂O molecules can be viewed as 12H¹⁺ + 6O²⁻, in which case, the 12H¹⁺ on each side cancel. Finally, 4Fe³⁺ + 6O²⁻ is equivalent to 2Fe₂O₃, which allows us to write the common chemical equation for the rusting of iron:

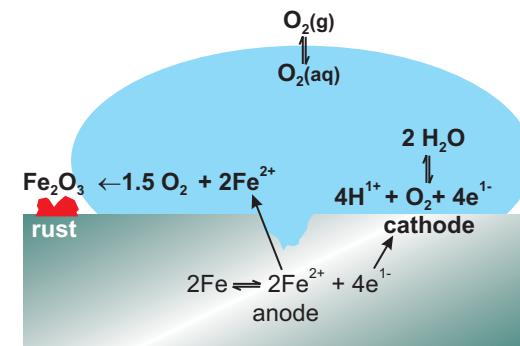
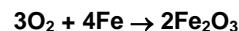


Figure 11.8 Corrosion of iron

The electrochemical reactions that occur when a slightly acidic water drop sits on top of a piece of iron

* The standard reduction potential is used here rather than the reduction potential of pure water because we are calculating the standard potential.

GALVANIZATION

When more than one metal is present, the more reactive metal (the one with a more negative \mathcal{E}°) reacts first. This fact is the basis of **galvanization**, the protection of one metal by the sacrifice of a more reactive metal. For example, the iron in an automobile body is *galvanized* by coating it with zinc, a more reactive metal (compare the \mathcal{E}° values in Table 11.1). When paint is scratched off the surface, the zinc coating is sacrificed ($\text{Zn} + \frac{1}{2}\text{O}_2 \rightarrow \text{ZnO}$) to preserve the iron and, therefore, the automobile body. Indeed, iron can be protected by placing it in contact with any more reactive metal.

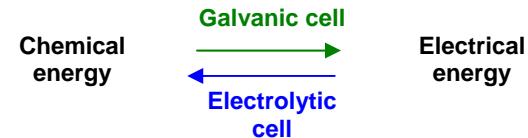
PASSIVATION

Metal surfaces can also be **passivated** with a protective coating of a metal oxide. One of the most common forms of *natural* passivation is the protection of aluminum. Aluminum is much more reactive than iron (see Table 11.1), yet it is used to make airplane bodies and outdoor furniture. Aluminum can be put to such uses, even though it corrodes, because, rather than dissolving, it forms a thin layer of Al_2O_3 on the outer surface that is impervious to further attack. The underlying aluminum metal is passivated by the protective coating. The galvanized iron in an automobile is also passivated because, as the sacrificial zinc is oxidized, it forms a zinc oxide coating, which then passivates the underlying iron.

11.8 ELECTROLYTIC CELLS

One of the major advantages of electrochemistry is that the free energy of the redox electrons can be adjusted by changing the voltage between the electrodes with an external power supply, such as a battery. In Example 11.5, we decided that Cu does not react with strong acids like HCl because \mathcal{E}° is negative, $\text{Cu} + 2\text{H}^{1+} \rightleftharpoons \text{Cu}^{2+} + \text{H}_2 \quad \mathcal{E}^\circ = -0.34\text{V}$. The negative value simply means that the donor orbital on Cu is at a lower free energy than the acceptor orbital on H^{1+} . Electrons do not flow uphill *spontaneously*, but they can be pushed uphill by connecting an external power supply to the cell. The power supply can provide the 0.34 V the electrons need to make this uphill climb. Forcing a nonspontaneous process to occur by the application of an external power supply is called **electrolysis**, and the cell in which it is accomplished is called an **electrolytic cell**. Thus, an electrolytic cell converts electrical energy into chemical energy, while a galvanic cell converts chemical energy into electrical energy.

Recharging batteries is a common example of electrolysis. Consider the lead-storage



battery discussed in Section 11.6 and represented in the margin. When the starter is used, the battery is a galvanic cell because electrons spontaneously flow from the Pb anode through the starter, where their energy is used to start the car, and then to the PbO₂ cathode. As this occurs, lead, lead oxide, and sulfuric acid are converted to lead sulfate and water. The ‘cranking power’ of the battery is the rate at which the reaction occurs. A battery rated with 550 amps of ‘cranking power’ generates ~1.7 g of PbSO₄ per second while the starter is in use. Clearly, the battery would not be able to perform for very long at that rate before all of the chemical reactants would be consumed, and the battery would be ‘dead’. To increase the life of the battery, part of the free energy derived from the combustion of the gasoline when the car is operating is used to run an electrical generator (alternator), which supplies the electrical needs of the car and recharges the battery. To recharge the battery, a voltage greater than the 12 V the battery delivers as a galvanic cell is applied across the electrodes in the reverse direction. The large voltage forces the battery to operate as an *electrolytic cell* as electrons are forced through the battery in the reverse direction, oxidizing PbSO₄ to produce PbO₂ at the anode and reducing PbSO₄ to Pb at the cathode. Thus, some of the free energy from the combustion of the gasoline is used to pump the electrons back uphill from lower energy orbitals into higher energy orbitals.

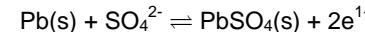
11.9 CHAPTER SUMMARY AND OBJECTIVES

Reduction is the gain of electrons, and oxidation is the loss of electrons. Spontaneous redox reactions involve a transfer of electrons from a donor (reducing agent) to an acceptor (oxidizing agent) that is lower in free energy. The free energy released by the reaction can be harnessed if the oxidation and reduction half-reactions are separated into compartments. Oxidation always occurs in the anode compartment and reduction always occurs in the cathode compartment. By measuring the cell potentials of the various half-reactions relative to the standard hydrogen electrode (SHE), we obtain the standard reduction potentials of the half-reactions. A large and negative standard reduction potential means that the reduced form is a very good reducing agent, while a large and positive standard reduction potential implies that the oxidized form is a good oxidizing agent.

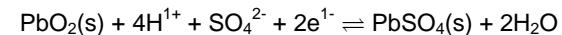
The cell potential is the potential difference (voltage) between the cathode and the anode: $\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}}$. If $\mathcal{E}_{\text{cell}} > 0$, the reaction is spontaneous, which means that energy can be extracted from it ($\Delta G < 0$). This type of cell is a galvanic cell. Galvanic

Discharging (Galvanic)

Anode



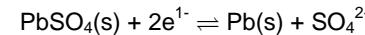
Cathode



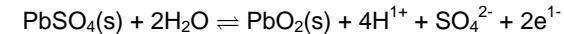
Electron flow: **anode → starter → cathode**

Charging (Electrolytic)

Cathode



Anode



Electron flow: **anode → alternator → cathode**

cells convert chemical potential energy into electrical potential energy. If $\xi_{\text{cell}} < 0$, the reaction is not spontaneous, and energy must be supplied to the cell for the reaction to occur. This type of cell is an electrolytic cell. Electrolytic cells convert electrical potential energy into chemical potential energy.

Metal corrosion is an electrochemical reaction that, in the case of iron, occurs on the iron surface in the presence of water, oxygen, and some acid. The overall reaction is the oxidation of iron metal by atmospheric oxygen to form iron(III) oxide. Galvanization and passivation are two ways to protect metal surfaces from corrosion.

Batteries are galvanic cells. The lead-storage battery in an automobile operates as a galvanic cell when the car is started or when the lights are on but the engine is not. However, it operates as an electrolytic cell when the engine is running, and the battery is being recharged.

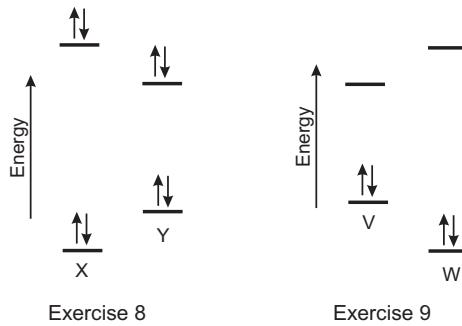
After studying the material in this chapter, you should be able to:

1. define oxidation and reduction and identify oxidizing and reducing agents (Section 11.1);
2. determine the number of electrons required to carry out an oxidation or a reduction (Section 11.1);
3. identify an oxidizing agent and a reducing agent based on an orbital energy diagram (Section 11.1);
4. write the half-reaction for a simple oxidation or reduction (Section 11.2);
5. identify the anode and cathode, indicate the direction of electron flow, and explain the function of the liquid junction in a galvanic cell (Section 11.3);
6. calculate standard cell potentials, given the standard reduction potentials of the half-reactions (Section 11.4);
7. use a table of standard reduction potentials to write balanced redox reactions and to predict if they would occur extensively (Section 11.5);
8. recognize common batteries and identify the anode and cathode (Section 11.6);
9. explain the corrosion of iron and how galvanization and passivation can be used to protect a metal from corroding (Section 11.7); and
10. explain the workings of an electrolytic cell (Section 11.8).

11.10 EXERCISES

- Define the oxidation and reduction processes.
- Describe oxidizing and reducing agents. What happens to each as it functions? What property makes a good oxidizing agent? What property makes a good reducing agent?
- Distinguish between donor and acceptor orbitals. Which orbital is on the oxidizing agent?
- Describe the factors that are important in determining the free energy of the following redox reaction: $\text{Pb(s)} + 2\text{Ag}^{1+}(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{Ag(s)}$.
- What change in potential does an electron experience when it moves from a potential of +0.5 V to one at -0.3 V? Is this a spontaneous process?
- What is a redox couple? Give three examples.
- The A¹⁺/A couple is 0.5 V more negative than the B²⁺/B couple. Which of the four species is the best oxidizing agent? Which is the best reducing agent? Write the balanced chemical equation for the spontaneous process that occurs when the two couples are connected in a galvanic cell.

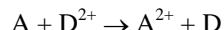
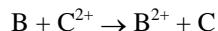
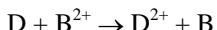
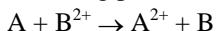
Use the following energy diagrams for X, Y, V, and W for Exercises 8 and 9



- Use the energy diagram for atoms X and Y to answer the following:
 - Draw the energy level diagram for the X²⁺ and Y²⁺ ions.
 - Write the standard half-reactions for the reduction of X²⁺ and Y²⁺, with the more negative reduction potential on top.
 - Of the four species, X, Y, X²⁺, Y²⁺, which is the best oxidizing agent? Which is the best reducing agent?
 - Write a balanced reaction, indicating the spontaneous reaction that occurs when X and Y are placed into solutions containing X²⁺ and Y²⁺.

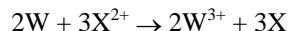
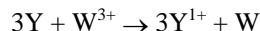
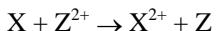
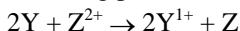
- Use the energy diagram for elements V and W to answer the following:
 - Write the standard reduction half-reactions for V, W, V²⁺ and W²⁺ and order them from most negative at top to most positive at the bottom.
 - Of the species, V²⁺, W²⁺, V, W, V²⁻, W²⁻, which is the best oxidizing agent? Which is the best reducing agent?
 - Indicate whether each of the following electron transfer reactions would be extensive:
 - $\text{V} + \text{W}^{2+} \rightarrow \text{V}^{2+} + \text{W}$
 - $\text{V}^{2-} + \text{W} \rightarrow \text{V} + \text{W}^{2-}$
 - $\text{W}^{2+} + \text{V}^{2+} \rightarrow \text{W} + \text{V}$
 - $\text{W}^{2+} + \text{V}^{2-} \rightarrow \text{W} + \text{V}$
 - $\text{V} + \text{W}^{2-} \rightarrow \text{V}^{2-} + \text{W}$
- Determine the oxidation state of nitrogen in each of the following molecules. See Section 4.4 for a review of oxidation states.
 - N₂
 - N₂H₄
 - NH₃
 - N₂O
 - N₂O₅
- Determine the oxidation state of carbon in each of the following:
 - CH₄
 - CH₂O
 - CO₂
 - CH₃F
 - CH₃OH
- Indicate whether each of the following chemical conversions requires an oxidizing agent, a reducing agent, or neither:
 - $\text{NO}_3^{1-} \rightarrow \text{NH}_3$
 - $\text{PO}_3^{3-} \rightarrow \text{PO}_4^{3-}$
 - $\text{AgCl} \rightarrow \text{Ag}^{1+} + \text{Cl}^{-}$
- Indicate whether each of the following chemical conversions requires an oxidizing agent, a reducing agent, or neither:
 - CO → CO₂
 - BaSO₄ → Ba
 - Hg₂Cl₂ → HgCl₂
- Determine the oxidizing and reducing agents and the number of electrons transferred in each of the following reactions:
 - $2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$
 - $\text{Pb} + \text{I}_2 \rightarrow \text{PbI}_2$
 - $\text{Hg}^{2+} + \text{NO}_2^{1-} + \text{H}_2\text{O} \rightarrow \text{Hg} + 2\text{H}^{1+} + \text{NO}_3^{1-}$
 - $2\text{MnO}_4^{1-} + 3\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 3\text{SO}_4^{2-} + 2\text{OH}^{1-}$
- Determine the oxidizing and reducing agents and the number of electrons transferred in each of the following reactions:
 - $3\text{C}_2\text{H}_5\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^{1+} \rightarrow 3\text{CH}_3\text{COOH} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O}$
 - $4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$
 - $5\text{Pb} + 2\text{MnO}_4^{1-} + 16\text{H}^{1+} \rightarrow 5\text{Pb}^{2+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$
 - $\text{C}_8\text{H}_{16} + 12\text{O}_2 \rightarrow 8\text{CO}_2 + 8\text{H}_2\text{O}$

16. The following processes are all spontaneous:



List the four redox couples that are involved in the above reactions in order of their standard reduction potentials in a manner similar to Table 11.1; *i.e.*, the most negative at the top.

17. The following processes are all spontaneous:



List the four redox couples that are involved in the above reactions in order of their standard reduction potentials with the most negative at the top.

18. Describe the role of the liquid junction (salt bridge) in an electrochemical cell. What type of ions (anions or cations) must flow into the cathode?

19. What is the difference between an anode and a cathode?

20. The standard reduction potentials for Hg^{2+} and Cr^{3+} are determined by measuring the voltage of the cell made by connecting a standard Cu^{2+}/Cu half-cell to the ‘Lo’ terminal of a voltmeter and a standard Hg^{2+}/Hg half-cell or standard Cr^{3+}/Cr half-cell to the ‘Hi’ terminal. The observed cell potentials were +0.54 V for Hg^{2+}/Hg and -1.10 V for Cr^{3+}/Cr .

- a) What are the standard reduction potential of mercury(II) and the *spontaneous* cell reaction between the Hg^{2+}/Hg and the Cu^{2+}/Cu couples.
b) What are the standard reduction potential of chromium(III) and the *spontaneous* cell reaction between the Cr^{3+}/Cr and the Cu^{2+}/Cu couples.
c) A Cr^{3+}/Cr half-cell and a Hg^{2+}/Hg half-cell are connected as a galvanic cell. Which compartment is the anode, and what is the cell voltage?

21. The standard reduction potentials for U^{3+} and In^{3+} are determined by measuring the voltage of the cell made by connecting a standard Ni^{2+}/Ni half-cell to the ‘Lo’ terminal of a voltmeter and a standard U^{3+}/U half-cell or standard In^{3+}/In half-cell to the ‘Hi’ terminal.

- a) If the voltmeter reading was -1.43 V when the U^{3+}/U half-cell was attached, what is the standard reduction potential of uranium(III)? Write the *spontaneous* cell reaction occurring between the U^{3+}/U and the Ni^{2+}/Ni half-cells.

- b) If the voltmeter reading was -0.11 V when the In^{3+}/In half-cell was attached, what is the standard reduction potential of indium(III)? Write the *spontaneous* cell reaction occurring between the In^{3+}/In and the Ni^{2+}/Ni half-cells.

- c) An In^{3+}/In half-cell and a U^{3+}/U half-cell are connected as a galvanic cell. Which compartment is the anode, and what is the cell voltage?

22. Describe *galvanization* and *passivation*. Give an example of each.

23. In the following pairs of metals, one is used to protect the other by galvanization. Indicate which metal would be sacrificed.

- a) Fe and Mg

- b) Ni and Cu

- c) Fe and Pb

24. Describe the differences between electrolytic and galvanic cells.

25. Indicate whether each of the following standard cell reactions would take place in a galvanic or an electrolytic cell.

- a) $H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$

- b) $Zn^{2+}(aq) + 2 I^-(aq) \rightarrow Zn(s) + I_2(s)$

- c) $Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq)$

- d) $2 Fe^{3+}(aq) + Cu \rightarrow 2 Fe^{2+}(aq) + Cu^{2+}(aq)$

26. Write net equations or ‘no appreciable reaction’ for the following:

- a) A copper strip is placed in a silver acetate solution.

- b) A lead bar is placed in aqueous bromine.

- c) H_2 is bubbled into a solution containing Ni^{2+} and Cu^{2+} ions.

- d) A mixture of metallic zinc and copper is placed in 1 M HCl.

- e) Metallic copper is placed in a solution of KI.

- f) Chlorine gas is bubbled into a solution containing Fe^{2+} ions.

- g) Lead is added to an acidified solution of $KMnO_4$.

27. Write net equations or ‘no appreciable reaction’ for the following:

- a) An aluminum bar is placed in 1 M HCl.

- b) Aqueous bromine is added to a solution of Fe^{2+} .

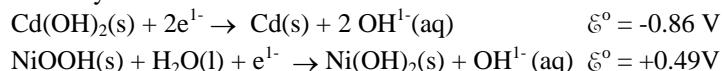
- c) A lead bar is placed in water.

- d) KBr is dissolved in an acidified solution of $Cr_2O_7^{2-}$.

- e) KF is dissolved in an aqueous bromine solution.

- f) Steel wool is placed into a solution of $NiSO_4$.

28. The standard reduction half-reactions involved in the nickel-cadmium or Nicad battery are



- a) Write the galvanic cell reaction and determine the cell voltage.
- b) Write the cell reaction for recharging a Nicad battery and determine the minimum voltage, to the nearest half of a volt, required to recharge a Nicad battery?

29. Lead acid batteries indicate that there should be no smoking during recharge because of the possibility of dangerous gases being released. Suggest what gas might be generated in the recharge cycle of a lead acid battery. (Hint: the gas reacts explosively with oxygen.) Write the half-reaction for its production.

30. The following redox couples are combined to make galvanic cells; in each case, indicate which couple is the anode and which is the cathode:

- a) H^{1+}/H_2 and Ag^{1+}/Ag
- b) H^{1+}/H_2 and Pb^{2+}/Pb
- c) Al^{3+}/Al and Cu^{2+}/Cu
- d) Fe^{2+}/Fe and Zn^{2+}/Zn

31. The following redox couples are combined to make galvanic cells; in each case, indicate which couple is the anode and which is the cathode:

- a) $\text{Br}_2/\text{Br}^{1-}$ and $\text{Cl}_2/\text{Cl}^{1-}$
- b) Sn^{2+}/Sn and Ag^{1+}/Ag
- c) I_2/I^{1-} and Ni^{2+}/Ni
- d) Zn^{2+}/Zn and $\text{Fe}^{3+}/\text{Fe}^{2+}$

32. Write the cell reaction and determine the cell potential for the galvanic cells constructed from the following redox couples (see Exercise 30):

- a) H^{1+}/H_2 and Ag^{1+}/Ag
- b) H^{1+}/H_2 and Pb^{2+}/Pb
- c) Al^{3+}/Al and Cu^{2+}/Cu
- d) Fe^{2+}/Fe and Zn^{2+}/Zn

33. Write the cell reaction and determine the cell potential for the galvanic cells constructed from the following redox couples (see Exercise 31):

- a) $\text{Br}_2/\text{Br}^{1-}$ and $\text{Cl}_2/\text{Cl}^{1-}$
- b) Sn^{2+}/Sn and Ag^{1+}/Ag
- c) I_2/I^{1-} and Ni^{2+}/Ni
- d) Zn^{2+}/Zn and $\text{Fe}^{3+}/\text{Fe}^{2+}$

34. Determine how many moles of electrons and how many coulombs ($C = nF$) must be transferred for each of the following processes:

- a) reduce 1.5 moles of silver ions to silver metal
- b) oxidize 0.22 moles of metallic nickel to nickel(II) ions
- c) produce 8.9 g of gold from Au^{3+} ions

35. Determine how many moles of electrons and how many coulombs ($C = nF$) must be transferred for each of the following processes:

- a) reduction of 1.3 mol Al^{3+} to Al
- b) oxidation of 3.4 mol Br^{1-} to Br_2
- c) oxidize 2.8 g of copper to Cu^{2+}

36. A standard galvanic cell, constructed with Al/Al^{3+} and Pb/Pb^{2+} couples, is discharged until 1.6 g of Pb forms.

- a) What are the cell reaction and its standard cell potential?
- b) How many moles of electrons flow through the circuit during the discharge? (Hint: grams of Pb \rightarrow moles of Pb \rightarrow moles of electrons.)
- c) How many coulombs flow through the circuit? (Hint: use $C = nF$)
- d) Assume that the cell potential does not change and determine the maximum work that could be done by the electrons during the discharge? (Hint: Use the answers to Parts a and d and Equation 11.3)

37. A standard galvanic cell, constructed with Ag^{1+}/Ag and Zn^{2+}/Zn couples, is discharged until 3.3 g of Ag forms. For hints, see Exercise 36.

- a) What are the overall cell reaction and the standard cell potential?
- b) How many moles of electrons must flow through the circuit?
- c) How many coulombs of charge flow through the circuit?
- d) Assume that the cell potential does not change and determine the maximum work that could be done by the electrons during the discharge?

Chapter 12

Acid-Base Chemistry

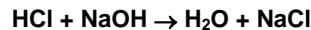
12.0 Introduction	12.6 The Acid Dissociation Constant, K_a
12.1 Lewis Acids and Bases	12.7 Solutions of Weak Bases
12.2 Brønsted Acids	12.8 The Acid-Base Table
12.3 Brønsted Acid-Base Reactions	12.9 pH and pK_a
12.4 Extent of Proton Transfer	12.10 Chapter Summary and Objectives
12.5 Acid and Base Strengths	12.11 Exercises

12.0 INTRODUCTION

The terms "acid" and "base" have been used for several centuries. Acids were characterized by their sour taste and their corrosive nature, while bases were substances that were slippery, had a bitter taste, and reacted with acids. However, these simple definitions had to be refined as the chemical properties of acids and bases became better understood. The first chemical definition of acids and bases was that of Svante Arrhenius.* An Arrhenius acid is a substance that produces H^{1+} ions when dissolved in water, while an Arrhenius base produces OH^{1-} ions. In this theory, an acid *ionizes* in water much as an ionic substance, and the equilibrium constant for the ionization is often referred to as the **acid ionization constant**. For example, dissolving HCl in water is represented as follows in Arrhenius acid-base theory:



The reaction of an acid with a base is called **neutralization**, and the products are water and a **salt**. The cation of a salt is derived from the base, and the anion comes from the acid. The following reaction is the neutralization of HCl with NaOH to produce the salt NaCl:



Arrhenius acid-base theory is very limited because its definitions are restricted to behavior in water. Consequently, broader definitions for these very important classes of compounds were developed. In this chapter, we examine the Lewis and the Brønsted-Lowry (or simply Brønsted) theories of acid-base chemistry. We begin our discussion of acids and bases with the more general Lewis definition and then use the more restricted Brønsted definition in a discussion of acid-base reactions in water.

THE OBJECTIVES OF CHAPTER 12 ARE TO:

- define acids and bases;
- show examples of Lewis and Brønsted acid-base reactions;
- explain how acids are named;

* Arrhenius acids and bases were first introduced in Section 10.5 where we used them as another class of electrolytes.

- discuss the factors dictating the extent of proton transfer in acid-base reactions;
- explain the factors dictating the relative strengths of acids;
- define K_a and show how the equilibrium constants of acid-base reactions are related to the K_a values of the acids involved in the equilibrium;
- explain the acid-base chart and how it is used to predict the extent of proton transfer in acid-base reactions; and
- define pH and pK_a .

12.1 LEWIS ACIDS AND BASES

A **Lewis base** contains a lone pair, a **Lewis acid** contains an empty orbital that can overlap with the lone pair, and a **Lewis acid-base reaction** is the formation of a coordinate covalent bond (bonds in which both bonding electrons are supplied by the same atom) between a Lewis acid and a Lewis base. A Lewis base is readily identified by the presence of a lone pair (Figure 12.1a). Bases are strengthened by negative charge. Lewis acids (Figure 12.1b) are often more difficult to identify. The following should help:

- A Lewis acid must be able to accommodate an additional electron region (the new bond), so, if it obeys the octet rule, a Lewis acidic atom must have less than four regions.
- Attack by a lone pair is facilitated by positive charge, so Lewis acidity is strengthened by positive charge.

The bond between two atoms is covalent only when the interacting orbitals have similar energies because large energy separations favor ionic bonds. Thus, the formation of a coordinate covalent bond in a Lewis acid-base reaction is facilitated when the energy of the empty orbital of the Lewis acid is close to that of the lone pair of the Lewis base. The energies of lone pairs are typically lower than those of empty orbitals, so the strongest interactions occur when the energy of the lone pair is high for a lone pair and the energy of the empty orbital is low for an empty orbital. For example, consider the cases of Na^{1+} and Ag^{1+} as shown in Figure 12.2. The energy of the empty orbital of Ag^{1+} is much lower than that of Na^{1+} ; *i.e.*, the energy of the empty orbital of Ag^{1+} is low for an empty orbital. Thus, the empty orbital on Ag^{1+} is sufficiently close to that of the lone pair on the Br^{1-} ion that the Ag-Br bond is covalent. However, the energy of the empty orbital on Na^{1+} is so high that the Na-Br bond is ionic. Thus, Ag^{1+} is a Lewis acid, but Na^{1+} is not. In general, H^{1+} and cations of metals with high effective nuclear charge (metals such as Ag and Pb that lie low and to the right of the periodic table) have empty orbitals that are relatively low in energy, so they are good Lewis acids, but cations of metals with low effective nuclear charges (such as those in Groups 1A and 2A) are very high in energy, so their bonds with

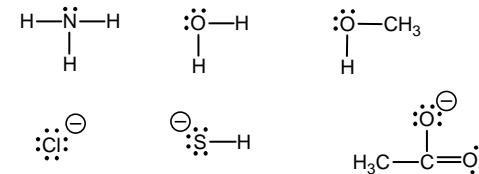


Figure 12.1a Some Lewis Bases

Atoms with lone pairs are Lewis basic. Negative charge strengthens their basicity.

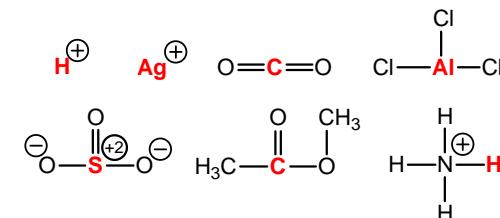


Figure 12.1b Some Lewis Acids

Atoms (highlighted in red) with fewer than four electron regions are Lewis acidic. Positive charge strengthens their acidity.

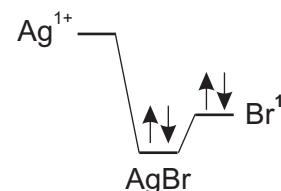
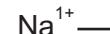


Figure 12.2 Metal ions with low-energy empty orbitals are Lewis acidic.

The empty orbital on Ag^{1+} is relatively low in energy, so it forms a covalent bond with the lone pair on Br^{1-} ion. The empty orbital on Na^{1+} is very high in energy, so its bonds to nonmetals are ionic. Therefore, Ag^{1+} is Lewis acidic, but Na^{1+} is not.

anionic substances are ionic, and they are not Lewis acidic. We conclude that

Strong Lewis acids have low-energy empty orbitals, and strong Lewis bases have high-energy lone pairs.

Oxidizing agents and Lewis acids are both characterized by empty valence orbitals that are low in energy, while reducing agents and Lewis bases both have high-energy electrons. Consequently, many Lewis acids are also oxidants and many Lewis bases are also reductants. Indeed, oxidants and Lewis acids are often defined as electron acceptors, and reductants and Lewis bases as electron donors. The obvious question becomes, “What determines whether electrons are transferred or shared when a lone pair comes into contact with an empty orbital?” As has been the case so often in our study of chemistry, the answer lies in their relative energies: electrons do whatever is most efficient at increasing their electrical potential in order to lower their energy. If the energy of the empty orbital is lower than that of the lone pair, the electrons simply transfer from the reductant to the more positive electrical potential on the oxidant in a redox reaction. However, if the empty orbital is at higher energy, the electrons lower their energy by forming a covalent bond between an acid and a base, which increases their electrical potential by exposing them to part of the nuclear charge on the acid. The example of H^{1+} , which is both an oxidant and an acid, is considered in Figure 12.3. If H^{1+} encounters a zinc atom, it behaves as an oxidant and accepts the higher energy electrons from the reductant zinc. However, electrons will not flow from a Br^{1-} ion to the higher energy orbital on H^{1+} , so the lone pair on Br^{1-} ion lowers its energy by forming an H-Br covalent bond. Br^{1-} is a base in the presence of H^{1+} , but it is a reductant in the presence of something like Cl_2 that has an empty orbital at lower energy ($2\text{Br}^{1-} + \text{Cl}_2 \rightarrow \text{Br}_2 + 2\text{Cl}^{1-}$).

Curved arrows are used to indicate the direction of electron pair attack in Lewis acid-base reactions.

- A curved arrow from a lone pair on one atom to another atom indicates that the lone pair becomes a covalent bond between the atoms.
- A curved arrow from a bond to an atom indicates that the bonding electrons become a lone pair on the atom.

Figure 12.4 demonstrates the use of curved arrows in Lewis acid-base reactions involving metals. The acidic nature of Ag^{1+} ions is demonstrated in Figures 12.4a and b, where the lone pair of the base (Cl^{1-} ion or NH_3 molecule) attacks the acid (Ag^{1+}) to produce a covalent bond. The curved arrow in each case points from the lone pair on the base to the silver ion and implies that the lone pair becomes a covalent bond between the acid and the

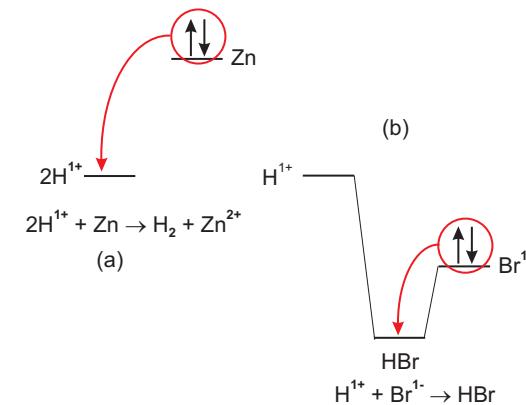


Figure 12.3 H^{1+} as oxidant and acid

a) Electrons transfer to orbitals at lower energy. The empty orbital on H^{1+} is at lower energy than the electrons on Zn, so the electrons transfer making H^{1+} an oxidizing agent in the presence of Zn.

b) Electrons are shared with orbitals at higher energy. The empty orbital on H^{1+} is at higher energy than the electrons on Br^{1-} , so the electrons are shared making H^{1+} an acid in the presence of Br^{1-} .

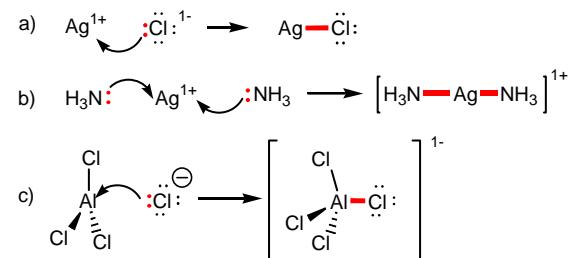


Figure 12.4 Metal ions as Lewis acids

- a) precipitation of AgCl
- b) formation of $\text{Ag}(\text{NH}_3)_2^{1+}$
- c) formation of AlCl_4^-

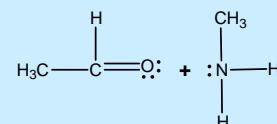
The red lone pairs become the red bonds.

base. The aluminum atom of AlCl_3 has only six valence electrons and three electron regions surrounding it, so AlCl_3 is a strong Lewis acid. The Lewis acid-base reaction of AlCl_3 with Cl^{1-} ion is shown in Figure 12.4c. The curved arrow shows that the lone pair on the base is converted into an Al-Cl bond. The increase in the number of electron regions results in geometry and hybridization changes as the number of electron regions surrounding the Al atom goes from three (trigonal planar, sp^2) to four (tetrahedral, sp^3).

Now consider the three-step reaction of SO_3 and H_2O to form H_2SO_4 , the reaction that is the primary cause of acid rain. The oxygen atom of the water molecule contains two lone pairs, so water is a Lewis base, while the sulfur atom in SO_3 has only three electron regions, which makes SO_3 Lewis acidic. As shown in Figure 12.5a, a lone pair on the oxygen atom in water is shared with the sulfur atom to form a new S-O σ bond. Simultaneously, the electrons in the S=O π bond are converted into a lone pair on the oxygen (curved arrow from the bond to the atom), and the hybridization of the sulfur atom goes from sp^2 to sp^3 (from trigonal planar to tetrahedral). The resulting structure places positive formal charge on the oxygen atom, which is eliminated by transferring a proton (shown in red in Figure 12.4b) from that oxygen atom to one that carries negative formal charge. The proton transfer is accomplished with two acid-base reactions with the solvent. In the first, a proton (red) is transferred from the oxygen atom with positive formal charge to a solvent molecule (water). In the second, a proton (blue) is transferred from the solvent to an oxygen atom with negative formal charge. Although Figure 12.5b shows only one water molecule, it is more likely that *two* are involved: one to remove the proton from the oxygen with positive charge and another to donate a proton to a lone pair on one of the other oxygen atoms.

Example 12.1

Use curved arrows to show the mechanism* of the Lewis acid-base reaction between the following and draw the Lewis structure of the product.



We first identify the Lewis acidic and basic sites. The nitrogen atom and the carbon atoms in the CH_3 groups each have four electron regions, so they are not Lewis acidic. H atoms in C-H bonds are not acidic, nor are they acidic in N-H bonds unless the nitrogen has a positive formal charge as in NH_4^+ . That leaves the carbon and oxygen atoms in the $\text{C}=\text{O}$

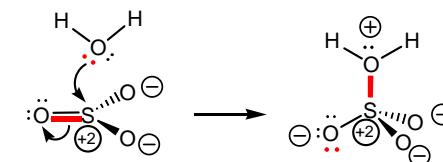


Figure 12.5a $\text{SO}_3 + \text{H}_2\text{O}$, Step 1

Red lone pair on water becomes S-O bond, and π electron pair in S=O bond becomes red lone pair on O. Lone pairs on two oxygen atoms have been omitted.

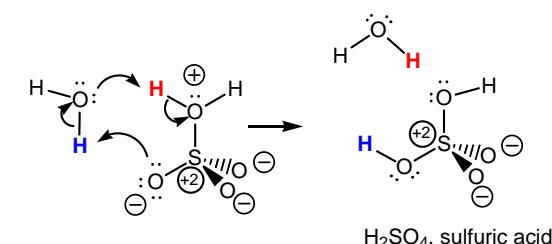
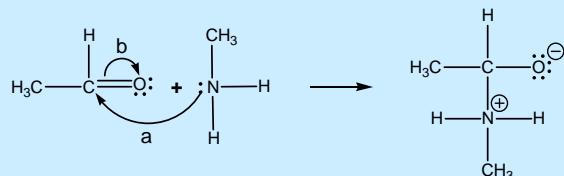


Figure 12.5b $\text{SO}_3 + \text{H}_2\text{O}$, Step 2

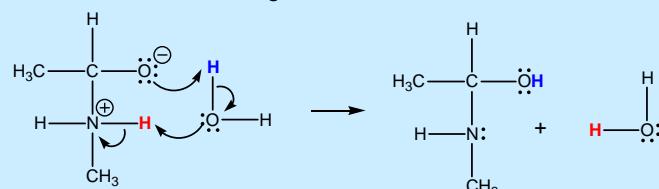
Water assists in a proton transfer to reduce formal charge.

* Recall from Chapter 9 that a reaction mechanism shows the individual steps required to convert the reactants to products. In Lewis acid-base reactions, each step is represented with curved arrows that show the movement of electrons to form either bonding pairs or lone pairs.

bond. The bond is polar with the negative end on oxygen and the positive end on carbon. The partial positive charge and only three electron regions make the carbon atom Lewis acidic. The lone pair on the nitrogen atom makes it Lewis basic. The attack is from the lone pair on N to the C atom in the C=O bond. The lone pair on the N atom is used to form a C-N bond (Arrow a below). The two additional electrons in the C-N bond would put 10 electrons around the C atom, so the π electrons in the C=O bond are converted into a lone pair on the oxygen atom (Arrow b).



The positive formal charge on the N atom makes the H atoms attached to it acidic, so the formal charge is eliminated by a solvent-assisted proton transfer similar to that shown in the reaction of SO_3 and water. The proton shown in red below is transferred from N to a water molecule as the N-H bonding pair is converted to a lone pair on N. Another proton (blue) is transferred from a water molecule to the O atom with negative formal charge. The resulting product has no formal charge.



The above reaction is an example of organic chemistry, which is introduced in the following chapter. Organic chemistry has many Lewis acid-base reactions with mechanisms that are almost identical to the one shown here; the only difference is the identity of the acid and the base.

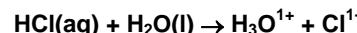
To summarize, a Lewis acid-base reaction results in the formation of a coordinate covalent bond between an acid and a base. The bonding pair comes from the lone pair of the base. The acid must have an empty orbital that can overlap with the filled orbital on the base to form the bond. If the very broad classification of Lewis is used to define acid-base reactions, then *a very large number of chemical reactions can be classified as either acid-base or redox reactions. In one, a base shares its electrons with an acid; in the other, a reductant transfers its electrons to an oxidant.**^{*}

* There are many similarities in the treatment of redox and acid-base chemistry that will be indicated in the margin as we proceed through this chapter.

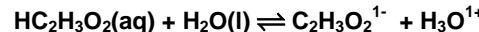
12.2 BRØNSTED ACIDS

Brønsted acids are proton donors, and **Brønsted bases** are proton acceptors. The Brønsted definition is a special case of the Lewis definition. In both, a base contains a lone pair that it shares with the acid in a covalent bond. All Lewis bases are Brønsted bases, and all Brønsted bases are Lewis bases. However, a Lewis acid is *any* species that can share the lone pair, while the species that shares the lone pair *must* be a proton in the Brønsted definition. A Brønsted acid is the species that contains the proton. A **Brønsted acid-base** reaction is a proton transfer from the acid to the base.[†]

In Chapter 10, we classified acids that are strong electrolytes as strong acids. **Strong acids** dissociate 100% in water. The dissociation of an acid in water is viewed as ionization in Arrhenius theory, but acids are not ionic compounds, and the term “ionization” is misleading. Brønsted theory views the dissociation of an acid in water as a proton transfer between the acid and water, which is a Brønsted base. The chemical equation for the proton transfer between hydrochloric acid, a strong acid, and water is*



The single arrow indicates that the above reaction is extensive and there are essentially no HCl molecules in the equilibrium mixture. Most acids are not strong electrolytes, but they do produce some ions in solution. These weak electrolytes are classified as **weak acids**. Consider the reaction of acetic acid, a weak acid, and water.



Acetic acid is a weak acid as only about 1% of the molecules react to produce acetate ions. HClO is an even weaker acid as less than 0.1% of HClO molecules transfer their protons to water to form of ClO¹⁻. Thus, the reaction of a weak acid and water is not extensive, which is represented by double arrows in the chemical equation.

In order for HX to be acidic, the H-X bond must break to produce H¹⁺ and X¹⁻ ions, but that can happen only if it is a polar bond. Thus, *a hydrogen atom must be covalently bound to a highly electronegative atom to be acidic*. There are a great number of compounds with hydrogen atoms covalently bound to atoms that are not very electronegative, but these compounds are not Brønsted acids. The most common examples are organic compounds because the C-H bond is not polar (C and H have very similar electronegativities). For example, the C-H bonds in CH₄ do not produce H¹⁺ when they break, so CH₄ cannot be a Brønsted acid. The H-Cl bond is very polar, so breaking the H-Cl bond does produce H¹⁺ ions, which makes HCl a Brønsted acid.

[†] Redox reactions involve the transfer of the basic unit of negative charge (the electron), while Brønsted acid-base reactions involve the transfer of the basic unit of positive charge (the proton).

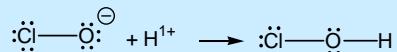
* As in Chapter 11, it is assumed that all ions are in aqueous solution, so the (aq) is omitted for clarity.

Acidic protons are often written first in the formula to indicate that they are acidic. For example, the hydrogen atoms in HCN and HSO_4^{1-} are acidic, while those in NH_3 and CH_4 are not. An important exception to this rule is NH_4^{1+} , which contains one acidic proton. $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid) contains one acidic hydrogen, written first in the formula, and three hydrogen atoms that are not acidic (Figure 12.6). However, *placing the acidic proton first in the formula can be misleading because it often places the proton next to an atom to which it is not bound*. For example, the acidic proton in $\text{HC}_2\text{H}_3\text{O}_2$ is bound to an oxygen atom not a carbon atom. Consequently, acetic acid is often written as CH_3COOH , which indicates an O-H bond and better represents the true structure of the acid. Similarly, H_2SO_4 contains two O-H bonds but no S-H bonds (Figure 12.4b).

Example 12.2

a) Draw the Lewis structure of HClO .

The Lewis structure of the ClO^{1-} ion shows that the negative charge is centered on the O atom, so the acidic proton is bound to it.



b) Draw the Lewis structure of H_2CO_3 .

The Lewis structure of the CO_3^{2-} ion places the negative formal charge on two of the oxygen atoms, so the acidic protons must be bound to them.



Although the chemical formulas frequently place the acidic proton next to the central atom of an oxoanion (chlorine and carbon above), the acidic proton is always attached to one of the oxygen atoms.

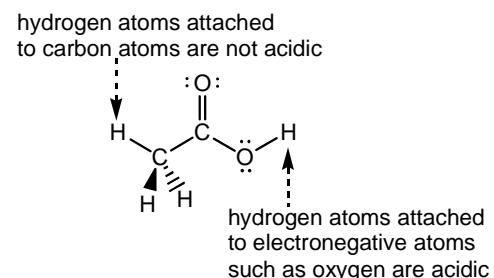


Figure 12.6 Only protons bound to highly electronegative atoms are acidic.

NAMING ACIDS

The manner in which an acid is named depends on whether it is a binary acid (an acid that contains only two elements, such as HCl and H_2S) or a polyatomic acid (an acid that contains more than two elements, such as HClO or H_3PO_4).

Binary Acids

Binary acids are derived from gases. The gases are named using the rules outlined in Section 5.3. For example, HCl(g) is hydrogen chloride, and HF(g) is hydrogen fluoride.

When they are dissolved in water, the names are changed in the following manner:

- 1) replace "hydrogen" with "hydro",
- 2) change the *-ide* ending to *-ic* and
- 3) add the word "*acid*".

Some examples are given in Table 12.1.

Acids Derived from Polyatomic Anions

Acids derived from polyatomic ions are **oxoacids**, *i.e.*, they are protonated oxoanions. The *acidic proton is always attached to an oxygen atom*. They are named as follows:

- 1) change the *-ate* ending of the polyatomic ion to *-ic** or
- 2) change the *-ite* ending of the polyatomic ion to *-ous** and
- 3) add the word "*acid*".

In summary, an *elementate* ion becomes an *elementic* acid, and an *elementite* ion becomes an *elementous* acid. If the acid is also an ion, its name is unchanged. For example, the HPO_4^{2-} and $\text{H}_2\text{PO}_4^{1-}$ ions are the monohydrogen phosphate ion and dihydrogen phosphate ion[†], respectively. Some examples of oxoacids are given in Table 12.2.

Example 12.3

a) Name the acid H_2CO_3 .

The CO_3^{2-} ion is the **carbonate** ion (Table 4.1), so the acid is **carbonic acid**.

b) Name the acid HCO_3^{1-} .

Acids that are ions are named as the ion, so HCO_3^{1-} is the **hydrogen carbonate ion** or the **bicarbonate ion**.

c) What is the formula of selenous acid?

The *-ous* ending tells us that the acid is derived from a polyatomic ion with an *-ite* ending; *i.e.*, the acid is derived from the **selenite** ion. Selenium is a Group 6A nonmetal, so its chemical properties are expected to be similar to those of sulfur. The sulfite ion is SO_3^{2-} , so selenite is SeO_3^{2-} and selenous acid is H_2SeO_3 . It contains two O-H bonds.

d) What is the formula of hydroselenic acid?

The name starts with **hydro**, so this is a binary acid of H and Se. Se is in Group 6A, so it is expected to form a -2 anion, which requires two protons. Hydroselenic acid is H_2Se .

Table 12.1 Examples of binary acid names

Formula	Name	Formula	Name
HBr(g)	hydrogen bromide	HBr(aq)	hydrobromic acid
HCl(g)	hydrogen chloride	HCl(aq)	hydrochloric acid
HCN(g)	hydrogen cyanide	HCN(aq)	hydrocyanic acid ^a
HF(g)	hydrogen fluoride	HF(aq)	hydrofluoric acid
HI(g)	hydrogen iodide	HI(aq)	hydroiodic acid

^a HCN is not a binary compound, but HCN is a gas and the name of the CN^{1-} ion (cyanide ion) ends in *-ide*, so, HCN(aq) is named in the same manner as the binary acids.

* If the non-oxygen atom is sulfur, replace *-ate* with *-uric* and *-ite* with *-urous*. If it is phosphorus, replace *-ate* with *-oric* and *-ite* with *-orous*.

[†] In an older, but still common, method, ions with acidic protons are named by using the prefix 'bi' instead of the word 'hydrogen'. Thus, HSO_4^{1-} is either hydrogen sulfate or bisulfate.

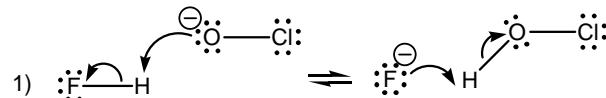
Table 12.2 Names of some oxoanions and their oxoacids

Ion Formula	Ion Name	Oxoacid Formula	Oxoacid Name
ClO^{1-}	hypochlorite ion	HClO^{a}	hypochlorous acid
ClO_2^{1-}	chlorite ion	HClO_2	chlorous acid
BrO_3^{1-}	bromate ion	HBrO_3	bromic acid
IO_4^{1-}	periodate ion	HIO_4	periodic acid
NO_3^{1-}	nitrate ion	HNO_3	nitric acid
NO_2^{1-}	nitrite ion	HNO_2	nitrous acid
PO_4^{3-}	phosphate ion	H_3PO_4	phosphoric acid
SO_4^{2-}	sulfate ion	H_2SO_4	sulfuric acid
SO_3^{2-}	sulfite ion	H_2SO_3	sulfurous acid

^a The proton in HClO is attached to the O not the Cl (Example 12.1), so it is often written as HOCl. However, the O is never written first in HClO_2 , HClO_3 , or HClO_4 , so we use HClO for the formula to be consistent with the other members of this group of acids.

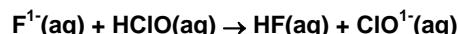
12.3 BRØNSTED ACID-BASE REACTIONS

The reaction between hydrofluoric acid and hypochlorite ion can be written in two ways



The top representation shows the Lewis formalism that uses curved arrows to show the direction of electron pair attack, *which is opposite to the direction of proton transfer*. The bottom representation is the way the reaction is typically written in the Brønsted formalism. We use both formalisms when writing acid-base reactions in this chapter.

In the reaction between HF and ClO⁻, a proton transfers from HF, the acid, to ClO⁻, the base. The curved arrows show that the H-F bonding pair remains on the fluorine atom as a lone pair, while a lone pair on the oxygen atom is converted to an H-O bonding pair. The resulting fluoride ion has a lone pair that it can use to bond to an acid, so it is a base. Thus, proton donation has converted the acid HF into the base F⁻. Proton transfer also converts the base (ClO⁻) ion into an acid (HClO), so the products of the acid-base reaction are also an acid and a base, which can also undergo an acid-base reaction to produce the original reactants in the back-reaction.



When the rates of the forward and reverse reactions are equal, the reaction reaches a dynamic equilibrium in which both reactions continue at the same rate with no net change in the equilibrium concentrations. Consequently, acid-base reactions are often written with double arrows to indicate the competing reactions.

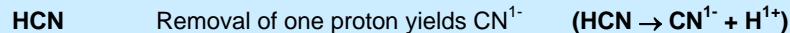
The acid in a Brønsted acid-base reaction loses a single proton to become a base, while the base accepts a single proton to become an acid. An acid and a base that differ by a *single proton* are conjugate to one another and form a **conjugate acid-base pair**.* F⁻ ion is the **conjugate base** of HF, and HClO is the **conjugate acid** of ClO⁻. We conclude the following:

The products of a Brønsted acid-base reaction are the conjugate base of the reacting acid and the conjugate acid of the reacting base. In other words, all Brønsted acid-base reactions consist of two conjugate acid-base pairs and nothing else.

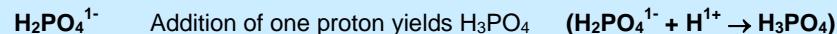
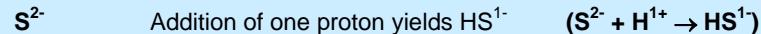
* In redox reactions, electron transfer converts an oxidant into a reductant and the reductant into an oxidant. The reductant and the oxidant that it becomes are called a redox couple. Redox reactions consist of two redox couples just as acid-base reactions consist of two conjugate acid-base pairs.

Example 12.4

- a) Write the conjugate base of each of the following acids:



- b) Write the conjugate acid of each of the following bases:

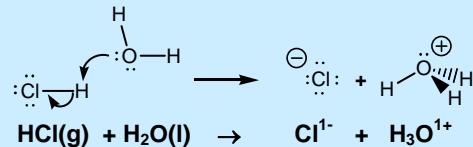


Note that H_2O was used as an example of both an acid and a base in Example 12.4. Substances that can function as either an acid or a base are said to be **amphiprotic**. $\text{H}_2\text{PO}_4^{1-}$ is another amphiprotic substance in Example 12.4.

Example 12.5

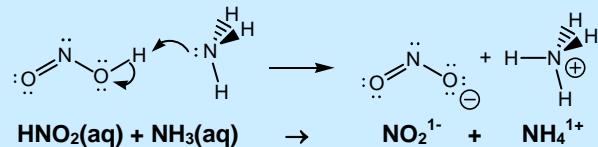
Draw Lewis structures of the reactants and products of the following reactions. Indicate the mechanism with curved arrows and include all nonzero formal charges.

- a) Hydrogen chloride gas is dissolved in water.



The two conjugate acid-base pairs are (HCl , Cl^{1-}) and (H_2O , H_3O^{1+}).

- b) Nitrous acid is added to a solution of ammonia.



The two conjugate acid-base pairs are (HNO_2 , NO_2^{1-}) and (NH_3 , NH_4^{1+}).

12.4 EXTENT OF PROTON TRANSFER

All acid-base reactions reach a dynamic equilibrium because the forward and reverse reactions do not stop at equilibrium. The position of the equilibrium is referred to as the **extent of proton transfer**: *if the concentration of at least one reactant in an acid-base reaction is much smaller than any of the product concentrations, then the reaction is an extensive proton transfer.* Consider the following generic* acid-base equilibrium:



If $K \gg 1$, the equilibrium concentration of at least one reactant (term in the denominator) is very small,[†] which means that the forward proton transfer is more extensive than the reverse. If $K \sim 1$, the concentrations of reactants and products are similar and the extents of proton transfer of the forward and reverse reactions are similar. If $K \ll 1$, the concentrations of at least one product (term in the numerator) is very small, so little proton transfer takes place because the reverse reaction is the more extensive proton transfer.

Recall from Section 9.11 that extensive reactions are frequently written with single arrows to emphasize that the back reaction can be neglected when calculating the amount of product that is formed. The value of K at which the reverse reaction can be ignored in an acid-base reaction varies with the reactant concentrations, but, for purposes of discussion, we will arbitrarily assume that the reaction can be written with a single arrow when $K \geq 10^3$.[§] However, extensive reactions do reach equilibrium and can be written with double arrows; the single arrow simply indicates that essentially all of at least one of the reactants disappears during the reaction. In this text, double arrows will always be used for reactions in which $K < 10^3$ to emphasize the importance of the back reaction in determining the equilibrium concentrations. For example, consider the following aqueous reaction:



K is greater than 10^3 , so the denominator of the equilibrium constant must be very small; *i.e.*, $[\text{HF}]$ and/or $[\text{ClO}^{1-}]$ are/is nearly zero at equilibrium. Thus, the proton transfer from HF to ClO^{1-} is extensive, and the reaction *could have been* written with a single arrow.

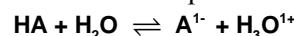
* 'HA' and 'HB' are used to indicate generic acids, and ' A^{1-} ' and ' B^{1-} ' are used to denote their conjugate bases.

[†] Concentrations of acids and bases are normally less than 1 M, so the terms in the numerator cannot make K a very large number. Instead, a large value of K is obtained because at least one of the terms in the denominator is very small.

[§] A value of K greater than 10^3 implies that over 95% of at least one reactant is consumed with normal concentrations.

12.5 ACID AND BASE STRENGTHS

The strength of an acid is determined by the ease with which it donates its proton. It is easier to remove a proton from a stronger acid than from a weaker acid. Since the H-A bond must be broken in order for HA to donate a proton, the strength of the bond is an important factor in dictating the strength of an acid. In general, *a strong H-A bond implies a weak acid*. For example consider the following reaction of a generic acid with water:



~4% of the acid molecules react when the acid is HF, but ~100% react when the acid is HCl. Thus, HCl donates its proton to water much more extensively than does HF, which means that HCl is a much stronger acid. The difference in acid strengths can be attributed to differences in bond energies: $D_{\text{H-F}} = 565 \text{ kJ/mol}$ and $D_{\text{H-Cl}} = 431 \text{ kJ/mol}$. H-Cl is the stronger acid because it has the weaker bond.

However, bond energies alone do not account for the relative strengths of all acids. For example, the C-H bond energy is ~413 kJ/mol, which is even weaker than the H-Cl bond, but hydrogen atoms attached to carbon are not acidic. The reason bond energies alone do not completely explain acid strengths is shown in Figure 12.7. The bond energy is the energy required to break the bond to form neutral atoms and, as shown in Figure 12.7a, this requires that each atom retains one of the bonding electrons. The acid strength, however, is a measure of how easily the bond is broken to form ions, and as shown in Figure 12.7b, this requires that one atom retains both bonding electrons, while the other atom retains none. The latter process is favored by large electronegativity differences between the two bound atoms (that is, by polar bonds). This is why our definition of a Brønsted acid indicates that the acidic proton must be covalently bound to an electronegative atom. Consequently, *the strength of an acid also increases with the electronegativity of the atom to which the proton is attached*. HCl is a strong acid because the HCl bond is very polar, while CH₄ is not acidic because the C-H bond is not polar. HF is a much weaker acid than HCl, even though the HF bond is much more polar, so the bond strength is the more important consideration in this case.

A large number of acids are oxoacids, but their acid strengths vary considerably even though the acidic proton is always attached to an oxygen atom. To understand the variation in their strengths, we need only examine the factors that govern the O-H bond energy. We will represent an oxoacid as XOH, where X is an atom that may have other atoms attached to it (often other oxygen atoms). The strength of the O-H bond depends

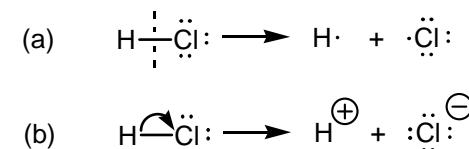


Figure 12.7 Two ways to break an HCl bond

(a) Each atom retains one of the bonding electrons. This is the type of bond breakage to which the bond energies apply. (b) The more electronegative atom retains both electrons. This is the type of bond breakage that accompanies an acid-base reaction.

upon the electron density in the bond, which, in turn, depends upon the electron withdrawing ability of X: *the more electron density X draws from the O-H bond, the weaker the bond becomes, and the stronger the acid becomes.* The following two factors dictate the electron withdrawing abilities of X:

1. **Oxidation state:** The ability of X to withdraw electrons from the O-H bond increases with its oxidation state, so the strength of an oxoacid increases with the oxidation state of X. For example, HNO₃ is a stronger acid than HNO₂ because the oxidation state of the nitrogen atom is greater in HNO₃ (+5) than in HNO₂ (+3).
2. **Electronegativity:** The amount of electron density withdrawn from the O-H bond increases with the electronegativity of X, as does the acid strength of the oxoacid. HClO₂ is a stronger acid than HBrO₂ because chlorine is more electronegative than bromine.

A strong acid is one that has a weakly bound hydrogen, but a strong base is one that forms a strong bond with hydrogen. Consequently, strong acids have weak conjugate bases, and weak acids have strong conjugate bases. In other words, *the strength of a base varies inversely with the strength of its conjugate acid.* For example, the fact that HClO₂ is a stronger acid than HBrO₂ means that BrO₂¹⁻ is a stronger base than ClO₂¹⁻. This is because Br is less electronegative than Cl, so less electron density is withdrawn from the oxygen atom in BrO₂¹⁻. The increased electron density lowers the electrical potential at the oxygen atom, which raises the energy of its lone pairs and makes BrO₂¹⁻ a stronger base.

If a proton transfer is extensive, then the forward reaction is more extensive than the reverse reaction, which means that the reacting acid gives up its proton more easily than the produced acid. We conclude that *an acid-base reaction is extensive when the reacting acid is stronger than the produced acid,** which has the following implications:

K >> 1: Reacting acid is stronger than produced acid, and proton transfer is extensive.

K ~ 1: Reacting and produced acids have comparable strengths.

K << 1: Reacting acid is weaker than produced acid, so little reaction takes place.

Example 12.6

K = 10⁵ for HC₂H₃O₂ + NH₃ ⇌ NH₄¹⁺ + C₂H₃O₂¹⁻. Which is the stronger acid, HC₂H₃O₂ or NH₄¹⁺? Which is the stronger base, NH₃ or C₂H₃O₂¹⁻?

K >> 1, so the reacting acid is stronger than the produced acid and the reacting base is stronger than the produced base. We conclude that acetic acid is a stronger acid than ammonium ion and ammonia is a stronger base than acetate ion.

* The equilibrium concentrations of the weaker acid and base are always greater than the equilibrium concentrations of the stronger acid and base because the stronger acid and base react more extensively to produce the weaker acid and base.

Example 12.7

Predict whether $K > 1$ or $K < 1$ for the following acid-base reactions:



Chlorine is more electronegative than bromine, so HClO_2 is a stronger acid than HBrO_2 .

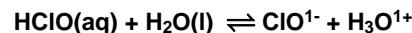
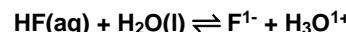
Thus, $K > 1$ because the produced acid is weaker than the reacting acid.



The oxidation state of the chlorine is +5 in HClO_3 and +1 in HClO , so HClO_3 is the stronger acid. Thus, $K < 1$ because the produced acid is stronger than the reacting acid.

12.6 THE ACID DISSOCIATION CONSTANT, K_a

In order to predict the extent of an acid-base reaction, we need know only the *relative* strengths of the reacting and produced acids. This is done by measuring how extensively each acid reacts with a reference base. The reference base is water, and the extent of the reaction is given by the value of the equilibrium constant for the reaction.* Consider the examples of HF and HClO with water.



The equilibrium constant for the reaction of an acid with *water*, is called the **acid dissociation** or **acid ionization constant** and given the symbol K_a . Water is the solvent, and in the dilute solutions common to most acid-base reactions, its concentration is essentially the same as in the pure liquid. In addition, its concentration is essentially unchanged by the reaction. Consequently, it is treated as a pure liquid, as indicated by '(l)' in the chemical equation. Pure liquids enter the equilibrium constant expression as 1 (unity), which is not shown. Therefore, the K_a expressions for HF and HClO are

$$K_a(\text{HF}) = \frac{[\text{F}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HF}]} = 7.2 \times 10^{-4} \quad \& \quad K_a(\text{HClO}) = \frac{[\text{ClO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HClO}]} = 3.5 \times 10^{-8}$$

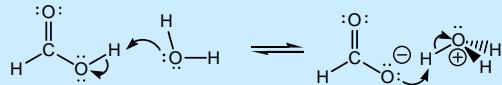
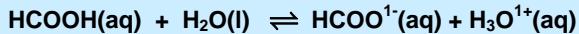
$K_a(\text{HF}) \ll 1$, so $[\text{F}^{1-}][\text{H}_3\text{O}^{1+}] \ll [\text{HF}]$ at equilibrium. Consequently, only a small fraction of the acid reacts with water, which means that HF is a weak acid. Furthermore, $K_a(\text{HClO}) < K_a(\text{HF})$, so HClO is a weaker acid than HF.

* Relative reducing or oxidizing strengths were measured by referencing the half-reaction to a reference half-reaction (the SHE). The extent of that reaction was given by the value of E° for the cell, which is a measure of the equilibrium constant of a redox reaction.

Example 12.8

The K_a of formic acid (HCOOH) is 1.8×10^{-4} . Write the chemical equation (Brønsted and Lewis) and the mathematical expression to which this number applies.

The K_a of formic acid is the equilibrium constant for the reaction of formic acid with water.



The equilibrium constant expression for the reaction is

$$K_a = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^{1+}]}{[\text{HCOOH}]} = 1.8 \times 10^{-4}$$

Example 12.9

Buffers are solutions of weak acids and their conjugate bases. Buffered solutions function to maintain the pH of a solution because the addition of an acid is neutralized by the weak base and the addition of a base is neutralized by the weak acid. What is the hydronium ion concentration in a buffered solution that is 0.10 M in HClO ($K_a = 3.5 \times 10^{-8}$) and 0.15 M in ClO^- ion?

We are given K_a , $[\text{HClO}]$, and $[\text{ClO}^-]$, so we substitute the known values into the K_a expression and solve for the hydronium ion concentration.

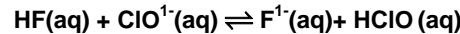
$$K_a = 3.5 \times 10^{-8} = \frac{[\text{ClO}^-][\text{H}_3\text{O}^{1+}]}{[\text{HClO}]} = \frac{(0.15)[\text{H}_3\text{O}^{1+}]}{0.10} = 1.5[\text{H}_3\text{O}^{1+}]$$
$$[\text{H}_3\text{O}^{1+}] = \frac{3.5 \times 10^{-8}}{1.5} = 2.3 \times 10^{-8} \text{ M}$$

Thus far we have used only the relative strengths of the reacting and produced acids to determine if a reaction is extensive, but the K_a values of the reacting and produced acids can be used to determine the value of the equilibrium constant for the reaction.

$$K = \frac{K_a \text{ reacting acid}}{K_a \text{ produced acid}} \quad \text{Eq. 12.1}$$

The equilibrium constant for an acid-base reaction equals the K_a of the reacting acid divided by the K_a of the produced acid. If the reacting acid is stronger than the produced acid, then $K_a(\text{reacting}) > K_a(\text{produced})$, in which case, $K > 1$ and the reaction is extensive.

Combining Equation 12.1 and our rule that Brønsted acid-base reactions for which $K > 10^3$ are extensive and can be written with single arrows, we can state that a reaction can be written with a single arrow when the K_a of the reacting acid is at least 10^3 times greater than that of the produced acid. As an example of the application of Equation 12.1, consider the following reaction:



HF ($K_a = 7.2 \times 10^{-4}$) is the reacting acid and HClO ($K_a = 3.5 \times 10^{-8}$) is the produced acid. $K_a(\text{HF}) > K_a(\text{HClO})$, so the reacting acid is stronger than the produced acid. We conclude that the equilibrium constant for the reaction between HF and ClO^{1-} is large, and the proton transfer is extensive. The value of the equilibrium constant can be determined with Equation 12.1 as follows:

$$K = \frac{K_a(\text{HF})}{K_a(\text{HClO})} = \frac{7.2 \times 10^{-4}}{3.5 \times 10^{-8}} = 2.1 \times 10^4$$

$K > 10^3$, so the reaction is extensive and could be written with a single arrow. That the above is indeed the equilibrium constant for the reaction can be verified by dividing the K_a expressions

$$K = K_a(\text{HF}) \times \frac{1}{K_a(\text{HClO})} = \frac{[\text{H}_3\text{O}^{1+}][\text{F}^{1-}]}{[\text{HF}]} \times \frac{[\text{HClO}]}{[\text{H}_3\text{O}^{1+}][\text{OCl}^{1-}]} = \frac{[\text{F}^{1-}][\text{HClO}]}{[\text{HF}][\text{OCl}^{1-}]}$$

The expression is indeed the equilibrium constant expression for the reaction.

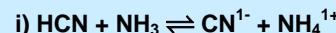
Example 12.10

K_a values: $\text{HCN} = 4.0 \times 10^{-10}$; $\text{HNO}_2 = 4.0 \times 10^{-4}$; $\text{HF} = 7.2 \times 10^{-4}$; $\text{NH}_4^{1+} = 5.6 \times 10^{-10}$.

- a) What is the strongest acid? Which has the strongest conjugate base?

The acid with the largest K_a is HF, so it is the strongest acid. The acid with the smallest K_a is HCN, so it is the weakest acid. Conjugate base strengths are opposite the acid strengths, so F^{1-} ion would be the weakest base and CN^{1-} ion the strongest base.

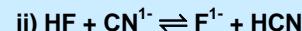
- b) Indicate whether each of the following aqueous reactions is extensive and could be represented with a single arrow.



We can use the K_a values to see that NH_4^{1+} ion, the produced acid, is a stronger acid than HCN, the reacting acid, so the reaction is not extensive. Using Equation 12.1 we obtain

$$K = \frac{K_a(\text{HCN})}{K_a(\text{NH}_4^{1+})} = \frac{4.0 \times 10^{-10}}{5.6 \times 10^{-10}} = 0.71$$

The reaction is not extensive, but the value of $K \sim 1$, so the equilibrium concentration of HCN will be only slightly higher than that of CN^{1-} .



$K_a(\text{HF}) \gg K_a(\text{HCN})$, so this reaction is extensive. Applying Equation 12.1, we obtain

$$K = \frac{K_a(\text{HF})}{K_a(\text{HCN})} = \frac{7.2 \times 10^{-4}}{4.0 \times 10^{-10}} = 1.8 \times 10^6$$

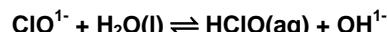
$K \gg 10^3$, so essentially all of one reactant will be consumed and the chemical equation could be written with a single arrow.

c) Which acid base reaction would be most extensive?

The most extensive reaction is between the strongest acid (HF) and the strongest base (CN^{1-}), which is Reaction ii in Part b.

12.7 AQUEOUS SOLUTIONS OF WEAK BASES

Water is also an acid, so it can react with weak bases to produce hydroxide ion and the conjugate acid of the weak base. Consider the reaction of hypochlorite ion with water:



The reaction involves the breaking of an O-H bond of water, which is called **hydrolysis**, so these reactions are also hydrolysis reactions. Most weak bases are found as salts, so salts such as KClO , NaF , KCN , and LiNO_2 all form basic solutions in water because their reaction with water produces hydroxide ion.

12.8 THE ACID-BASE TABLE

The acid-base table shown in Table 12.3 (next page) lists several acids and their K_a values in descending order. Thus, stronger acids are at the top of the table, and stronger bases are at the bottom of the table. The K_a 's of the acids are given in the center column.

Stronger acids are located above weaker acids, so proton transfer is extensive when the reacting acid is above (stronger than) the produced acid. Stated somewhat differently, *the reaction between an acid and a base is extensive when the acid is above the base on the acid-base table* (Figure 12.8). Protons transfer spontaneously ‘downhill’ in our acid-base table just as electrons transferred spontaneously ‘downhill’ in our table of standard reduction potentials. Compare Figures 11.3 and 12.8 to see the similarities of the two reaction types.

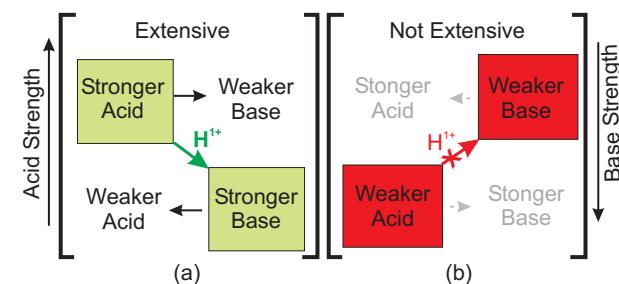


Figure 12.8. Reactivity from the relative position of reactants and products on an acid-base table

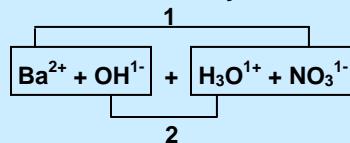
(a) The reaction of a stronger acid and base to produce a weaker acid and base is extensive. (b) The reaction of a weaker acid and base to produce a stronger acid and base is not extensive. The diagonal arrow represents the direction of the proton transfer and the horizontal arrows point toward the products of the reaction. The proton transfer is extensive when it is ‘downhill’ from the strong acid to the strong base, but only little reaction occurs when it is ‘uphill’ from the weak acid to the weak base.

Any acid (HA) that is above H_3O^{1+} in Table 12.3 is a strong acid ($K_a \gg 1$) and reacts extensively with water to produce H_3O^{1+} and its conjugate base (A^{1-}), which is why solutions of strong acids are strong electrolytes. Just as a solution of sodium chloride is represented as $\text{Na}^{1+} + \text{Cl}^{1-}$, hydrochloric acid is represented as $\text{H}_3\text{O}^{1+} + \text{Cl}^{1-}$. Hydrofluoric acid is a weak acid ($K_a \ll 1$) and a weak electrolyte (only about 4% of the molecules in a 0.1 M solution of HF are in the form of H_3O^{1+} and F^{1-} ions), so it is written as HF, *not* as $\text{H}_3\text{O}^{1+} + \text{F}^{1-}$ because HF represents the predominant species in an aqueous solution. A *solution of a strong acid is represented by the hydronium ion and its conjugate base, but a solution of a weak acid is written as the unreacted (undissociated) acid*. Note that in each case, the solution is represented by the principle species present; that is, the one(s) present with the greatest concentration(s).

Example 12.11

Write net equations for the following reactions. Determine the value of the equilibrium constant. Use a single arrow for reactions in which $K \geq 10^3$.

- a) Solutions of barium hydroxide and nitric acid are mixed.



Nitric acid is a strong acid, so it must be written as $\text{H}_3\text{O}^{1+} + \text{NO}_3^{1-}$.

- All nitrates are soluble (Solubility Rule 2), so Ba^{2+} and NO_3^{1-} do not react; they are spectator ions.
- H_3O^{1+} is the strongest acid that can exist in water (all of the acids above H_3O^{1+} react with water to produce H_3O^{1+}), and OH^{1-} is the strongest base in water (any base below OH^{1-} reacts with water to produce OH^{1-}). Consequently, they react extensively.



The preceding chemical equation is the general equation for the reaction of any strong acid and any strong base. H_3O^{1+} is the reacting acid and H_2O is the produced acid, so $K = (1.0)/(1.0 \times 10^{-14}) = 1.0 \times 10^{+14}$, which is so large that the reaction is usually written with a single arrow rather than double, equilibrium arrows; but it is still an equilibrium process.

In the remainder of this example, the ions and/or molecules that comprise the solutions are shown in the margin.

Table 12.3 An Acid-Base Table

Acid	K_a	Base
HClO_4	$\gg 1$	ClO_4^{1-}
HX	$\gg 1$	X^{1-} ($\text{X}=\text{I}, \text{Br}, \text{Cl}$)
H_2SO_4	$\gg 1$	HSO_4^{1-}
HNO_3	$\gg 1$	NO_3^{1-}
H_3O^{1+}	1.0	H_2O
H_2SO_3	1.5×10^{-2}	HSO_3^{1-}
HSO_4^{1-}	1.2×10^{-2}	SO_4^{2-}
H_3PO_4	7.5×10^{-3}	$\text{H}_2\text{PO}_4^{1-}$
HF	7.2×10^{-4}	F^{1-}
HNO_2	4.0×10^{-4}	NO_2^{1-}
$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}	$\text{C}_2\text{H}_3\text{O}_2^{1-}$
H_2CO_3	4.3×10^{-7}	HCO_3^{1-}
HSO_3^{1-}	1.0×10^{-7}	SO_3^{2-}
H_2S	1.0×10^{-7}	HS^{1-}
$\text{H}_2\text{PO}_4^{1-}$	6.2×10^{-8}	HPO_4^{2-}
HClO	3.5×10^{-8}	ClO^{1-}
NH_4^{1+}	5.6×10^{-10}	NH_3
HCN	4.0×10^{-10}	CN^{1-}
HCO_3^{1-}	4.7×10^{-11}	CO_3^{2-}
HPO_4^{2-}	4.8×10^{-13}	PO_4^{3-}
HS^{1-}	1.3×10^{-13}	S^{2-}
H_2O	1.0×10^{-14}	OH^{1-}
NH_3	$<<10^{-14}$	NH_2^{1-}
OH^{1-}	$<<10^{-14}$	O^{2-}

Stronger
Acids

Weaker
Bases

Weaker
Acids

Stronger
Bases

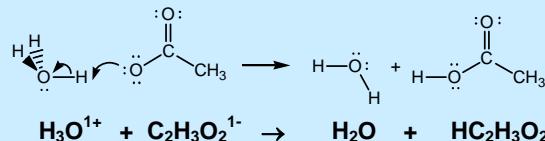
Acids and bases that lie between the lines drawn above water as a base and below water as an acid exist in aqueous solution, i.e., they are weak acids and bases. Those above or below the lines react extensively with water to produce either H_3O^{1+} or OH^{1-} ; i.e., they are strong acids and bases.

The arrows on the sides indicate the result of extensive proton transfer: stronger acids are converted into weaker acids and stronger bases are converted into weaker bases.

b) Solutions of sodium acetate and hydrochloric acid are mixed.

Hydrochloric acid is a strong acid and is written as $\text{H}_3\text{O}^{1+} + \text{Cl}^{1-}$.

1. Sodium chloride is soluble (Solubility Rule 1), so Na^{1+} and Cl^{1-} are spectator ions.
2. Acetate ion is a weak base, but it is well below H_3O^{1+} on the acid-base chart. Consequently, an extensive proton transfer reaction occurs.

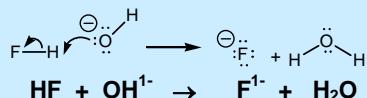


This reaction is representative of a strong acid reacting with a weak base. These types of reactions are extensive and are, therefore, usually written with single arrows. For the above reaction, $K = (1.0)/(1.8 \times 10^{-5}) = 5.6 \times 10^4$.

c) Solutions of sodium hydroxide and hydrofluoric acid are mixed.

HF is a weak acid, so it is written in molecular form.

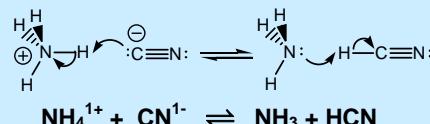
1. NaF is soluble (Solubility Rule 1), so Na^{1+} is a spectator ion.
2. HF is a weak acid, but OH^{1-} is a strong base, located well below the weak acid, so an extensive reaction is predicted.



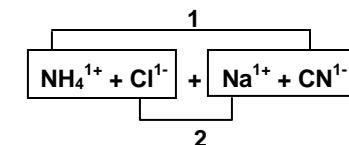
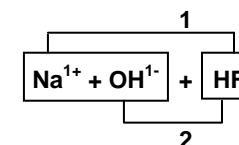
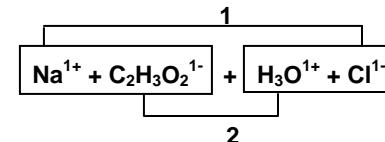
This is a reaction between a weak acid and a strong base. Reactions of weak acids with hydroxide ion are extensive because hydroxide ion is a very strong base. Consequently, they are typically written with a single arrow. $K = (7.2 \times 10^{-4})/(1.0 \times 10^{-14}) = 7.2 \times 10^{10}$.

d) Solutions of ammonium chloride and sodium cyanide are mixed.

1. NH_4CN is soluble (Solubility Rule 1), but NH_4^{1+} is also a weak acid and CN^{1-} is a weak base. Checking the acid-base table, we see that NH_4^{1+} and CN^{1-} are close to one another, so we expect the equilibrium constant to be close to 1.
2. NaCl is soluble, so Na^{1+} and Cl^{1-} are spectator ions.

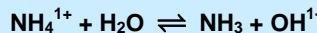


This is an example of a reaction of a weak acid and a weak base. Double arrows are used because the reacting acid (NH_4^{1+}) and the produced acid (HCN) are of comparable strengths, so the reverse reaction is important in determining the amount of product. For this reaction, $K = (5.6 \times 10^{-10})/4.0 \times 10^{-10} = 1.4$, so $[\text{NH}_3][\text{HCN}] \sim [\text{NH}_4^{1+}][\text{CN}^{1-}]$ at equilibrium.



e) **Solutions of ammonium nitrate and sodium bromide are mixed.**

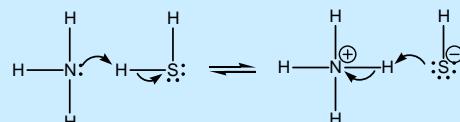
- No precipitate is predicted. NH_4^{1+} ion is a weak acid, but Br^{-} ion is a weaker base than water,* so NH_4^{1+} would react with water, not bromide ion in aqueous solution. Thus, the only reaction to take place would be the following:



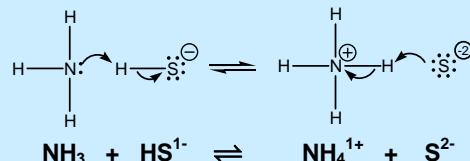
- NaNO_3 is soluble, so Na^{1+} and NO_3^{-} are spectator ions.

f) **Hydrogen sulfide is added to an excess of aqueous NH_3 .**

This is a weak acid/weak base reaction. H_2S is a diprotic acid (having two protons); but, in Brønsted acid-base reactions, the protons are removed one at a time. H_2S is a stronger acid than NH_4^{1+} , but the equilibrium constant ($K = (1.0 \times 10^{-7})/(5.6 \times 10^{-10}) = 1.8 \times 10^2$) is not greater than 10^3 , so double arrows are used.



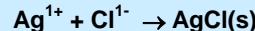
HS^{-} is amphiprotic because it is not only the conjugate base of H_2S , but it is also the conjugate acid of the S^{2-} ion. However, a check of the acid-base table indicates that HS^{-} is such a weak acid that it does not react extensively with the remaining (excess) NH_3 ($K = (1.3 \times 10^{-13})/(5.6 \times 10^{-10}) = 2.3 \times 10^{-4}$). HS^{-} is the predominant sulfur-containing species.



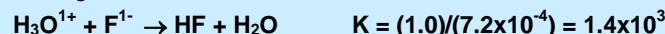
g) **Solutions of silver fluoride and hydrochloric acid are mixed.**

Hydrochloric acid is a strong acid and must be written as $\text{H}_3\text{O}^{1+} + \text{Cl}^{-}$.

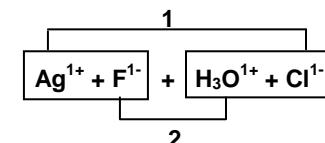
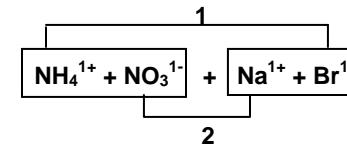
- Silver chloride is insoluble, so it precipitates from the solution (Solubility Rule 3).



- This is a strong acid-weak base reaction.

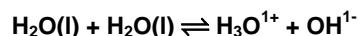


Both reactions are extensive.



12.9 pH AND pK_a

Water is both an acid and a base and can react with itself.



Water is a pure liquid and enters the equilibrium constant as unity. The equilibrium constant for this reaction is called the **ion product constant for water** and given the symbol **K_w**.

$$K_w = [\text{H}_3\text{O}^{1+}] [\text{OH}^{1-}] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Eq. 12.2

In pure water, the hydronium and hydroxide ion concentrations are the same because they are produced in a 1:1 ratio from water. Consequently, in pure water at 25 °C,

$$[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = \sqrt{K_w} = 1.0 \times 10^{-7} \text{ M}$$

Eq. 12.3

Solutions for which Equation 12.3 is valid are called **neutral**; solutions in which $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$ are called **acidic**; and solutions in which $[\text{H}_3\text{O}^{1+}] < [\text{OH}^{1-}]$ are called **basic** or **alkaline**.

The hydronium ion concentration is an important characteristic of the solution, but it is normally a small number. To avoid the use of exponentials in discussions of hydronium ion concentrations, we define the **pH** as

$$\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$$

Eq. 12.4

The exponent of $[\text{H}_3\text{O}^{1+}]$ is usually negative, so the sign of $\log[\text{H}_3\text{O}^{1+}]$ is usually negative. The negative sign in Equation 12.4 assures that the pH is *usually* positive. Because of the negative sign, *a high pH implies a low hydronium ion concentration, and a low pH implies a high hydronium ion concentration*. However, Equation 12.2 shows solutions with low hydronium ion concentrations have high hydroxide ion concentrations, so *a high pH also implies a high hydroxide ion concentration and a low pH implies a low hydroxide ion concentration*. A neutral solution is one in which $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7} \text{ M}$, so the pH of a neutral solution is determined to be $\text{pH} = -\log(1.0 \times 10^{-7}) = 7.0$. The hydronium ion is greater in an acidic solution, so the pH of an acidic solution is less than 7.0. The hydronium ion concentration is less in a basic solution, so the pH of a basic solution is greater than 7.0. These conclusions are summarized in Table 12.4.

Table 12.4 Solution type versus pH

Solution pH	solution type
above 7	basic
equal to 7	neutral
below 7	acidic

Rearranging Equation 12.2, we obtain the hydronium ion concentration in an aqueous solution as a function of the hydroxide ion concentration,

$$[\text{H}_3\text{O}^{1+}] = \frac{K_w}{[\text{OH}^{1-}]} = \frac{1.0 \times 10^{-14}}{[\text{OH}^{1-}]} \quad \text{Eq. 12.5}$$

K_a values are frequently used as a measure of an acid's ability to donate a proton, but the large exponential associated with many of the values is awkward. Consequently, a scale similar to the pH scale for $[\text{H}_3\text{O}^{1+}]$ has been defined for acids:

$$\text{p}K_a = -\log K_a \quad \text{Eq. 12.6}$$

A high pK_a indicates a weak acid. For example, the fact that the pK_a of acetic acid (4.74) is less than the pK_a of HCN (9.21) means that acetic acid is a stronger acid.

Example 12.12

- a) What is the pH of a solution in which $[\text{H}_3\text{O}^{1+}] = 1.3 \times 10^{-5} \text{ M}$? What is $[\text{OH}^{1-}]$?

$$\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log (1.3 \times 10^{-5}) = -(-4.89) = 4.89$$

$\text{pH} < 7$, so this is an *acidic* solution.

Solving Equation 12.2 for $[\text{OH}^{1-}]$, we obtain

$$[\text{OH}^{1-}] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^{1+}]} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10} \text{ M}$$

- b) What is the pH of a 0.10 M HCl solution?

Hydrochloric acid is a strong acid, so all of the HCl is converted into hydronium and chloride ions. Thus, $[\text{H}_3\text{O}^{1+}] = 0.10 \text{ M}$ (the concentration of the acid), which means that the pH of the solution is $-\log(0.10) = 1.00$.

- c) The pH of a 0.10 M solution of HBrO is 4.82, and the pH of a 0.10 M solution of HClO is 4.27. Which is the stronger acid?

Both acids have the same concentration, so the one with the greater hydronium ion concentration is the stronger acid. The acid with the lower pH has the greater hydronium ion concentration, so HClO is the stronger acid. This is expected because chlorine is more electronegative than bromine. An appreciation of how weak these acids are can be gained by comparing their pH to that of the 0.10 M HCl solution discussed in Part b above. The pH of the 0.10 M strong acid solution is 1.0, while the pH of these acid solutions is greater than 4.0. A difference of over 3 pH units means that the concentration of the hydronium ion in a 0.10 M strong acid solution is over 1,000 (10^3) times greater than in these two weak acid solutions.

d) What is the pH of a 0.022 M Ba(OH)₂ solution?

First, determine the hydroxide ion concentration from the concentration of Ba(OH)₂ and the fact that there are two moles of hydroxide ion in each mole of Ba(OH)₂.

$$[\text{OH}^{1-}] = \frac{0.022 \text{ mol Ba(OH)}_2}{\text{L of solution}} \times \frac{2 \text{ mol OH}^{1-}}{\text{mol Ba(OH)}_2} = 0.044 \text{ M}$$

We use Equation 12.5 to obtain the hydronium ion concentration

$$[\text{H}_3\text{O}^{1+}] = \frac{1.0 \times 10^{-14}}{0.044} = 2.3 \times 10^{-13} \text{ M}$$

and Equation 12.4 to determine the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log(2.3 \times 10^{-13}) = 12.64$$

Example 12.13

The pK_a of phenol is 10.0 while the pK_a of the hydrogen sulfite (bisulfite) ion is 7.0. Which acid is the stronger acid?

The strength of an acid increases as its pK_a decreases, so the bisulfite ion is the stronger acid because it has the lower pK_a.

Example 12.14

Indicate the solution with the greater hydronium ion concentration in each pair.

a) 0.10 M HNO₂ or 0.15 M HNO₂?

The acids are identical, so the only difference is concentration. The more concentrated acid (0.15 M HNO₂) has the greater hydronium ion concentration.

b) 0.10 M KF or 0.15 M KF?

Both are solutions of the same weak base, so the hydroxide ion concentration and pH increase with the concentration of the base. Thus, the less concentrated base (0.10 M KF) has the lower OH¹⁻ concentration and the greater H₃O¹⁺ concentration.

c) 0.05 M benzoic acid (pK_a = 4.19) or 0.05 M lactic acid (pK_a = 3.85)?

Lactic acid has the lower pK_a, so it is the stronger acid and has the greater H₃O¹⁺ concentration.

d) a solution with pH = 3 or one with a pH = 5?

The solution with the lower pH (pH = 3 solution) has the higher H₃O¹⁺ ion concentration.

e) **0.1 M Ba(OH)₂ or 0.15 M KOH?**

Both are strong base solutions. $[\text{OH}^-] = 2(0.10) = 0.20 \text{ M}$ in the Ba(OH)₂ solution, but it is only 0.15 M in the KOH solution. The 0.15 M KOH has the lower hydroxide ion concentration, so it has the greater hydronium ion concentration.

12.10 CHAPTER SUMMARY AND OBJECTIVES

A Lewis base is a substance with an electron pair that can be used to form a covalent bond. A Lewis acid is a substance with an empty orbital that can overlap with the electron pair on the base to form a bond. The Lewis definition is the most general acid-base definition. A Brønsted acid is a proton donor, and a Brønsted base is a proton acceptor. All Brønsted bases are Lewis bases and *vice versa*. The *proton is a Lewis acid* because it will readily accept a pair of electrons to share in a covalent bond, but the *proton defines all Brønsted acids*.

As the strength of the H-A bond increases the strength of HA as an acid decreases and the strength of its conjugate base, A¹⁻, increases. Many acids contain the unit H-O-X. For these oxoacids, the acid strength increases as the electronegativity and/or the oxidation state of X increases. The relative strength of an acid is measured by its acid dissociation constant, K_a, which is the equilibrium constant for the reaction of the acid with water. If K_a >> 1, the acid is a strong acid; if K_a << 1, the acid is a weak acid. The equilibrium of a Brønsted acid-base reaction is equal to the K_a of the reacting acid divided by the K_a of the produced acid.

The products of a Brønsted acid-base reaction are the conjugate base of the reacting acid and the conjugate acid of the reacting base. The reaction is extensive when the produced acid and base are weaker than the reacting acid and base, which is quantified by the expression K = K_a(reacting)/K_a(produced).

The pH of a solution is often used instead of the hydronium ion concentration to avoid the awkwardness of using large, negative exponentials. The pH is defined as -log[H₃O¹⁺]. Solutions with pH = 7 are said to be neutral, while solutions with pH > 7 are basic and those with pH < 7 are acidic. Exponentials can also be avoided when referring to the K_a of the acid by using pK_a, which is defined as -log K_a. A high pK_a implies a weak acid.

After studying the material presented in this chapter, you should be able to:

1. define acids and bases using both the Lewis and Brønsted definitions (Sections 12.1 and 12.2);
2. identify the acid and the base in a reaction (Sections 12.1 and 12.2);
3. explain how acids are named (Section 12.2);
4. discuss the factors dictating the extent of proton transfer in an acid-base reaction (Sections 12.3 and 12.4);
5. explain the factors dictating the relative strengths of acids (Section 12.5);
6. define K_a (Sections 12.6);
7. use the acid-base table to write acid-base reactions and to predict the extent of proton transfer (Section 12.7);
8. determine the equilibrium constant for an acid-base reaction from the K_a values of the reacting and produced acids (Section 12.7);
9. define pH and determine the pH of a solution from the hydronium ion concentration (Section 12.8);
10. determine the hydronium ion concentration in a solution given the hydroxide ion concentration and *vice versa* (Section 12.8); and
11. define pK_a and determine the pK_a of an acid from its K_a (Section 12.8).

12.11 EXERCISES

1. Distinguish between an Arrhenius, a Brønsted, and a Lewis acid.
2. Define a Lewis acid and a Lewis base.
3. What is a salt?
4. What is a conjugate acid-base pair?
5. Use curved arrows to show the mechanisms of the following Lewis acid-base reactions. Identify the Lewis acid and the Lewis base. What is the hybridization of the boron before and after reaction (a)? What is the hybridization of the carbons before and after reaction b? Note that reaction (b) is a two-step reaction like that shown in Figure 12.4.

a) $\text{BF}_3 + \text{NH}_3 \rightarrow \text{F}_3\text{B}-\text{NH}_3$ **b)** $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$
6. Use curved arrows to show the mechanisms of the following Lewis acid-base reactions. Identify the Lewis acid and the Lewis base. What is the hybridization of the boron before and after reaction (a)? What is the hybridization of the sulfurs before and after reaction b? Note that reaction (b) is a two-step reaction like that shown in Figure 12.4.

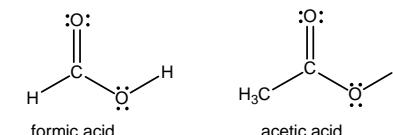
a) $\text{B}(\text{OH})_3 + \text{OH}^{1-} \rightarrow \text{B}(\text{OH})_4^{1-}$ **b)** $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$
7. The potential energy diagram below is for following the acid-base reaction:
 $\text{HA(aq)} + \text{B(aq)} \rightarrow \text{A}^{1-}(\text{aq}) + \text{HB}^{1+}(\text{aq})$

a) Which is the stronger acid?
b) Which is the stronger base?
c) What is the magnitude of the equilibrium constant for the reaction ($K > 1$ or $K < 1$)?
d) Draw a probable transition state (Section 9.7).
8. What is the conjugate acid of each of the following?

a) F^{1-} **b)** OH^{1-} **c)** HSO_3^{1-} **d)** S^{2-}
9. What is the conjugate base of each of the following?

a) HClO **b)** NH_4^{1+} **c)** H_3PO_4 **d)** HSO_3^{1-}
10. CH_3 and CH_2 groups are said to be *electron donating* groups because they place electron density on the atoms to which they are attached. Which is a stronger base CH_3NH_2 or NH_3 ? Explain.

11. Which is the stronger acid, formic acid or acetic acid? Which acid has the greater pK_a ? Explain your answers. Refer to Exercise 10 for information about CH_3 groups.



12. Which is the stronger base, NH_3 or NF_3 ? Explain.
13. List the following compounds in order of increasing acidity. (Recall that from Exercise 10 that CH_3 groups are electron donating.)

H-O-H H-O-Cl H-O-CH₃ H-O-I
14. Indicate the stronger acid in each of the following pairs and explain your choice:
 - H_3AsO_4 or H_3AsO_3
 - H_2SeO_4 or H_2SO_4
 - CH_4 or NH_3 (see Table 9.1 on page 176)
15. Indicate the stronger acid in each of the following pairs and explain your choice:
 - H_2SeO_3 or HSeO_3^{1-}
 - HIO_4 or HIO_2
 - CH_3COOH or CF_3COOH
16. Use curved arrows and Lewis structures to indicate the mechanisms of the following acid-base reactions:

a) $\text{HClO}_2 + \text{H}_2\text{O}$ **b)** $\text{PO}_4^{3-} + \text{HCN}$ **c)** $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^{1-}$
17. Use curved arrows and Lewis structures to indicate the mechanisms of the following acid-base reactions.

a) $\text{HF} + \text{S}^{2-}$ **b)** $\text{NH}_3 + \text{HNO}_2$ **c)** $\text{H}_2\text{SO}_3 + \text{C}_2\text{H}_3\text{O}_2^{1-}$
18. Equal amounts of benzoic acid and sodium acetate are mixed. At equilibrium, the concentration of the benzoate ion is just slightly greater than that of the acetate ion. What can be concluded about the relative acid strengths of acetic acid and benzoic acid?
19. Consider the reaction, $\text{HBrO} + \text{CN}^{1-} \rightleftharpoons \text{BrO}^{1-} + \text{HCN}$ $K = 5$
 - Which is the weaker of the two acids in the above reaction?
 - Which is the weaker of the two bases in the above reaction?
 - Given that $K = 0.08$ for $\text{HBrO} + \text{ClO}^{1-} \rightleftharpoons \text{BrO}^{1-} + \text{HClO}$ predict where on the acid-base table should HBrO be placed, above HClO , between HClO and HCN , or below HCN ?

20. Consider the following reaction: $\text{H}_2\text{C}_2\text{O}_4 + \text{F}^{1-} \rightleftharpoons \text{HC}_2\text{O}_4^{1-} + \text{HF}$ $K \sim 100$
- Which of the two bases is stronger?
 - Which of the two acids is stronger?
 - What is the approximate value of K_a for $\text{H}_2\text{C}_2\text{O}_4$?
21. The K_a of nitrous acid (HNO_2) is 4.0×10^{-4} .
- Write the reaction to which this equilibrium constant applies.
 - Express the K_a of nitrous acid in terms of concentrations.

For Exercises 22 and 23, use Equation 12.1 and Table 12.3 to determine the value of the equilibrium constant and write the equilibrium constant expression for each reaction.

22. a) $\text{H}_2\text{CO}_3 + \text{SO}_4^{2-} \rightleftharpoons \text{HCO}_3^{1-} + \text{HSO}_4^{1-}$
b) $\text{H}_2\text{S} + \text{NH}_3 \rightleftharpoons \text{HS}^{1-} + \text{NH}_4^{1+}$
c) $\text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^{1-} + \text{OH}^{1-}$
23. a) $\text{NO}_2^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^{1-}$
b) $\text{HSO}_3^{1-} + \text{HCO}_3^{1-} \rightleftharpoons \text{SO}_3^{2-} + \text{H}_2\text{CO}_3$
c) $\text{H}_3\text{PO}_4 + \text{OH}^{1-} \rightleftharpoons \text{H}_2\text{PO}_4^{1-} + \text{H}_2\text{O}$

For Exercises 24 and 25, write net equations for the acid-base reactions that occur when the given aqueous solutions are mixed. Determine the value of the equilibrium constant. Use single arrows for extensive reactions ($K > 1000$) but double arrows otherwise.

24. a) $\text{HNO}_2 + \text{NaOH}$ b) $\text{NH}_4\text{Cl} + \text{Na}_2\text{SO}_3$
c) $\text{NaClO} + \text{NaH}_2\text{PO}_4$ d) $\text{HBr} + \text{NH}_3$
e) $\text{HF} + \text{NaCN}$ f) $\text{H}_3\text{PO}_4 + \text{NaC}_2\text{H}_3\text{O}_2$
g) $\text{HClO}_4 + \text{NaH}_2\text{PO}_4$
25. a) $\text{NaC}_2\text{H}_3\text{O}_2 + \text{HCN}$ b) $\text{KOH} + \text{HI}$
c) $\text{H}_2\text{S} + \text{K}_2\text{HPO}_4$ d) $\text{NaOH} + \text{HClO}$
e) $\text{NaNO}_2 + \text{H}_2\text{CO}_3$ f) $\text{NH}_4\text{Cl} + \text{KOH}$
g) $\text{HNO}_3 + \text{KF}$

26. Indicate whether each of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte:
- HF
 - NaF
 - HCl
 - CH_3Cl

27. Indicate whether each of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte:
- NH_3
 - C_6H_6
 - HClO
 - NH_4Cl
28. What is meant by a neutral solution?
29. Which of the following compounds could be used to lower the pH of a solution?
- K_2S
 - NH_4Cl
 - KCl
 - KHSO_4
 - HF
30. Indicate whether each of the following solutions is acidic, basic, or neutral:
- 0.1 M KNO_2
 - a solution with a pH of 3
 - a solution in which $[\text{OH}^{1-}] = 10^{-4}$ M
 - a solution in which $[\text{OH}^{1-}] = 10^{-8}$ M
31. Indicate whether each of the following solutions is acidic, basic, or neutral:
- 0.10 M CH_3COOH
 - 0.10 M NaCN
 - 0.10 M KBr
 - a solution in which $[\text{H}_3\text{O}^{1+}] = 10^{-5}$ M
32. Indicate which solution in each pair has the lower pH:
- 0.1 M HClO_2 or 0.2 M HClO_2
 - 0.1 M K_3PO_4 or 0.2 M K_3PO_4
 - 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ or 0.1 M HNO_2
 - 0.1 M NaOH or water
33. Calculate the pH of each of the following strong acid solutions:
- 0.0032 M HCl
 - 0.016 M HCl
 - 1.5 M HNO_3
34. Calculate the pH of each of the following strong acid solutions:
- 0.80 M HCl
 - 2.1×10^{-5} M HClO_4
 - 2.1×10^{-3} M HCl
35. Calculate the pH of the following basic solutions:
- 0.0032 M NaOH
 - 0.016 M KOH
 - 0.040 M Ba(OH)_2
36. Write the expression for K_a for each of the following acids and the chemical equation to which it applies.
- NH_4^{1+}
 - H_3PO_4
 - HSO_3^{1-}
 - CH_3COOH

37. Determine the pK_a of each of the following weak acids:
a) HF b) HClO c) HS^{1-}
38. Determine the pK_a of each of the following weak acids:
a) $\text{H}_2\text{PO}_4^{1-}$ b) H_2O c) H_2S
39. The pK_a of acid HA is greater than that of acid HB.
a) Which is the stronger acid?
b) Which is the stronger base, B^{1-} or A^{1-} ?
40. The pK_a of acid HA is greater than that of acid HB.
a) Which has the higher pH, 0.1 M HA or 0.1 M HB?
b) Which has the higher pH, 0.1 M KA or 0.1 M KB?
41. What is the K_a of an acid with a pK_a of 4.87?
42. Formic acid (HCOOH) is a weak acid. Write the K_a reaction and determine the value of K_a if $[\text{HCOOH}] = 0.10 \text{ M}$ and $[\text{HCOO}^{1-}] = [\text{H}_3\text{O}^{1+}] = 0.0042 \text{ M}$. Above which acid in Table 12.3 would formic acid be placed?
43. Phenol ($\text{C}_6\text{H}_5\text{OH}$) is a weak acid with $\text{K}_a = 1.0 \times 10^{-10}$.
a) Write the reaction to which this number applies.
b) What is the pK_a of phenol?
c) What is the concentration of phenol in a solution in which $[\text{C}_6\text{H}_5\text{O}^{1-}] = 3.2 \times 10^{-6} \text{ M}$ and $\text{pH} = 6.00$?
44. Determine the hydronium ion concentration in a solution in which the concentrations of acetic acid and acetate ion are equal. What is the pH of this solution? The K_a of acetic acid is 1.8×10^{-5} .

Chapter 13

Organic Chemistry

- 13.0 Introduction*
- 13.1 Hydrocarbons*
- 13.2 Naming Simple Hydrocarbons*
- 13.3 Isomers*
- 13.4 Functional Groups*

- 13.5 Introduction to Organic Reactions*
- 13.6 Polymers*
- 13.7 Chapter Summary and Objectives*
- 13.8 Exercises*

13.0. INTRODUCTION

Organic chemistry is the study of molecules that feature carbon as the principal atomic building block. An entire branch of chemistry is devoted to carbon because carbon atoms can bond together in long chains to produce an enormous number of organic compounds. Organic compounds are found everywhere - as structural and genetic materials of plants and animals, as drugs, plastics, dyes and textiles, paper and paper products, and on and on. This diversity could make the study of organic chemistry overwhelming, but the rules for understanding organic molecular structure and reactivity are based on familiar principles that have been covered earlier in this text: Lewis structures, resonance, and Lewis acid-base theory. In addition, organic compounds have been organized into a relatively few classes according to their structural and chemical characteristics. In this chapter, we explore fundamental concepts of the structure and properties of several classes of organic molecules.

THE OBJECTIVES OF CHAPTER 13 ARE TO:

- explain how to name simple organic molecules;
- show how to represent organic molecules in both skeletal and condensed structures;
- define and identify structural isomers of simple molecules;
- characterize several common functional groups;
- explain the mechanism for the reaction of a hydrogen halide and an alkene;
- distinguish between addition and condensation polymers and show examples of each; and
- explain the role of hydrogen bonding in the structures of proteins and DNA.

13.1 HYDROCARBONS

Carbon atoms always have four bonds: four single bonds, two single and one double bond, two double bonds, or a single bond and a triple bond. Although carbon is the basic building block, organic compounds usually have hydrogen atoms as well. Oxygen and nitrogen are also common, but almost any other element can be found in organic compounds. In this section, we deal with the class of compounds known as **hydrocarbons**, which are compounds that contain only carbon and hydrogen.

Alkanes are the simplest organic compounds. All of the carbon atoms in an alkane are sp^3 hybridized and tetrahedral, and all bonds are sigma bonds, which makes alkanes relatively unreactive. They have the general formula C_nH_{2n+2} , where n is an integer. Figure 13.1 shows CH_4 , C_2H_6 and C_3H_8 , the three simplest alkanes. The line-wedge-dash representations attempt to give a three-dimensional view of the organic molecules. However, groups connected by a single bond can rotate relative to one another, so the structures of alkanes are very dynamic, and there is not much to be gained by attempting to show a three-dimensional structure. Instead, several shorthand notations are used for drawing organic molecules. These shorthand notations are based on the following facts:

- carbon atoms form the backbone of organic molecules;
- carbon atoms always have four bonds in their molecules; and
- organic compounds usually contain many C-H bonds.

Figure 13.2 shows four ways of representing a C_4H_{10} molecule. Figure 13.2a is the line-wedge-dash representation. Figure 13.2b is the Lewis structure, which shows all atoms in a plane and all angles at 90° . Structures like those shown in Figure 13.2c, which give the number of hydrogen atoms but do not show the C-H bonds explicitly, are called **condensed structures**. The number of carbon atoms and the number of C-H bonds in organic molecules can be quite large, so organic molecules are often represented by **skeletal structures**, Figure 13.2d, that show neither the carbon atoms nor the hydrogen atoms attached to them explicitly. Rather, they show only the bonds connecting the carbon atoms. All other atoms, including hydrogen atoms attached to non-carbon atoms, are included explicitly. The fact that carbon always has four bonds is used to determine whether an intersection or end of a line segment represents a C, a CH, a CH_2 , or a CH_3 . For example, Figure 13.2d shows two ends and two intersections, so the molecule contains four carbon atoms. Only one bond is drawn to the carbon atom at each end, so there must

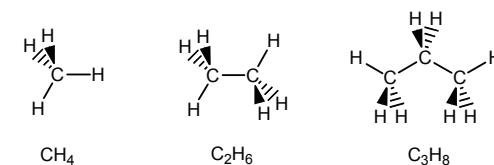


Figure 13.1 The simplest alkanes

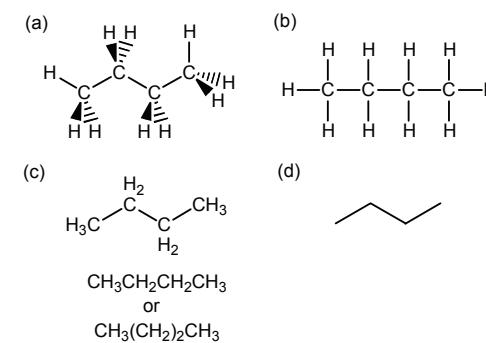


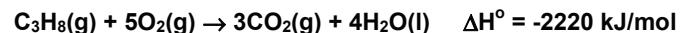
Figure 13.2 Four representations of C_4H_{10}

- a) Line-wedge-dash representation;
- b) Lewis structure;
- c) condensed structures; and d) skeletal structure

be three additional bonds, which are assumed to be C-H bonds, which makes the end positions CH₃ groups. There are two bonds drawn to the two carbon atoms in the middle, so there must also be two C-H bonds to each. These intersections represent CH₂ groups.

There is only one way to connect the atoms in each of the alkanes shown in Figure 13.1, but there are multiple ways to connect the atoms in all other alkanes. Consider the four-carbon alkane C₄H₁₀. Figure 13.2 and Figure 13.3a show C₄H₁₀ as a **straight or continuous chain** hydrocarbon (no carbon bound to more than two other carbons). However, C₄H₁₀ can also exist as a **branched** hydrocarbon (at least one carbon atom bound to three or four other carbon atoms), as shown in Figure 13.3b. The two structures shown in Figure 13.3 have the same formula, C₄H₁₀, but they are different molecules. Different molecules with the same formula are called **isomers**. The two molecules shown in Figure 13.3 are the two isomers of C₄H₁₀. The number of isomers can be very large for a formula containing a large number of carbon atoms. Isomers are prevalent in organic chemistry and are one of the reasons there is such a diversity of organic molecules. We consider isomers in more detail in Section 13.3.

The two major sources of alkanes are natural gas (mostly CH₄ and C₂H₆) and petroleum (a mixture of thousands of substances, mainly hydrocarbons that were formed from the decomposition of plants and animals). Although alkanes are not very reactive, they do burn. As discussed in Section 9.3, combustion of alkanes such as C₃H₈ (propane, home heating and cooking), C₄H₁₀ (butane, lighter fluid), and C₈H₁₈ (octane, a component of gasoline) are an important source of heat and power. As an example, the combustion of propane is



C-H and C-C bond cleavage during a combustion reaction is homolytic,* so each atom in the bond retains one of the bonding electrons to produce two species, called **free radicals**, that have unpaired electrons (Figure 13.4). Free radicals are highly reactive, but they are stabilized when the unpaired electron is on an atom that is attached to other carbon-containing groups. Thus, free radicals formed from highly branched carbon atoms, such as (CH₃)₃C·, are more stable and less reactive than those formed from straight chain hydrocarbons. Indeed, straight chain hydrocarbons react so fast and violently that they can cause an engine to ‘knock’. The octane rating of a gasoline indicates the extent of knocking it causes. The reference molecules are shown in Figure 13.5. The straight chain hydrocarbon C₇H₁₆ causes substantial knocking and is assigned an octane rating of 0,

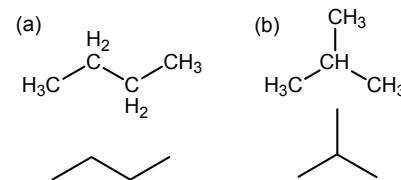


Figure 13.3 Straight or continuous chain (a) and branched (b) isomers of C₄H₁₀

* Bond breaking in which one bonding electron resides on each atom after the bond is broken is called **homolytic** bond cleavage. If both bonding electrons remain on one atom after the bond breaks, the cleavage is said to be **heterolytic**.

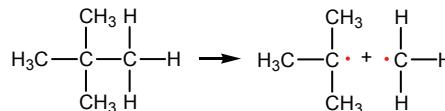


Figure 13.4 Free radicals have unpaired electrons

Homolytic bond cleavage of a C-C bond produces two free radicals. The radicals are stabilized when the carbon atom with the unpaired electron is bound to one or more carbon atoms, so (CH₃)₃C· is more stable and less reactive than H₃C·.

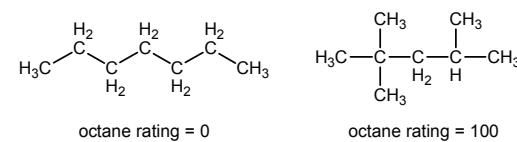


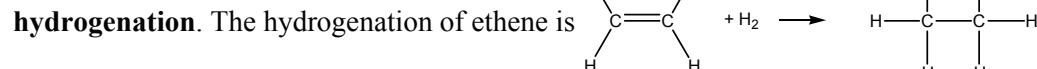
Figure 13.5 Reference molecules used in establishing the octane rating of a gasoline

while the highly branched alkane C₈H₁₈ causes little knocking and is assigned an octane rating of 100. A gasoline with an octane rating of 87 causes the same knocking as a mixture that is 87% in the branched alkane and 13% of the straight chain alkane.

Alkenes are organic compounds that contain carbon-carbon double bonds. The two simplest alkenes, C₂H₄ and C₃H₆, are shown in Figure 13.6. It might appear that the C₃H₆ molecules shown in Figures 13.6b and 13.6c are different, but they can be interchanged by a simple rotation, so they are representations of the same molecule and not isomers. Now consider the representations of C₄H₈ shown in Figure 13.7. The double bond can be placed after either the first (Figure 13.7a) or second carbon (Figure 13.7c). However, placing the double bond after the third carbon (Figure 13.7b) is the same as placing it after the first carbon atom because the two molecules can be interchanged by a simple rotation. We conclude that Figure 13.7 shows only *two* isomers of C₄H₈ (Figures 13.7a and 13.7c).

Alkenes with several double bonds are called **polyenes**, and polyenes with alternating single and double bonds have delocalized π systems. As the number of delocalized bonds in a polyene increases, the energy spacing between their π MOs decreases (Section 8.6) as does their HOMO-LUMO gap (the energy separation between the highest occupied and lowest unoccupied MOs). In large π systems, the HOMO-LUMO gap drops into the visible region of the spectrum ($\Delta E = h\nu$) and the polyene absorbs visible light. Indeed, most dyes are polyenes of this type. Figure 13.8 shows β -carotene, which contains 21 alternating single and double bonds, so its π system is delocalized. The HOMO-LUMO energy gap is such that β -carotene absorbs blue light and reflects orange light. β -carotene is the compound responsible for the orange color of carrots.

Alkenes are far more reactive than alkanes. Most of the chemical reactivity of alkenes comes from the fact that the pi bond can act as an electron pair source (it is a Lewis base) and can initiate the formation of new chemical bonds. As an example, hydrogen can add across the double bond of an alkene to produce an alkane in a process called



Alkenes are said to be **unsaturated** because hydrogen atoms can be added to them. Similarly, *polyenes* are said to be *polyunsaturated*. Alkanes, on the other hand, have no multiple bonds, so no more hydrogen atoms can be added to them. Therefore, alkanes are said to be **saturated**.

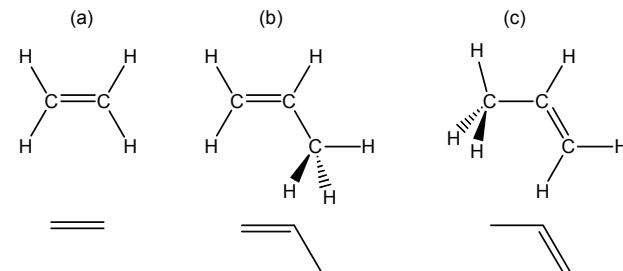


Figure 13.6 Ethene and propene

(a) C₂H₄, (b) and (c) are identical structures of C₃H₆. The skeletal structures are shown beneath the Lewis structures.

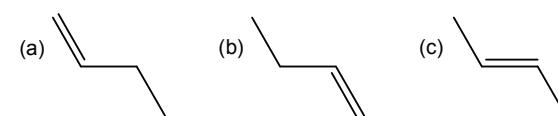


Figure 13.7 Isomers of C₄H₈

(a) and (b) are identical molecules. (c) is the second other isomer.



Figure 13.8 β -carotene

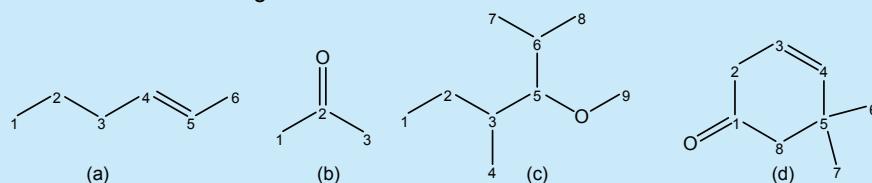
The π electrons are delocalized over the 21 alternating single and double bonds.

Alkynes are hydrocarbons that contain at least one triple bond. The simplest alkyne is C₂H₂ (see margin), which is commonly known as acetylene. Carbon atoms involved in triple bonds have only two electron regions and are sp hybridized and have 180° bond angles. The presence of π electrons makes them Lewis basic as well, and their chemistry is similar to that described above for alkenes. Alkynes are also unsaturated.

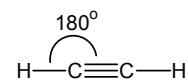
Example 13.1

Write condensed structures corresponding to the skeletal structures shown below.

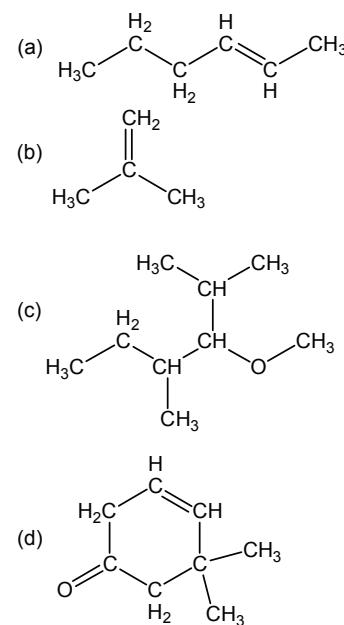
Note that the numbers of the carbon positions are included for discussion purposes only. Position numbers are not usually included and those given here do not represent the normal method of numbering.



- a) The positions labeled 1 and 6 each have only one bond drawn to them, but carbon atoms must have four bonds, so each must contain three C-H bonds. As a result, positions 1 and 6 are CH₃ groups. Two bonds are drawn to positions 2 and 3, so they must each be CH₂ groups. Three bonds are drawn to positions 4 and 5, so they are CH groups. The condensed structure of (a) is shown in the margin.
- b) The positions labeled 1 and 3 each have only one bond drawn to them, so the other three bonds to each must be C-H bonds. Thus, positions 1 and 3 are CH₃ groups. There are already four bonds drawn to position 2, so it is a carbon atom with hydrogen atoms attached. The condensed structure of (b) is shown in the margin.
- c) Positions 1, 4, 7, 8, and 9 are all CH₃ groups. Position 2 is a CH₂ group. Positions 3, 5 and 6 each show three bonds, so they are CH groups. The condensed structure of (c) is shown in the margin.
- d) Position 1 has four bonds and is a carbon atom with no hydrogen atoms attached. Positions 2 and 8 are CH₂ groups. Positions 3 and 4 each show three bonds and are CH groups. Positions 6 and 7 must be CH₃ groups, because there is only one bond shown to each carbon. Position 5 already has four bonds shown, so there are no C-H bonds required. The condensed structure of (d) is shown in the margin. It contains two CH₃ groups and an oxygen atom attached to a six-carbon ring. Cyclic structures like the six-carbon ring are very common in organic chemistry.



C₂H₂, Acetylene



13.2 NAMING SIMPLE HYDROCARBONS

Straight or continuous chain alkanes are named by indicating the number of carbon atoms in the chain with the appropriate **root name** as given in Table 13.1 and adding **ane** to indicate that the compound is an alkane. For example, the straight chain alkane C₇H₁₆ contains seven carbon atoms in the chain, so its root name from Table 13.1 is *hept*. It is an alkane, so its name ends in *ane*. Thus, C₇H₁₆ is heptane.

All of the carbon atoms in a branched chain alkane are not in the same chain, so they are named by identifying the *longest continuous chain* with the appropriate root name and then identifying the type and positions of any side chains that are attached to the longest continuous chain. Side chains can be any type of group, but we restrict our discussion to alkyl groups. **Alkyl groups** are formed by removing one hydrogen atom from an alkane. The resulting alkyl group binds to a longer chain at the position of the removed hydrogen. Alkyl groups are parts of compounds; they are not compounds themselves. The name of the alkyl group is obtained by adding -yl to the root name. The two simplest alkyl groups are:



The dash before the formula indicates where they bond to a longer chain. Propyl, butyl, pentyl, etc., groups also exist, but there are more than one of each of these alkyl groups. For example, there are two different propyl groups that differ by the position of the removed hydrogen, which can come from a terminal carbon atom or from the middle carbon atom. We restrict our discussion of naming organic compounds to compounds that contain methyl and/or ethyl groups to avoid this complexity.

The carbon atoms in the longest continuous chain are numbered starting at the end closest to the side chain, and the position of the alkyl group is indicated by the number of the carbon atom to which it is attached. The name of the alkyl group and the name of the longest chain are combined into one word. For example, 2-methylhexane has a six-carbon chain with a CH₃ group attached to the second carbon from the end. To name alkanes with more than one side chain, simply place the names of the alkyl groups separated by hyphens in front of the root name. For example, 2-methyl-3-ethylheptane contains a seven carbon continuous chain with a CH₃ group on the second carbon and a C₂H₅ group attached to the third carbon. Two identical groups are indicated with the prefix *di* and their positions separated with a comma. For example, 2,2-dimethylheptane and 3,4-diethyloctane. The procedure for naming branched alkanes is summarized in the margin.

Table 13.1 Roots of names of simple organic compounds and the names of the corresponding alkanes

Number of C atoms	Root of name	Formula of alkane	Name of alkane
1	meth	CH ₄	methane
2	eth	C ₂ H ₆	ethane
3	prop	C ₃ H ₈	propane
4	but	C ₄ H ₁₀	butane
5	pent	C ₅ H ₁₂	pentane
6	hex	C ₆ H ₁₄	hexane
7	hept	C ₇ H ₁₆	heptane
8	oct	C ₈ H ₁₈	octane
9	non	C ₉ H ₂₀	nonane
10	dec	C ₁₀ H ₂₂	decane

To name branched chain alkanes,

- Identify the longest continuous chain, select the appropriate root from Table 13.1 and add the ending -ane.
- Number the atoms in the longest continuous chain, starting at the end of the chain closest to the branch.
- The name of the alkane is the number of the position of the side chain followed by a hyphen, then the name of the alkyl group followed by the name obtained in step one.

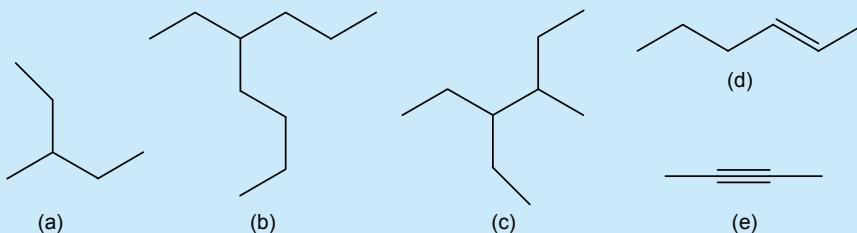
To name simple alkenes and alkynes,

- Identify the longest continuous chain *that contains the multiple bond* and determine the root of the name from Table 13.1.
- Start at the end of the chain closest to the multiple bond and number the atoms in the longest continuous chain.
- Use the number of the first carbon in the multiple bond as a prefix followed by a hyphen followed by the root with an -ene or –yne ending for alkene and alkyne, respectively. For example, 1-butyne has four carbon atoms and a triple bond between the first and second.

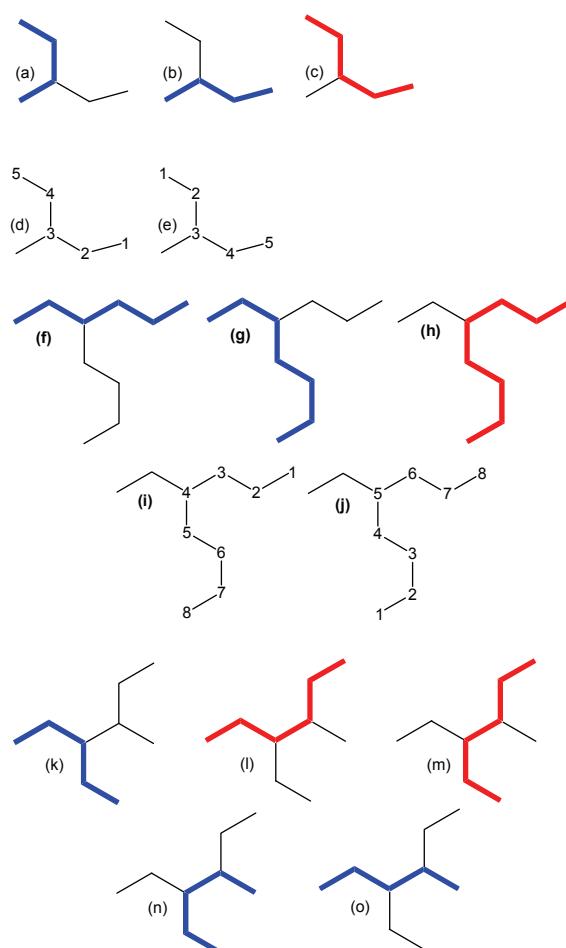
Alkenes and alkynes are named in a similar manner, but with the additional requirement that the position of the multiple bond(s) must be established. The procedure for naming simple alkenes and alkynes is summarized in the margin.

Example 13.2

Name the following organic molecules:



- a) The continuous chains of this branched alkane are highlighted with thick lines in the margin. The continuous chains in (a) and (b) contain only four carbons, while the longest continuous chain (c) contains five carbons. Because the longest continuous chain contains five carbon atoms, the compound is named as a pentane. We next identify the type and position of the attached group. The attached group contains only one carbon atom and is, therefore, a methyl group. (d) and (e) show that the methyl group is located on the third carbon, regardless of the end at which the numbering is started. The name of the compound is therefore 3-methylpentane.
- b) This is also a branched alkane. The continuous chains are shown in the margin with thick lines. (f) is a six-carbon chain; (g) is a seven-carbon chain; and (h) is an eight-carbon chain. The longest chain contains eight carbons, so this compound is named an octane. The branch contains two carbon atoms and is therefore an ethyl group. The ethyl group is located on the fourth carbon if the numbering is as in (i), but it is attached to the fifth carbon if numbering is as in (j). The compound is named so that the branch is at the lower number. Consequently, this compound is 4-ethyloctane.
- c) This molecule is a branched alkane with two branches. The continuous chains are shown as thick lines in the margin. The chains in (k), (n) and (o) each contain five atoms, while (l) and (m) are each six-carbon chains. This branched chain alkane is, therefore, named as a hexane, 3-ethyl-4-methylhexane.
- d) This is an alkene containing a six-carbon chain, so it is a hexene. The chain is numbered starting at the end closest to the double bond, so it is a 2-hexene. As we will see in Example 13.5 of the next section, there are actually two different compounds that are 2-hexene. The complete name that identifies the 2-hexene is given there.
- e) The triple bond comes after the second carbon in a four-carbon chain, so this compound is 2-butyne.

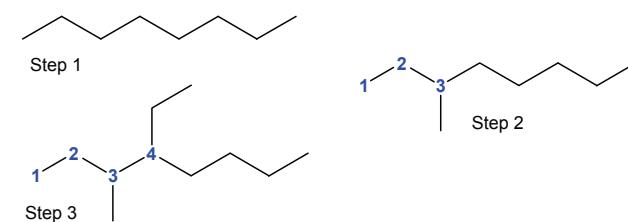


Example 13.2

Example 13.3

Draw the skeletal structure of 3-methyl-4-ethyloctane.

1. Draw the eight-carbon continuous chain of an octane. See margin.
2. Attach a methyl group to the 3 position.
3. Add an ethyl group to the 4 position.



13.3 ISOMERS

Isomers are different molecules that have different structures and properties but the same molecular formula. There are two types: *constitutional isomers* and *stereoisomers*.

CONSTITUTIONAL ISOMERS

Constitutional isomers have the same molecular formula but differ in the connectivity of the atoms; that is, they differ in how the atoms are connected to one another. For example, the carbon atoms of the two isomers of butane shown in Figure 13.3 are connected to one another in different ways, so they are constitutional isomers. Also, consider the two Lewis structures for the molecules having the molecular formula C_2H_6O shown in Figure 13.9. The structure in Figure 13.9a contains C-O-C linkage, which makes it is an *ether*, while that in Figure 13.9b contains a hydroxyl group (-OH), which makes it an *alcohol*. Alcohols and ethers are very different. Alcohols are able to hydrogen bond to one another while ethers cannot. The hydrogen bond can dramatically affect the solubility properties and the physical properties of alcohols. As an example, Figure 13.9a is dimethyl ether, which boils at $-23^{\circ}C$, while Figure 13.9b is ethanol, a hydrogen-bonding molecule that boils at $78^{\circ}C$.

Now consider the six structures for molecules having the formula $C_4H_{10}O$ (Figure 13.10). Figures 13.10a and 13.10b contain a C-O-C linkage, so they are ethers, while the remaining structures all contain hydroxyl groups, which make them alcohols. Note that, as the number of carbon atoms in the molecular formula increases, the number of constitutional isomers also increases. For $C_{12}H_{26}O$, there are well over one hundred isomers! The existence of so many constitutional isomers gives rise to a wealth of structural diversity in organic chemistry. While there is no simple mathematical relationship between the molecular formula and the number of constitutional isomers, you can be certain that molecules with a large number of carbon atoms will have a large number of constitutional isomers.

Example 13.3

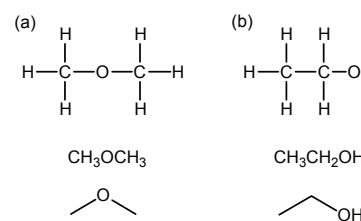


Figure 13.9 Constitutional isomers of C_2H_6O

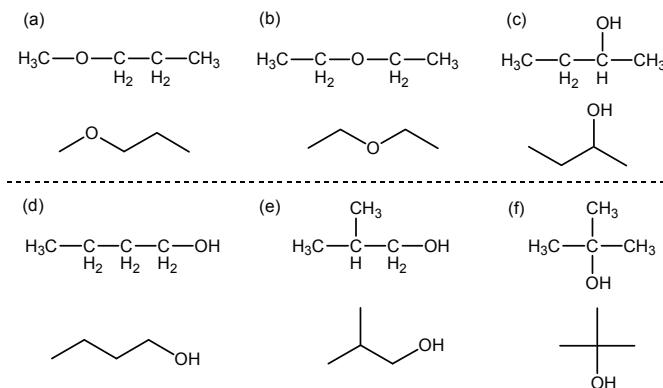


Figure 13.10 Six constitutional isomers of $C_4H_{10}O$

Example 13.4

Draw the constitutional isomers of the alkane C_6H_{14} .

Our strategy is to start with the six-carbon continuous chain isomer and then successively reduce the length of the longest continuous chain by one carbon atom, while adding alkyl groups to maintain six carbons. We do this until the branching chains are longer than our continuous chain, at which point we are done. In the following, the first number is the length of the longest chain, and the subsequent number(s) are the lengths of the alkyl groups.

6 + 0: Isomer **a** in the margin is the six-carbon chain with no side chains.

5 + 1: One methyl group must be attached to a five-carbon chain. The methyl group cannot be added to a terminal carbon (positions 1 or 5) because that would simply lengthen the chain and produce Isomer a. In addition, the 2 and 4 positions of a five-carbon chain are identical. Therefore, there are two isomers that have a five-carbon chain and one methyl group. **Isomer b** places the methyl group at position 2, and **Isomer c** places it at position 3.

4 + 2: An ethyl group cannot be added to a four-carbon chain without lengthening the chain, so there is no $4 + 2$ isomer. If the ethyl group is placed at positions 1 or 4, the result is Isomer a. If it is placed at either position 2 or position 3, Isomer c is produced.

4 + 1 + 1: The methyl groups cannot be added to the terminal carbons (positions 1 and 4), which leaves only positions 2 and 3. Adding one methyl to each position produces **Isomer d**, and adding both methyl groups to the same position yields **Isomer e**. Note that the 2 and 3 positions are identical, so there is no 3,3-dimethylbutane.

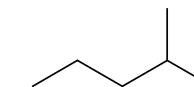
3 + 2 + 1: The three-carbon chain is shown in blue in Figure (f) in the margin. Adding an ethyl group to position 2 lengthens the chain to four atoms to produce Isomer e.

3 + 3: As shown in (g), adding a propyl group (three carbon alkyl group) to position 2 of a three-carbon chain (blue bonds) lengthens the chain to five carbons. The resulting isomer is identical to Isomer b.

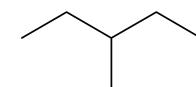
We conclude that there are no isomers of C_6H_{14} that have longest chains of less than four atoms and that there are five constitutional isomers of C_6H_{14} .



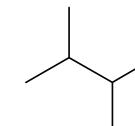
(a) hexane



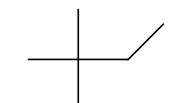
(b) 2-methylpentane



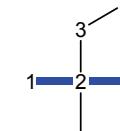
(c) 3-methylpentane



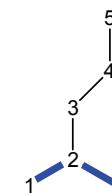
(d) 2,3-dimethylbutane



(e) 2,2-dimethylbutane



(f) 2,2-dimethylbutane
Isomer (e)



(g) 2-methylpentane
Isomer (b)

STEREOISOMERS

Stereoisomers have the same connectivity but differ in the *spatial* arrangement of their atoms. We will consider two types of stereoisomers: *geometric isomers* and *enantiomers*.

Geometric isomers

Sigma bonds are cylindrical, and the groups bound by them rotate around the bond to adopt different relative positions. Figure 13.11a shows just two of the relative positions of the fluorine atoms during a rotation about the sigma bond. However, groups connected by double bonds cannot rotate relative to one another without breaking the π bond because the rotation would move the two p orbitals used in the π bond away from one another and remove their overlap. Consequently, the transformation in Figure 13.11b cannot occur without breaking the C=C bond, so the two molecules are **geometric isomers**. A geometric isomer in which two groups are on the same side of a double bond is the **cis isomer**, while a geometric isomer in which the groups are on opposite sides of a double bond is called a **trans isomer**.

Example 13.5

Draw and name the two geometric isomers of 2-hexene.

2-hexene is $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ and, as shown in the margin, it can exist in both a *trans* and a *cis* form. In the *trans* form, the two C-C bonds (dark lines) are on opposite sides of the double bond; but, in the *cis* isomer, they are on the same side. Thus, the molecule shown in Example 13.2d is named *trans*-2-hexene to show that it is the geometric isomer in which the C-C bonds are on opposite sides of the double bond.

Name the molecule shown in the figure labeled Example 13.5b.

There are two carbon atoms with a double bond, so the compound is an ethene. Two chlorine atoms make it a dichloroethene. The two chlorine atoms are on the same side of the double bond, so the molecule is *cis*-dichloroethene.

Alkenes can convert between the *cis* and *trans* isomers if enough energy is supplied to break the π bond. For example, consider the molecule *retinal*, which is derived from β -carotene (Figure 13.8) in the body. Like β -carotene, retinal absorbs visible light, and the energy of the absorbed photon promotes an electron from a π to a π^* orbital. The result is that the excited state contains one electron in the π orbital and one in the π^* orbital, which results in a bond order of zero for the π bond shown in red in Figure 13.12; i.e., the bond is a single bond in the excited state. Rotation can occur about the resulting single bond and convert the *cis* isomer (Figure 13.12a) to the *trans* isomer (Figure 13.12b). This simple process is the driving force responsible for vision.

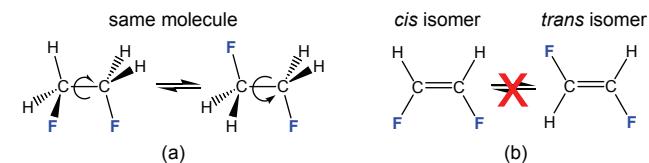
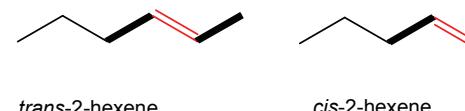


Figure 13.11 Rotation can occur about single bonds but not about double bonds.

a) The two structures of $\text{C}_2\text{H}_4\text{F}_2$ are not isomers because the groups can rotate around the single bond. b) The two structures of $\text{C}_2\text{H}_2\text{F}_2$ are isomers because the groups cannot rotate around a double bond.



Example 13.5a



Example 13.5b

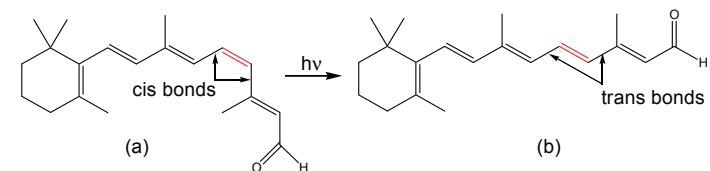


Figure 13.12 *cis* (a) and *trans* (b) isomers of retinal

Enantiomers

There is additional complexity in the structures of organic molecules that possess carbon atoms with four *different* groups attached to them. Such carbon atoms are said to be **stereocenters**. The central carbon shown in red in molecule **A** in Figure 13.13 is a stereocenter because it contains four different groups: H, OH, CH₃, and Cl. Molecule **B** in Figure 13.13 is its *mirror image*. Molecules **A** and **B** are different molecules! That they are different can be seen by rotating molecule B by 180° about the C-C bond (**B1** → **B2** in Figure 13.13). The rotation makes the OH and CH₃ groups of the two molecules (**A** and **B2**) superimposable. However, the H and the Cl groups are still reversed in the two molecules. Consequently, molecules **A** and **B** are not superimposable. *Molecules with a stereocenter cannot be superimposed on their mirror images.* Pairs of molecules that are non-superimposable mirror images are called **enantiomers**. Enantiomers are stereoisomers because their spatial arrangements are different while their connectivities are identical. Molecules **A** and **B** are enantiomers.

Switching any two groups about a stereocenter results in its mirror image. Thus, each stereocenter can have only two enantiomers, and a molecule with n stereocenters has 2ⁿ stereoisomers. For example, a molecule with fifteen stereocenters can have 2¹⁵ = 32,768 stereoisomers - a very large number of different molecules with the same formula and connectivity!

Enantiomers have the same melting and boiling points, but they often have very different biological activities. In fact, some biological processes proceed only for *one* enantiomer. For example, the enantiomers of carvone (Figure 13.14) have different odors. One enantiomer has the odor of spearmint, while the other has the odor of caraway. This is because each enantiomer is recognized by different receptors in the nose.

A tragic example of different biological reactivity of enantiomers is the drug thalidomide (Figure 13.15). One stereoisomer acts as a sedative and anti-nausea drug, while its enantiomer prevents the growth of blood vessels and modifies the immune system, which can lead to severe birth defects if taken by pregnant women. Unfortunately, a form of this drug containing both enantiomers was prescribed to pregnant women in Europe between 1959 and 1962, and the result was thousands of badly deformed newborns. Today, however, the very properties of the isomer that caused birth defects in babies is being exploited as a possible cure for leprosy, AIDS, cancer, and other diseases.

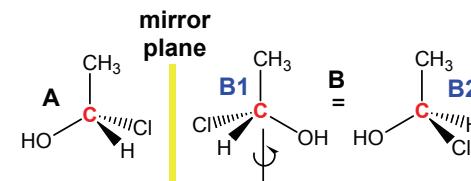


Figure 13.13 Enantiomers

Molecules A and B are mirror images. B1 and B2 are not different molecules; they simply show B before and after a rotation of 180° about the C-C bond. Molecules A and B are non-superimposable mirror images, so they are enantiomers.

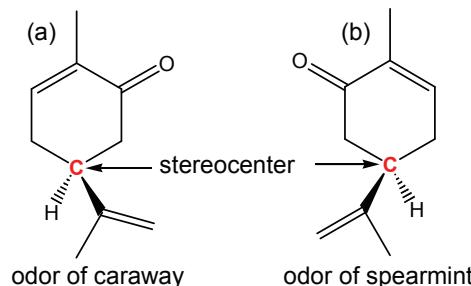


Figure 13.14 Enantiomes of Carvone with different odors

Note that the ring counts as two different groups due to the groups in it or attached to it. Going around the ring clockwise from the stereocenter, the double bond is encountered first in (a), but the C=O group is encountered first in (b).

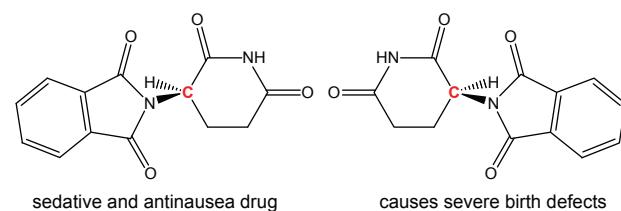


Figure 13.15 Thalidomide

Two enantiomers of thalidomide with dramatically different biological activity. The stereocenter is the carbon in red.

Example 13.6

How many stereocenters does sucrose (Figure 13.16) possess?

The two bonds in a ring represent different groups when the ring is not symmetrical. Neither ring in sucrose is symmetrical, so all nine carbon atoms in the two rings are stereocenters.

13.4 FUNCTIONAL GROUPS

Functional groups are sets of connected atoms within a molecule that have a specific reactivity. They usually contain electronegative atoms or multiple bonds that allow them to function as Lewis acids or bases. We have already discussed one reactive site, the C=C double bond. We now examine the properties of four other functional groups that add reactivity to organic molecules:

- alcohols (C-OH)
- carbonyls (C=O)
- carboxylic acids (COOH)
- amines (R_3N)

ALCOHOLS

Alcohols are compounds with the general formula R-OH. When R is an alkyl group, the alcohol is named by replacing the ‘e’ in the -ane ending of the corresponding alkane with -ol. Thus, the alcohol that results from replacing a hydrogen atom in methane with a hydroxyl group is called methanol. The position of the hydroxyl group is indicated with the number of the carbon atom to which it is attached. The continuous chain must be numbered by starting at the end closest to the hydroxyl group.

Alcohols contain hydroxyl groups, so, like water, they can behave both as Brønsted acids and as Lewis bases. Recall from our discussions on acid strengths that increasing the electron density in the O-H bond strengthens the bond and decreases the acid strength (Section 12.5). Furthermore, increasing the electron density also makes the oxygen lone pairs more basic. *Alkyl groups are electron donating*, so electron density in the O-H bond of R-OH increases when R = alkyl group. Consequently, *alcohols are weaker acids and stronger bases than water*.



Many household products contain alcohols. Some commonly encountered alcohols are

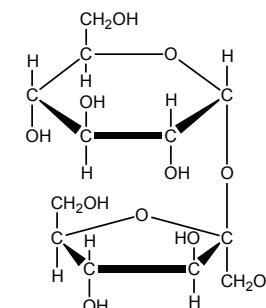
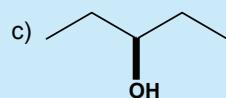
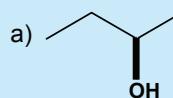


Figure 13.16 Sucrose (table sugar)

shown in Figure 13.17. Vitamin A is an alcohol. Cholesterol is an alcohol that is normally synthesized by the liver and is important as a constituent of cell membranes. However, high levels of cholesterol in the blood have been implicated in the formation of plaque on the walls of arteries (arteriosclerosis).

Example 13.7

Name the following alcohols.



- a) The hydroxyl group is attached to a four-carbon chain, so it is a butanol. Numbering the carbon atoms starting at the end closest to the hydroxyl group shows that it is attached to carbon number 2. Thus, the name is 2-butanol.
- b) The hydroxyl group is attached to the first carbon of a four-carbon chain, so the name of the compound is 1-butanol.
- c) The hydroxyl group is attached to carbon 3 of a five-carbon chain, so the name of the compound is 3-pentanol.

CARBONYL GROUPS

The C=O group is called a **carbonyl group**. The reactivity of carbonyl groups can be understood in terms of a second resonance structure in which the π electrons from the double bond are found on the electronegative oxygen atom as a lone pair (Figure 13.18). As a result, the oxygen becomes negatively charged, and the carbon becomes positively charged. Carbon atoms with a positive charge, which are called **carbocations**, are electron deficient and are excellent Lewis acids. The resonance structure shown in Figure 13.18b is not very important in the description of most carbonyls because it contains nonzero formal charge, but it does explain carbonyl reactivity, and we will use it to explain carbonyl chemistry. *Carbonyls are common in organic chemistry, and their Lewis acidity gives rise to dozens of chemical reactions that differ only in the species acting as the Lewis base.* Indeed, we have already examined the Lewis acidity of a carbonyl in the previous chapter in our discussion of Lewis acids and bases (Example 12.1).

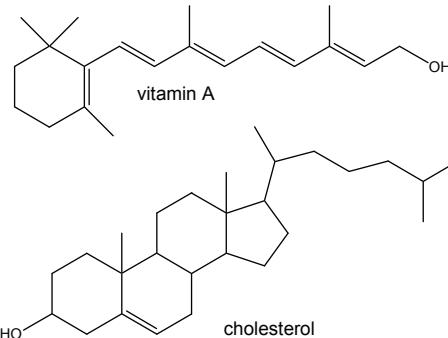
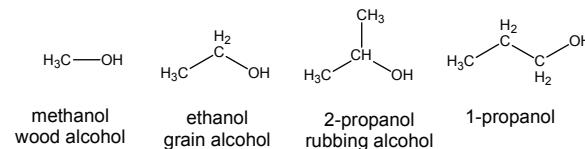


Figure 13.17 Some common alcohols

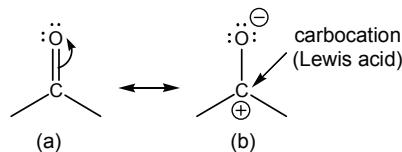


Figure 13.18 Two resonance structures of a carbonyl
(a) Resonance form that is most important in describing the bonding in carbonyls. (b) Resonance form used to explain carbonyl reactivity.

CARBOXYLIC ACIDS

Carboxyl groups consist of a hydroxyl group attached to a carbonyl group (Figure 13.19) and have the general formula RCOOH. The carbonyl oxygen removes electron density from the O-H bond, which makes carboxyl groups acidic (Figure 13.20).

Carboxylic acids are named by identifying the longest continuous chain that contains the carboxyl group and replacing the ‘e’ in the name of the corresponding alkane with *-oic* and adding the word *acid*. Thus, the four-carbon acid C₃H₇COOH is butanoic acid and the six-carbon acid C₅H₁₁COOH is hexanoic acid if there is no branching. The most common exception is CH₃COOH, which is referred to as acetic acid rather than ethanoic acid. When R = H, the acid is called formic acid, HCOOH. The anions of acids are named by replacing the *-ic* ending of the acid with *-ate*. Thus, C₅H₁₁COO¹⁻ is the hexanoate ion, HCOO¹⁻ is the formate ion, and CH₃COO¹⁻ is the acetate ion.

Carboxylic acids with long chains are called **fatty acids**. The long chains of animal fatty acids are saturated, while many of the vegetable fatty acids are unsaturated. As discussed at the end of Section 13.1, saturated chains contain no carbon-carbon double bonds, while unsaturated chains contain carbon-carbon double bonds. **Soaps** are the salts of fatty acids. CH₃(CH₂)₁₆COOH is stearic acid, a saturated fatty acid found in animal tissue, while CH₃(CH₂)₁₆COONa is sodium stearate, a soap. Soaps contain a hydrophobic tail (CH₃-(CH₂)_n-) and a polar head (COO¹⁻), so they are also detergents (Section 10.4).

AMINES AND AMIDES

Organic derivatives of ammonia that are not bound to a carbonyl group are called **amines**. Two examples of simple amines are methyl amine, CH₃NH₂, and dimethyl amine, (CH₃)₂NH. When the nitrogen is bound to a carbonyl group, it is called an **amide**. The groups around the N atom in amides are coplanar, so the N is sp² hybridized. The planarity of the amide group is accounted for with the resonance structure in Figure 13.21. Amine groups are present in many naturally occurring materials, four of which are shown in Figure 13.22. Note that caffeine also contains two amide nitrogens.

Compounds containing an amine and a carboxylic acid are called **amino acids**. However, like ammonia, amines are good Brønsted and Lewis bases, so they can react with carboxylic acids. As shown in Figure 13.23, amino acids can exist in a charge-separated form, in which the carboxylic acid has given up its proton, and the amine has gained a proton. In the human body, most of the amino acids are found in the charge-separated form. In all biologically important amines, the amine group is connected to the

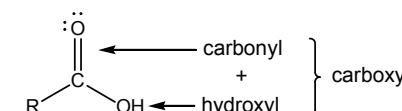


Figure 13.19 A carboxylic acid

A carboxylic acid contains a carboxyl group = a carbonyl + a hydroxyl group. R is used to represent an unspecified group.

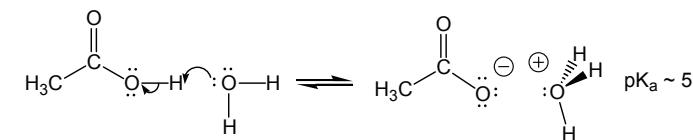


Figure 13.20 Reaction of acetic acid and water

Acetic acid is ~10¹³ times stronger as an acid than is ethanol.

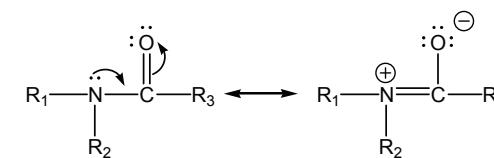


Figure 13.21 Resonance structures of amides

All of the groups in the figure lie in a plane, so the N atom must be sp² hybridized as shown in the structure on the right.

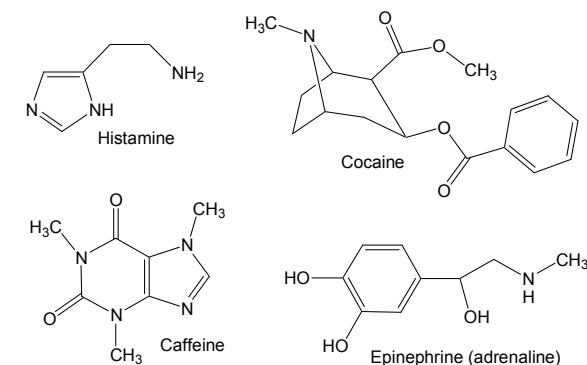


Figure 13.22 Some naturally occurring amines

carbon that is next to the carboxyl carbon. In almost all biologically relevant amino acids, the carbon to which the amine is attached is a stereocenter, although only one of the two enantiomers is biologically active.

13.5 INTRODUCTION TO ORGANIC REACTIONS

Organic chemists design molecules with specific sizes, shapes, and functionalities and then develop procedures to make them. Procedures for making almost any organic molecule can be developed because so many organic reactions proceed by a few well understood *mechanisms*. The mechanism of a reaction is the series of elementary steps through which the reaction proceeds from reactants to products. Organic reaction mechanisms are based on the ideas used to draw resonance forms and are guided by the principles of the octet rule and Lewis acid-base theory. In this section, we introduce a few fundamental organic reactions and their mechanisms. These are not new concepts; rather, they are the application of the fundamentals presented in Chapter 12 to a new field.

ADDITION REACTIONS OF ALKENES

Hydrogen halides *add across* the double bond of alkenes. This is called an **addition reaction** because two reactants combine to produce one product. The reaction of an alkene with a hydrogen halide is shown in Figure 13.24. The π electrons in a double bond are Lewis basic, so they attack the proton of the strongly acidic H-X molecule to form a C-H bond (Figure 13.24a). The H-X bond breaks as the C-H bond forms, and the loss of the π electrons produces a carbocation at the other carbon in the double bond. The carbocation is strongly acidic, so it is attacked by X^{1-} (Figure 13.24b) to produce the product shown in Figure 13.24c. The positive charge on a carbocation is stabilized by electron donating alkyl groups, so the carbocation usually forms on the carbon atom with the most alkyl groups (fewest hydrogen atoms) bound to it.

FORMATION OF ESTERS FROM ALCOHOLS AND CARBOXYLIC ACIDS

An ester is the product of the reaction between a carboxylic acid and an alcohol in a process called **esterification**. Water is the other product of the reaction. Reactions like this, in which two reactants combine to produce two products, are called **condensation reactions**. The net reaction is shown in Figure 13.25.

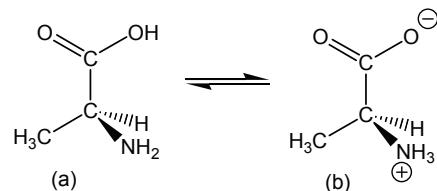


Figure 13.23 Alanine

a) Alanine is an amino acid. b) At pH ~ 7, alanine exists in a charge-separated form because the basic amine gains a proton and the carboxylic acid loses a proton.

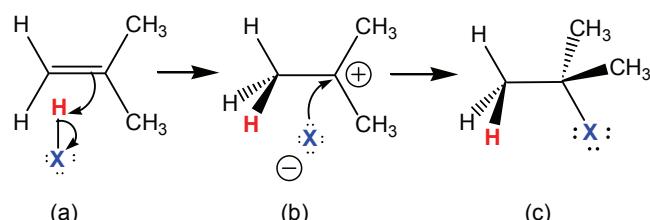


Figure 13.24 Hydrohalogenation of an alkene

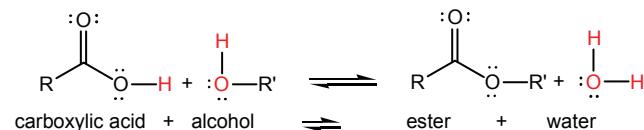


Figure 13.25 Esterification

The water molecule that is produced is highlighted in red.

Refer to Figure 13.26 for the following discussion of the mechanism for esterification.

- Step 1** The Lewis acidic carbonyl carbon (Section 13.4) is attacked by a lone pair on the oxygen of the alcohol. The red lone pair in (a) becomes the red bond in (b).
- Step 2** The solvent (green water) transfers a proton from the oxygen of what was the alcohol to the O-H group of the original acid. The blue lone pair in (b) becomes the blue bond in (c), while the blue bond in (b) becomes the blue lone pair in (c).
- Step 3** A water molecule is lost as the carbonyl π bond reforms to yield the ester. The red bond in (c) is converted into the red lone pair on the leaving water molecule in (d).

FORMATION OF AMIDES FROM ESTERS AND AMINES

Amides (nitrogen atom attached to a carbonyl group) can be formed in the reaction of an amine with a carboxylic acid or an ester (Figure 13.27). The mechanism for the reaction of an amine with an ester (Figure 13.28) is identical to that for esterification (Figure 13.26) except for the identity of the Lewis base.

- Step 1** The Lewis acidic carbon of the carbonyl is attacked by a lone pair on the nitrogen of the amine.
- Step 2** The solvent (green water) transfers a proton from the nitrogen atom to the non-carbonyl oxygen atom of what was the ester.
- Step 3** An alcohol molecule leaves as the carbonyl π bond reforms to yield the amide.

There are dozens of reactions between Lewis basic atoms of different molecules and Lewis acidic carbonyl carbons, but these reactions all have mechanisms that are very similar. This mechanistic similarity enables chemists to propose new chemical reactions.

13.6 POLYMERS

Polymers (from the Greek for ‘many units’) are large molecules made by forming covalent bonds between building blocks called *monomers* (single units). Successive reactions of the monomer units result in the growth of a long chain - the polymer (Figure 13.29d). Polymers can be synthetic (rubber, fibers, plastics) or natural (rubber, proteins, nucleic acids, carbohydrates). The special properties of polymers are related to their very high molecular weights. Synthetic polymers are classified as *condensation polymers* or *addition polymers*, depending on the mechanism by which they are formed. Polymers can be prepared by different mechanisms, but we will examine only those mechanisms that are similar to the reactions we have already studied in this chapter.

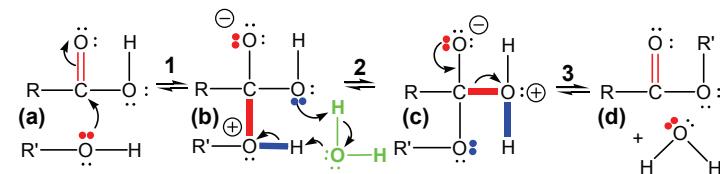


Figure 13.26 Mechanism of esterification

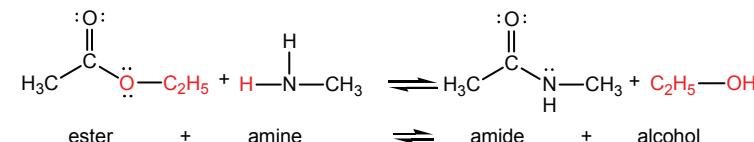


Figure 13.27 Amide formation

The water molecule that is produced is highlighted in red.

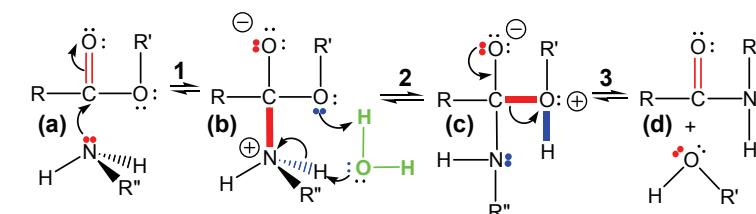


Figure 13.28 Mechanism for amide formation

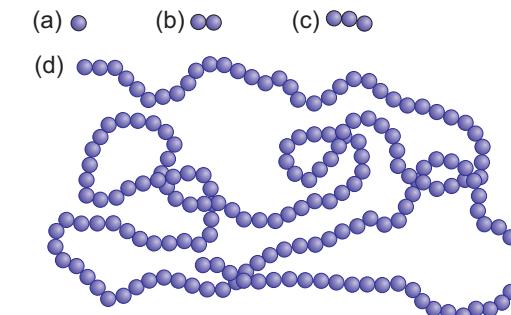


Figure 13.29 Combining mers (units)

One mer is a monomer (a), two mers form a dimer (b), three mers make a trimer (c), and many mers combine to form a polymer (d).

ADDITION POLYMERS

Addition polymers are formed in addition reactions and include such familiar materials as polyethylene, Teflon®, polyvinyl chloride (PVC), and polystyrene. Most addition polymers are derived from alkene monomers (Figure 13.30). The polymers differ in the identity of the R groups attached to the alkene. The properties of the polymers are dictated by both the length of the chain, ‘x’ in Figure 13.30, and the identity of the R groups attached to the alkene. Table 13.2 shows some common addition polymers and their uses.

POLY(ISOBUTYLENE)

One way in which an addition polymer of an alkene can be formed is by initiating the reaction with a small amount of hydrohalic acid. The mechanism is very similar to the addition of the hydrogen halide to a double bond discussed in Section 13.5 and shown in Figure 13.24. The C=C π bond is a weak base, and it can donate a pair of electrons to the strong acid (H^{1+}) to form a C-H bond. The resulting carbocation is a very strong Lewis acid and reacts with any base present. In the hydrohalogenation reaction, the halide ion serves as the base. In the polymerization reaction, however, only a small amount of hydrohalic acid is used to initiate the reaction, so very little halide ion is available. As shown in Figure 13.31, it is the C=C π bond of the alkene monomer, which is a far more plentiful base, that attacks the carbocation. The resulting carbocation reacts with yet another alkene. The polymer is formed by successive reactions of C=C π bonds with the carbocation at the end of the chain. Each successive reaction lengthens the polymer chain. The carbocation is formed much more easily on carbons with alkyl groups than on carbons with hydrogen atoms. As a result, the carbocation forms on the carbon atom with the fewest hydrogen atoms bound to it.

Natural rubber is a polymer of isoprene (Figure 13.32) that can now be made in the chemistry laboratory. Butyl rubber is a polymer made from isobutylene and isoprene. The United States produces over 500 million pounds of butyl rubber each year.

CONDENSATION POLYMERS

Condensation polymers are produced in condensation reactions. The requirement for forming condensation polymers is that *each of two reacting monomers must have two reactive centers*. The mechanisms are identical to those of the other condensation reactions (esters and amides) we have already discussed. The only difference is that, in polymer chemistry, the products continue to react to form larger molecules.

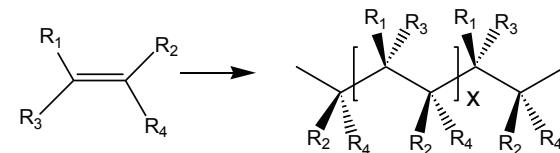


Figure 13.30 Alkene polymerization

Alkene monomers can polymerize to give the corresponding polymer. X is an integer that can be in the *millions*.

Table 13.2 Some common addition polymers and their uses
The numbering on the R-groups is shown in Figure 13.30.

R ₁	R ₂	R ₃	R ₄	Polymer Name	Common Uses
H	H	H	H	Polyethylene	plastic bottles and bags
H	H	H	CH ₃	Polypropylene	carpets
H	CH ₃	H	CH ₃	Poly(isobutylene)	tires
H	H	H	Cl	Poly(vinyl chloride)	plumbing and hoses
H	H	H	C ₆ H ₅	Polystyrene	insulation
F	F	F	F	Polytetrafluoroethylene (Teflon)	cooking utensils

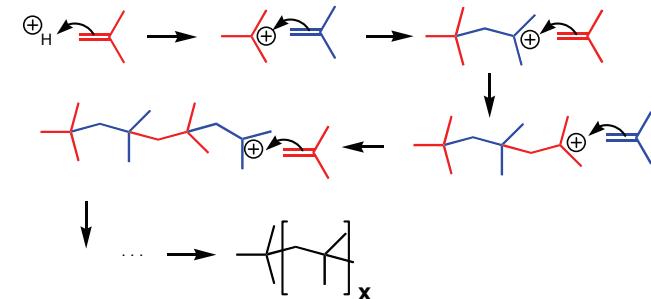


Figure 13.31 Polymerization of isobutylene

“x” is an integer that can be as high as 20,000 in a commercial polymer.

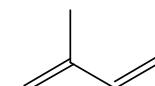


Figure 13.32 Isoprene

POLYESTERS

The reaction of an acid and an alcohol yields an ester, and the reaction of a *diacid* and a *diol* (an alcohol with two OH groups) results in the formation of a **polyester**. The monomers used to make poly(ethylene terephthalate) (PET) are shown in Figure 13.33. The mechanism of the reaction is identical to that of esterification, except that each reaction results in a molecule that still has reactive sites at each end. Successive reactions at these terminal sites lengthen the chain. PET goes by the trade names *Mylar*[®], *Dacron*[®], and *Terylene*[®]. The United States produces 4.5 billion pounds of PET per year. It is used in clothing, upholstery, tires, and many other products.

NYLONS

The reaction of an ester with an amine results in an amide, and the reaction of a *diester* with a *diamine* results in a **polyamide**. Polyamides formed in this type of reaction are also known as **nylons**.

Nylon 66 gets its name from the fact that it is formed from the condensation of a six-carbon diamine with a diester containing a six-carbon chain (Figure 13.34a). The amide that is formed (Figure 13.34b) has an amine group at one end of the molecule and an ester at the other end. These two reactive groups can each react with another acid or amine to produce a longer chain that still has reactive sites at both ends. This process continues, and the chain grows with each reaction.

POLYPEPTIDES AND PROTEINS

An amino acid is both an amine and a carboxylic acid, and amino acids can condense in a manner very similar to that discussed for nylons. The resulting molecule is called a peptide. **Peptides** are simply amides that are formed from the reaction of amino acids. Figure 13.35 shows the condensation of three amino acids: glycine + alanine + serine. The reaction of glycine and alanine results in a *dipeptide*; addition of the serine forms a *tri peptide*. This process continues to form a *polypeptide* and, eventually, a protein. **Polypeptides** are polyamides that form by polymerization of amino acids.

Proteins are high molecular weight polypeptides. Proteins often contain 100 or more amino acids. Although each amino acid has a stereocenter, only one of the two enantiomers is biologically active. It is estimated that the human body contains over 100,000 different kinds of protein molecules! The structure of a polypeptide can be envisioned as a *backbone* of amide linkages off which hang the various groups (referred to as *side chains*) that characterize the individual amino acids. The backbone of the tripeptide

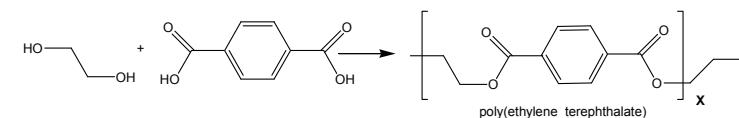


Figure 13.33 Polyester

The reaction of a diol and a diacid results in a polyester.

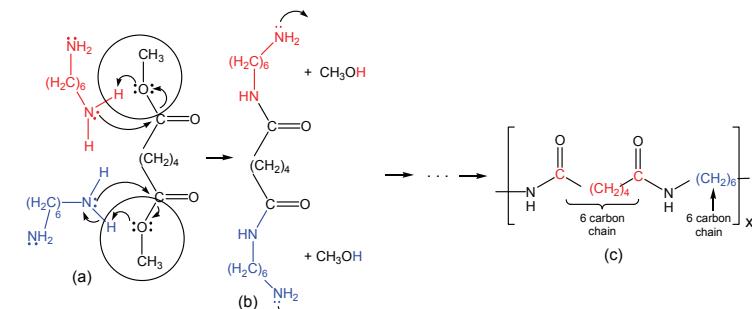


Figure 13.34 Formation of nylon 66

a) Lone pairs on N atoms of two diamine molecules attack carbonyl carbons of one diester to form C-N bonds, while a proton transfer (shown in circles) from amine to oxygen of diester produces CH_3OH , which leaves to produce an amide. b) The diamide that is formed still has two amine groups that can attack two more diester molecules. c) The chain grows with each successive reaction. The product of this reaction is the nylon 66 polymer.

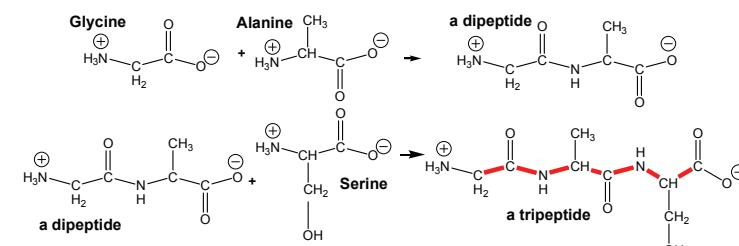


Figure 13.35 Polypeptides

The condensation of amino acids results in polypeptides. The red bonds in the tripeptide highlight the peptide 'backbone'. Note that the side chains of the amino acids appear to hang off the backbone.

is emphasized in Figure 13.35 by the bonds shown in red. As we shall see in the next section, the overall structure (shape) of proteins is often represented as a ribbon diagram. Ribbon diagrams emphasize the secondary structure of a protein by superimposing a ‘ribbon’ on the atoms of the polypeptide backbone.

SECONDARY STRUCTURES

Interactions such as hydrogen bonding and dipolar interactions that occur between groups within a polypeptide or protein are responsible for certain features of its three-dimensional shape known as its **secondary structure**. An example of secondary structure is the α -helix. The α -helix is adopted in order to optimize hydrogen-bonding interactions between different monomer units. The strongest interaction occurs when each amide N-H group forms a hydrogen bond to the C=O group of the amide four units away in the peptide sequence (Figure 13.36 below). The resulting α -helix is shown in Figure 13.37. The relatively short hydrogen bond between the first and fourth amino acids causes the intervening amino acids to form a loop. Multiple loops (four are shown in Figure 13.37) form an α -helix. In biology, specific amino acids can be placed at distinct positions around the core of the α -helix to give a protein its specific function. *The three-dimensional shapes associated with secondary structures, like the α -helix, are essential for the biological function of proteins.*

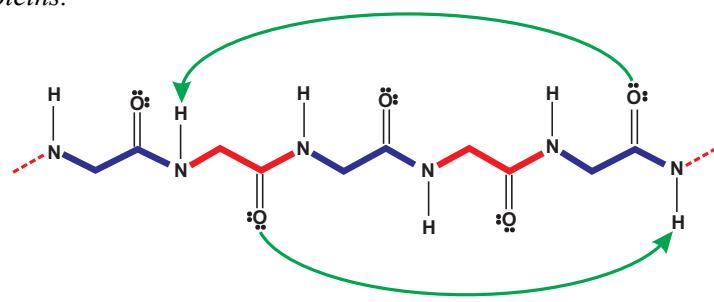


Figure 13.36 Hydrogen bonds responsible for the α -helix structure

Each amide linkage is highlighted with red or blue bonds. Green arrows indicate two of the hydrogen bonds responsible for the α -helix structure as the molecule bends and twists to bring the O and H atoms close enough to interact.

DNA STRUCTURE: THE DOUBLE HELIX

A nucleotide consists of a phosphate, a sugar*, and a N-containing base. A nucleic acid is a polymer formed from nucleotide residues (Figure 13.38). If the sugar is deoxyribose, the nucleic acid is **Deoxyribose Nucleic Acid** or DNA. Only four nitrogen-containing bases are found in DNA: adenine (A), thymine (T), cytosine (C), and guanine (G).

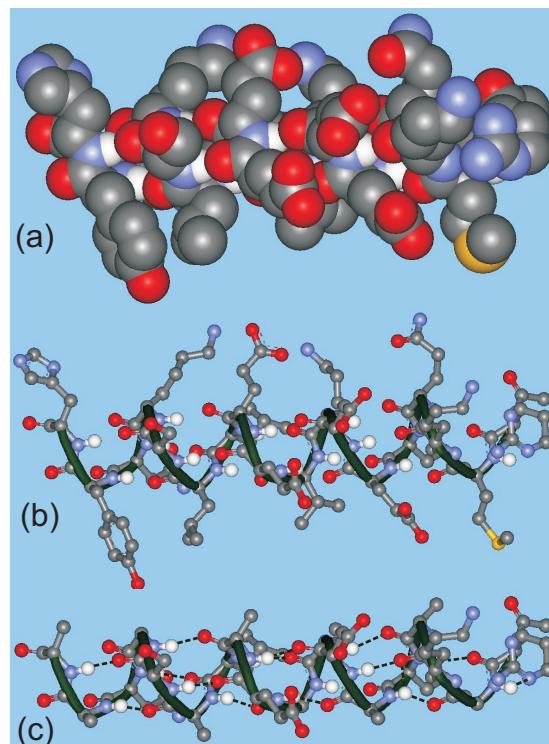


Figure 13.37 Portion of an α -helix

Color code: red = oxygen; blue = nitrogen; grey = carbon; white = hydrogen; yellow = sulfur. Note only those hydrogen atoms involved in hydrogen bonding are shown.

- (a) Space-filling model
- (b) Ball-and-stick model with green ribbon to show polypeptide backbone
- (c) Ball-and-stick model in which the side chains have been removed, and hydrogen bonds are shown as dashed lines.

* Sugars are carbohydrates with the formula $C_x(H_2O)_x$, where x is an integer greater than three. Ribose is a sugar with the formula $C_5H_{10}O_5$, but, as its name suggests, deoxyribose has one less oxygen.

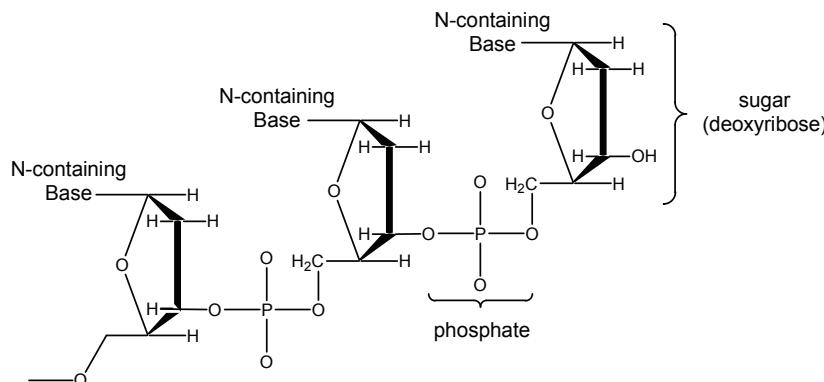


Figure 13.38 Three residues of a DNA molecule

Each nucleotide contains the sugar deoxyribose, a phosphate group, and one of four N-containing bases. In the above, three deoxyribose units are connected by two phosphate groups. The N-containing base can be different in each.

The N-containing bases interact with one another by hydrogen bonding, but the interactions are between specific pairs of bases only. The bases that interact with one another are called **base pairs**. Interactions between base pairs is specific due to the structures of the bases. As shown in Figure 13.39, Adenine and Thymine form a base pair (A-T), as do Cytosine and Guanine (C-G). It is the sequence of these bases along the DNA backbone that forms the genetic code. Thus, who we are is spelled out using an alphabet containing only four different chemical letters (**A**, **T**, **C** and **G**). The alphabet may be small, but the words are not: the human cell contains about three billion base pairs! *The biological importance of relatively weak interactions, such as hydrogen bonds and dipole-dipole interactions, cannot be overemphasized.*

The secondary structure of DNA, shown in Figure 13.40, is known as the **double helix**. The backbone of each strand (shown as ribbons in the figure) is composed of the phosphate groups of the nucleotide residues. The nitrogen containing base of each residue is matched by its base-pair partner in the other strand. The strong hydrogen bonding between the base pairs maintains the double helix.

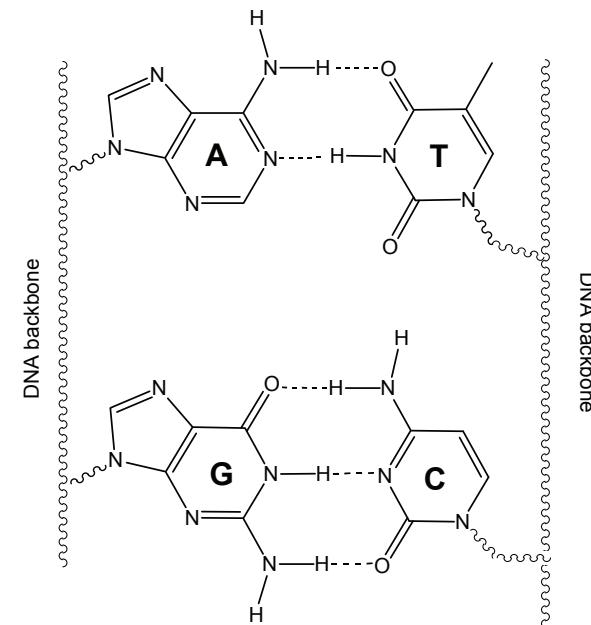


Figure 13.39 Hydrogen bonds responsible for DNA double helix

The two units in each base pair hydrogen bond specifically with one another. The genetic code is carried by the sequence of the base pairs along the DNA backbone. This base pair specificity allows DNA to reproduce strands that are identical to the original strands. A = adenine, T = thymine, G = guanine, and C = cytosine.

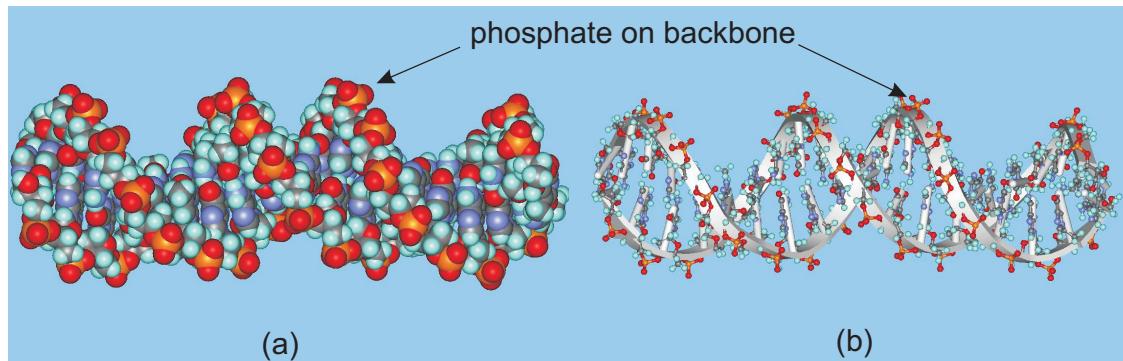


Figure 13.40 Space-filling (a) and ball-and-stick (b) models of a short piece of DNA

Color code Phosphorus = orange; Oxygen = red; Nitrogen = dark blue; Hydrogen = light blue; carbon = grey. The double helix is shown as a ladder in (b). The sides of the ladder (ribbon) show the phosphate backbone, while the rungs represent one base of each base pair. Hydrogen bonding between rungs is responsible for the double helix structure. The arrows point to identical phosphates on the backbone.

13.7 CHAPTER SUMMARY AND OBJECTIVES

Organic chemistry is the study of carbon-based compounds. The two simplest classes of organic compounds are the alkanes and the alkenes.

- Alkanes contain only sp^3 hybridized carbon atoms and sigma bonds. They are not very reactive. The names of all alkanes end in –ane. The positions of any alkyl groups are indicated by the number of the carbon atom in the longest continuous chain to which they are attached. Thus, 2-methylpentane has a five carbon continuous chain with a methyl group attached to the second carbon.
- Alkenes contain carbon-carbon double bonds. The π electrons of the double bond make alkenes weak Lewis bases. They react with hydrohalic acids to produce alkyl halides. Their names end in –ene. The position of the double bond is given as the atom number of the atom in the double bond with the smallest number. For example, 2-butene is a four-carbon alkene with the double bond between the second and third carbon atoms.

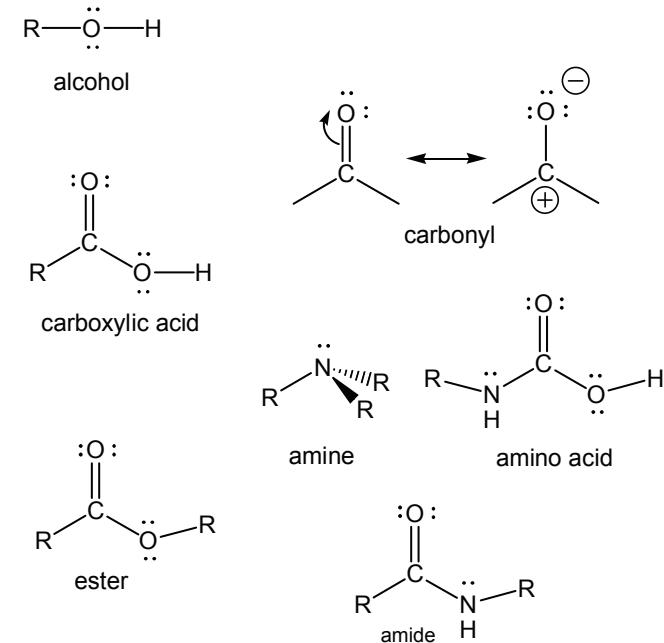
Organic compounds with identical formulas can exist as isomers.

- Constitutional isomers differ in the connectivity of the atoms in the molecule. There are five constitutional isomers of hexane, C_6H_{14} .
- Stereoisomers have the same connectivity, but the atoms have different geometric arrangements. Geometric isomers can be found in compounds containing double bonds and can be either *cis* or *trans*. Enantiomers are non-superimposable mirror images of one another. Enantiomers must contain a stereocenter, a carbon with four *different* groups attached to it. The physiological activity of the enantiomers can be very different.

Functional groups are groups of atoms that are reactive.

- Alcohols contain the hydroxyl group. They are weaker acids and stronger bases than water. The names of all alcohols end in *-ol*. The position of the hydroxyl group in the longest continuous chain is indicated by a prefix. Thus, 3-hexanol is a six-carbon chain with a hydroxyl group attached to the third carbon.
- Carbonyl groups are C=O groups. Their reactivity can be understood in terms of a resonance form containing a carbocation, which is a very strong Lewis acid.
- Carboxylic acids contain a carbonyl and a hydroxyl group bonded to one another. They are Brønsted acids, but they also have the carbonyl functionality described above. The names of carboxylic acids all end in *-oic acid*. Thus, octanoic acid is C₇H₁₅COOH. Fatty acids are carboxylic acids with long chains.
- Amines are organic derivatives of ammonia. Like ammonia, they are Lewis bases. Molecules containing both carboxylic acids and amines are known as *amino acids*.
- Esters are the product of the reaction of a carboxylic acid and an alcohol. In the reaction mechanism, the lone pair of the alcohol attacks the carbocation on the acid, a proton is transferred from the alcohol to the carboxylic acid, and the resulting water molecule is lost.
- Amides are the product of the reaction of a carboxylic acid or an ester with an amine. The reaction mechanism for the reaction between an amine and an ester is identical to the formation of the ester from a carboxylic acid and an alcohol, except that the amine is the Lewis base that attacks the carbocation of the ester. After proton transfer, it is an alcohol that leaves the molecule.

Polymers are large molecules formed by bonding smaller units, called monomers, together in long chains. Alkene polymers are called addition polymers. They can be formed by the reaction of the alkene with a small amount of a hydrohalic acid. Common synthetic polymers include polyethylene, PVC, and polystyrene. Condensation polymers result when molecules containing two functional groups react. Thus, a polyester is prepared by reacting a dicarboxylic acid with a diol. Nylons are polyamides made by reacting a diester with a diamine. Polypeptides are polyamides made by reacting amino acids. Proteins are large polypeptides. Three-dimensional structures, such as the protein α -helix and the DNA double helix, are the result of hydrogen bonding and are vital to the function of biomolecules.

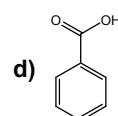
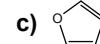
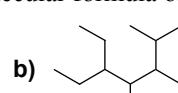
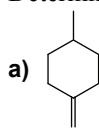


After studying the material presented in this chapter, you should be able to:

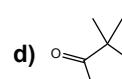
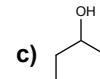
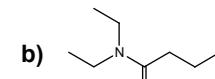
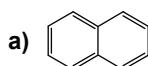
1. convert skeletal structures into condensed structures (Section 13.1);
2. name alkanes and simple alkenes (Section 13.2);
3. draw constitutional isomers for simple organic molecules (Section 13.3);
4. identify stereocenters and draw the enantiomer of a molecule with a stereocenter (Section 13.3);
5. recognize an alkene and distinguish between *cis* and *trans* isomers (Section 13.2);
6. recognize an alcohol and name simple alcohols (Section 13.4);
7. recognize a carbonyl group and draw the carbocation resonance form and explain its reactivity (Section 13.4);
8. recognize a carboxylic acid and explain its acidity (Section 13.4);
9. name simple carboxylic acids (Section 13.4);
10. identify amines and explain their reactivity (Section 13.4);
11. predict the product of the addition of a hydrohalic acid to an alkene (Section 13.5);
12. predict the structure of the ester formed by the reaction of a carboxylic acid and an alcohol (13.5);
13. predict the structure of the amide formed by the reaction of an ester and an amine (Section 13.5);
14. identify the repeat unit of an addition polymer (Section 13.6);
15. predict the repeat unit of a nylon from the reacting diester and diamine (Section 13.6);
16. draw the structure of the peptide resulting from the reaction of two amino acids (Section 13.6); and
17. predict the repeat unit of a polyester from the reacting diacid and diol (Section 13.6).

13.8 EXERCISES

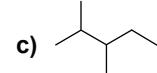
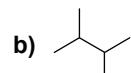
1. What is the difference between saturated and unsaturated hydrocarbons?
2. Differentiate between alkane, alkyl, and alkene.
3. How do a condensed structure and a skeletal structure differ?
4. There are two different propyl groups. Suggest the way in which they differ.
5. Why are alkenes more reactive than alkanes? Are alkenes Lewis acids or Lewis bases? Explain.
6. Determine the molecular formula of each of the following:



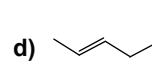
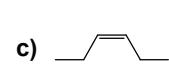
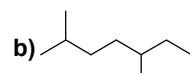
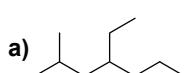
7. Determine the molecular formula of each of the following



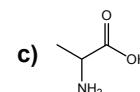
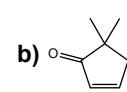
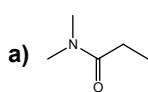
8. Name the following alkanes and alkenes:



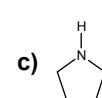
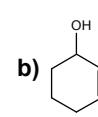
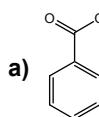
9. Name the following alkanes and alkenes:



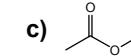
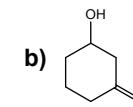
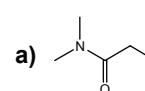
10. Identify the functional groups in the following:



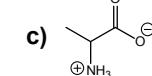
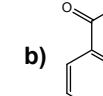
11. Identify the functional groups in the following:



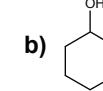
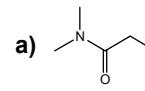
12. Identify the Lewis acid sites in the following molecules:



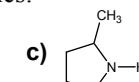
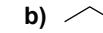
13. Identify the Lewis acid sites in the following species:



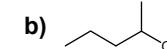
14. Identify the Lewis base sites in the following molecules:



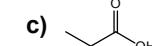
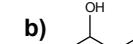
15. Identify the Lewis base sites in the following molecules:



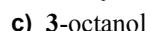
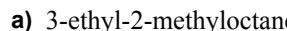
16. Name the following compounds:



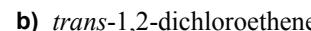
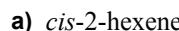
17. Name the following compounds:



18. Draw skeletal structures for the following:



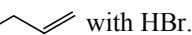
19. Draw skeletal structures for the following:



20. Use skeletal structures to show the constitutional isomers of C₅H₁₂ (an alkane).

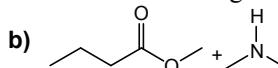
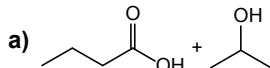
21. Use skeletal structures to show six constitutional isomers of C₅H₁₂O that are alcohols.

22. Distinguish between addition and condensation reactions. Give an example of each.

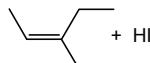
23. Predict the product reaction of  with HBr.

24. Write a step-wise mechanism for the reaction of the polar molecule I-Cl and .

25. Draw skeletal structures of the products of the following reactions:



26. Draw the skeletal structure of the product of the following reaction:

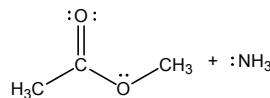


27. Define *polymer*. Why is nylon 66 called a *condensation polymer*?

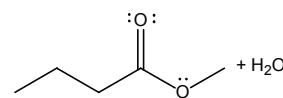
28. What is the difference between a polyamide and a polypeptide?

29. Name five common polymers and describe their uses.

30. Show the step-wise mechanism for the following reaction. Be sure to include all nonzero formal charge.



31. An important reaction of esters is the reverse of the esterification reaction shown in Figure 13.26. In this reaction, an ester reacts with water to produce a carboxylic acid and an alcohol. Write a step-wise mechanism for the following reaction:



32. Draw the Lewis structure of the product of the reaction of a proton and a carboxylic acid. What affect would this reaction have on the reactivity of the carbonyl carbon center?

33. Hydrogen chloride can add to formaldahyde (H₂CO).

a) Draw the Lewis structure of formaldehyde.

b) Draw the resonance form of formaldehyde that accounts for its reactivity

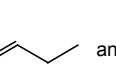
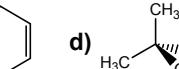
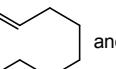
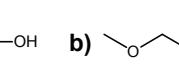
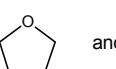
c) Use arrows to suggest how the HCl might attack formaldehyde.

d) Draw the Lewis structure of the reaction product.

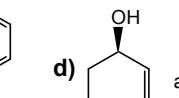
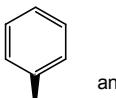
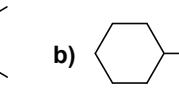
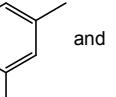
34. What force is responsible for the formation of the α -helix structure in proteins?

35. The double helix of DNA is held together by interactions between base pairs. Draw the base pairs and explain why they are ‘pairs’.

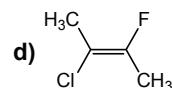
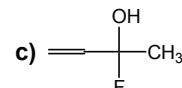
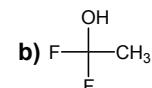
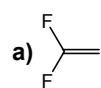
36. Identify each of the following pairs of molecules as constitutional isomers, stereoisomers, or identical molecules:



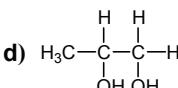
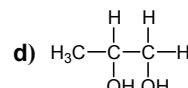
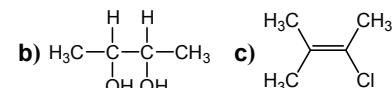
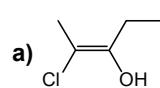
37. Identify each of the following pairs of molecules as constitutional isomers, stereoisomers, or identical molecules:



38. Indicate whether or not each of the following molecules has a stereoisomer. For those that do, indicate whether the isomer is a geometrical isomer or an enantiomer.



39. Indicate whether or not each of the following molecules has a stereoisomer. For those that do, indicate whether the isomer is a geometrical isomer or an enantiomer.



Chapter 14

Inorganic Chemistry

- 14.0 Introduction
- 14.1 Ligands and Coordination
- 14.2 The d Orbitals and Ligand Fields
- 14.3 Isomers
- 14.4 Metals in Biology

- 14.5 Transition Metals as Catalysts
- 14.6 Transition Metals as Electronic and Magnetic Materials
- 14.7 Chapter Summary and Objectives
- 14.8 Exercises

14.0 INTRODUCTION

In Chapter 13 we discussed organic chemistry, which is based on the chemistry of carbon. That leaves the chemistry of over a hundred elements to be broadly characterized as **inorganic chemistry**. Many of these elements have a very rich chemistry of their own, but we cannot begin to do justice to all of inorganic chemistry in this last chapter. We, therefore, take a segment of these elements, the *transition elements*, and present a very small portion of their chemistry here. As we shall see in this chapter, transition elements are vital to the function of living organisms and to the treatment of disease; they also serve as catalysts and electronic and magnetic materials.

The **transition elements** are the B-group elements that fall between Group 2A and Group 3A on the periodic table. They are usually characterized as having partially filled **d** sublevels. They are all metals and are frequently referred to as the **transition metals**. Often they are found as *complexes* in which the metal is bound to several molecules or ions that we call **ligands**. Ligands are Lewis bases, and transition metal cations are Lewis acids, so the metal ligand bond is a coordinate covalent bond. The compounds that transition metals form are frequently called **coordination compounds**. For example, $[\text{Co}(\text{NH}_3)_6][\text{PtCl}_4]$ is a coordination compound that consists of *two* complex ions, $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{PtCl}_4]^{2-}$, which have ammonia molecules and chloride ions as ligands. Many transition metal compounds are brightly colored, such as the deep blue color of a solution of solvated Cu^{2+} ions, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Transition metal compounds also have interesting magnetic properties that are strongly influenced by the nature of the ligands attached to the metal, even though the unpaired electrons reside on the metal.

The objectives of Chapter 14 are to:

- define ligands and discuss their bonding to metals;
- discuss some common shapes adopted by transition metal complexes;
- explain why the d orbitals in coordinated metals do not all have the same energy;
- use the fact that the d orbitals are at different energies to account for the rich color of many transition metal compounds;
- distinguish between high spin and low spin metal ions;
- describe the possible isomers of octahedral coordination compounds;
- describe the function of several transition metal ions in biology; and
- demonstrate some of the functions of transition metal compounds as catalysts and as electronic and magnetic materials.

14.1 LIGANDS AND COORDINATION

The molecules or ions that bind to a metal are called **ligands**. Typically, ligands contain lone pairs that can be used to form covalent bonds, so they function as Lewis bases. Ligands vary in size from small molecules, such as H_2O and NH_3 , and simple ions, such as Cl^{1-} and Br^{1-} , to very large molecules, such as proteins. The formation of a metal-ligand bond is called *coordination*, but it can be viewed as a Lewis acid-base reaction between a metal ion with unfilled d orbitals, and a ligand with a lone pair of electrons. The number of donor atoms bound to a metal is called its **coordination number**. The most common coordination numbers of transition metals are four, five and six. The spatial arrangement of the ligands around the metal is referred to as the metal's **coordination geometry**. Figure 14.1 shows the coordination geometries for the common coordination numbers.

Some ligands contain more than one lone pair capable of coordinating to a metal. If such a ligand bonds to two different metals, it is called a **bridging ligand**. The cyanide ion is a good bridging ligand because it can bond to the metal through the carbon and through the nitrogen, $\text{M}-\text{C}\equiv\text{N}-\text{M}'$. Ligands that can use two lone pairs to form bonds with metals are said to be **bidentate**, those using four are **tetridentate**, etc. If the different lone pairs of the ligand bind to the same metal, the ligand is called a **chelating*** ligand. Figure 14.2 shows three common chelating ligands.

Ethylenediamine coordinates through the two lone pairs on the nitrogen atoms, as shown in Figure 14.2a. Because it coordinates to the metal with two lone pairs, it is a **bidentate ligand**. The **tetridentate ligand** porphyrin (Figure 14.2b) binds with the lone

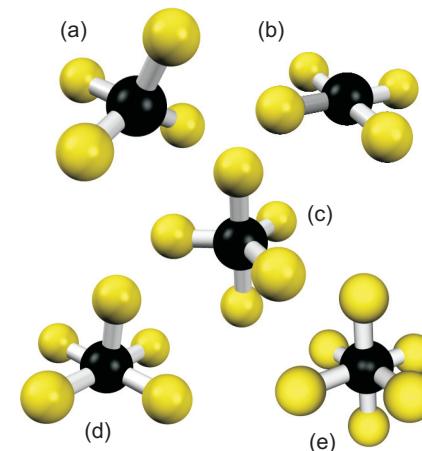


Figure 14.1 Common coordination geometries

Four-coordinate metals are typically tetrahedral (a) or square planar (b). Five-coordinate metals are usually trigonal bipyramidal (c) or square pyramidal (d). Six-coordinate metals are octahedral (e).

* The word 'chelate' is derived from the Greek for 'crab's claw' because the ligand-metal bonds appear to 'pinch' the metal like a 'crab's claw'.

pairs on the four nitrogen atoms. The metal is in the center of the large planar ligand. Metal porphyrin complexes, which are common in biochemistry, can differ because of the metal in the center or because of the identity of the R groups on the porphyrin ligand. One of the best known metal porphyrins is *heme*, a porphyrin with Fe^{2+} in the center. Heme is part of the oxygen carrying protein in blood. Another common example is chlorophyll, the light-gathering green pigment in plants. Chlorophyll is a porphyrin *derivative* with Mg^{2+} at the center.

The ethylenediaminetetraacetate ion, or simply EDTA, can coordinate to metals at six sites, so it is hexadentate. It bonds to metals using the lone pairs on the two nitrogen atoms and the four oxygen atoms that carry the negative charge (Figure 14.2c). The EDTA ligand can wrap itself around a metal ion and occupy all of the sites of an octahedral ion (Figure 14.2d). This property is extremely useful for coordinating to heavy metals and removing them from the environment. For example, heavy metal ions, such as Pb^{2+} and Hg^{2+} , are poisonous because they bind to proteins and cause the protein to stop functioning properly. $\text{Na}_2[\text{Ca}(\text{EDTA})]$ is prescribed for heavy metal poisoning because the EDTA binds so strongly to the Pb^{2+} and Hg^{2+} ions that they displace the Ca^{2+} ion from $\text{Ca}(\text{EDTA})^{2-}$. Once bound to the EDTA, the heavy metals can no longer bind to proteins and are passed from the body. EDTA bonds more strongly to Pb^{2+} and Hg^{2+} than to Fe^{2+} , so the beneficial Fe^{2+} is not removed by this treatment.

14.2 THE d ORBITALS AND LIGAND FIELDS

Recall from Chapter 2 that the orbitals of a sublevel all have the same energy. Thus all five d orbitals have the same energy. However, that is true only for a *free atom or monatomic ion*. The situation is quite different for a metal coordinated to ligands. If the six ligands in an octahedral coordination geometry are assumed to lie on the x, y and z axes as shown in Figure 14.3, then the five d orbitals of the metal fall into two groups: *one group of orbitals is directed along the bonding axes, while the other is directed between the metal-ligand bonds*. The z^2 orbital is directed *along* the z-axis, and the x^2-y^2 orbital *along* the x- and y-axes, while the xy, xz, and yz orbitals lie *between* the axes.* The six ligands are Lewis bases, and each ligand approaches the metal with a lone pair to be used to form a covalent bond. The lone pairs on the ligands generate an electric field, called the **ligand field**. Interaction with the ligand field raises the energies of the z^2 and x^2-y^2 orbitals above that of the xy, xz, and yz orbitals (Figure 14.4). That is, the energies of the d orbitals that lie

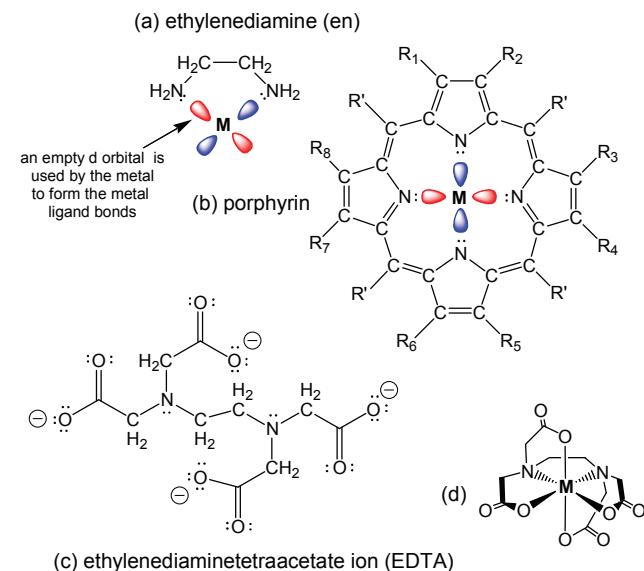


Figure 14.2 Three common chelating ligands

a) A metal is chelated with ethylenediamine. b) A square planar metal porphyrin (the R-groups can be varied). c) EDTA is a very strong chelating agent that can coordinate at six positions. d) The coordination of EDTA to a metal.

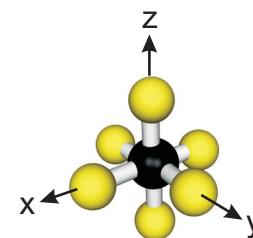


Figure 14.3 Coordinate system used to describe the bonding in six- coordinate metals

* The d orbitals are designated as either a subscripted d (d_{z^2} , $d_{x^2-y^2}$, d_{xy} , d_{xz} and d_{yz}) or by the orbital designation without the d (z^2 , x^2-y^2 , xy , xz , and yz). We use the latter method in this text for ease of reading.

on the bond axes (where they point directly at the ligands) are higher than the energies of those that lie between the axes (where they do not point directly at the ligands). The symbol Δ is used to represent the energy difference between the two sets of d orbitals. The magnitude of Δ depends on both the metal and the ligand, and it dictates many of the properties of the complex. Ligands that cause Δ to be large are called **strong-field ligands**, while ligands for which Δ is small are called **weak-field ligands**. In our discussions, we will use the CN^{1-} ion as an example of a strong-field ligand, and the Cl^{1-} ion and H_2O molecule as examples of weak-field ligands.

Many transition metal complexes are colored, and this color can often be used as an indicator of the magnitude of Δ . Recall from our discussion in Chapter 2 that color results from the absorption of light energy corresponding to electronic transitions that promote electrons from lower energy levels into higher energy levels. The frequency of the absorbed light, v , and the difference between the two energy levels, ΔE , are related by $\Delta E = hv$, where h is Planck's constant. It is often the case that the color of transition metal complexes is due to electrons changing d orbitals.

White light is the result of all visible colors. When white light shines on a colored substance, however, some of the colors are absorbed. Those colors that are not absorbed can be either reflected or transmitted to the eye. We perceive this reflected or transmitted portion as the color of the substance. Consequently, the characteristic color of a material is not the color of light that it absorbs; rather it is the mixture of the remaining, unabsorbed colors that are observed. In other words, it appears as its *complementary color*.* The approximate relationship between observed and absorbed colors is summarized in Table 14.1. Furthermore, the energy of a photon is proportional to its frequency, and so the frequency of the photon that is absorbed is a direct indicator of the magnitude of Δ . The relative energies of the visible photons are given in the last column of Table 14.1. Thus, a transition metal compound that appears yellow absorbs photons in the violet, while a transition metal compound that appears red absorbs green light. The energy of violet light is greater than that of green light, so we conclude that Δ is larger for the compound that appears yellow.

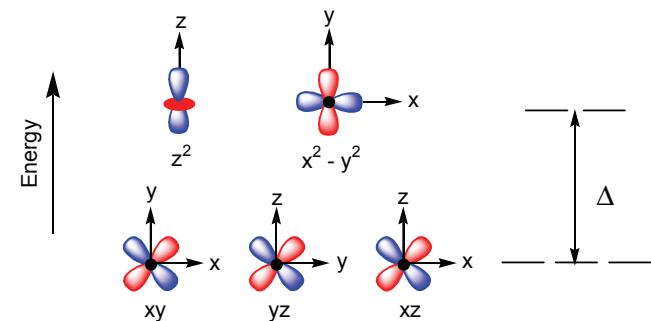


Figure 14.4 Relative energies of the d orbitals

* A color and its complement contain all colors. Thus, a paint consisting of a mixture of a color and its complementary color will absorb all visible light and appear black.

Table 14.1. Complementary colors

A compound observed to be	Absorbs photons in the	Increasing photon energy
green	red	lowest
blue	orange	
violet	yellow	
red	green	
orange	blue	
yellow	violet	highest

Example 14.1

CoBr₂ is a green solid while CoCl₂ is a blue solid. Which is a stronger field ligand, chloride ion or bromide ion?

The stronger field ligand is the one with the larger value of Δ . CoBr₂ appears green, which means that it absorbs red light. CoCl₂ appears blue, so it absorbs orange photons. Orange photons have more energy than red photons, so Δ is larger for CoCl₂, and chloride is the stronger field ligand. [Note that the Co²⁺ ion is octahedral and surrounded by six anions in the solid, even though the formula indicates only two per cobalt. This is analogous to NaCl where each Na⁺ is surrounded by six Cl⁻ ions.]

The magnitude of Δ can also influence the number of unpaired electrons on the metal, which is usually designated by the spin of the atom, ion, or molecule. The **spin** of a species is the sum of the individual electron spins. If there are no unpaired electrons, then there is no spin because the sum of the m_s quantum numbers of paired electrons is zero ($\frac{1}{2} - \frac{1}{2}$); that is, the two spins cancel because their magnetic fields are opposed. However, if the two electrons have the same spin, then they sum as: $\frac{1}{2} + \frac{1}{2} = 1$. Similarly, three electrons with the same spin result in a species with a spin of $(3)(\frac{1}{2}) = \frac{3}{2}$. As we shall see in Section 14.6, it is the spin associated with an atom, molecule, or ion that dictates its magnetic properties.

Consider the case of Mn²⁺, which has a 3d⁵ valence electron configuration. In the absence of any ligands, the five d orbitals all have the same energy; and the five electrons would be unpaired, as shown in Figure 14.5a. However, in the presence of ligands the **d** orbitals no longer have the same energy. Electrons seek the lowest energy situation, but the orbital energy is not the only consideration. Recall that Hund's rule states that electrons remain unpaired in a sublevel as long as empty orbitals are available. They do not pair because paired electrons are closer than unpaired electrons and the energy of two negatively charged electrons increases when they are close (like charges repel). The amount by which their energy increases is called the **pairing energy (PE)**. Thus, three electrons enter the three low-energy d orbitals without pairing, but the other two electrons can either pair with the first set at the cost of the pairing energy (PE) or they can remain unpaired and enter the set of orbitals at higher energy at the cost of the orbital energy difference (Δ). If $\Delta < PE$, it costs less energy for the electrons to occupy the higher energy orbitals (Figure 14.5b). However, when $\Delta > PE$, it costs less energy for the electrons to pair (Figure 14.5c).

Consequently, when Mn²⁺ is surrounded by weak-field ligands, such

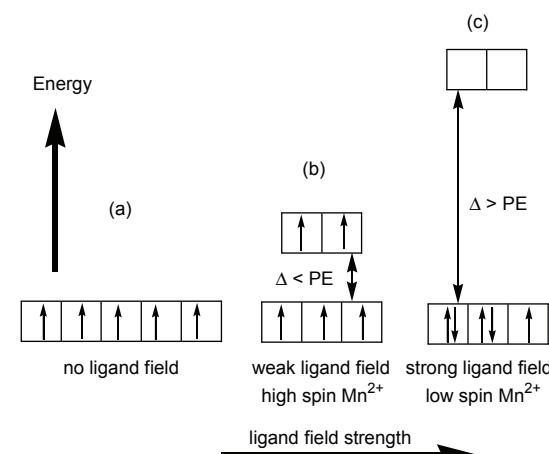


Figure 14.5 High and low spin Mn(II)

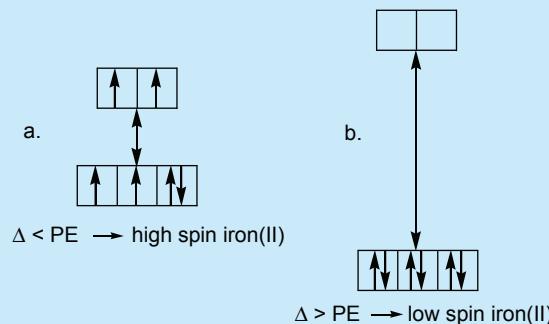
Δ and the number of unpaired electrons in a Mn²⁺ ion as a function of ligand field strength. PE is the pairing energy.

as chloride ions, the higher energy set of d orbitals is close in energy to the lower set ($\Delta < PE$), and no pairing occurs. Each of the five electrons has a spin of $+1/2$, which gives the ion a total spin of $(5)(1/2) = 5/2$, and $MnCl_6^{4-}$ is said to be **high spin**. However, if the ligands are strong-field ligands, such as cyanide ions, occupation of the higher energy set of orbitals requires more energy than does pairing, so the electrons pair. In this case, there are three electrons with spins of $+1/2$ and two with spins of $-1/2$ for a total spin of $(3)(1/2) + (2)(-1/2) = 1/2$, and $Mn(CN)_6^{4-}$ is said to be a **low spin** ion.

Example 14.2

- a) When $FeSO_4$ dissolves in water, it forms the $Fe(H_2O)_6^{2+}$ ion. Given that water is a weak-field ligand, how many unpaired electrons would be present in the $Fe(H_2O)_6^{2+}$ ion?

Iron has a $4s^23d^6$ valence electron configuration, and it loses the two 4s electrons to form iron(II). Consequently, Fe^{2+} is $3d^6$. Water is a weak-field ligand, so $\Delta < PE$, and the iron is expected to be high spin. The corresponding diagram is shown below in Figure a. Because $\Delta < PE$, each of the d orbitals is occupied before any pairing occurs. The result is that there are four unpaired electrons.



- b) When CN^- ion is added to a solution of $Fe(H_2O)_6^{2+}$, the deeply colored $Fe(CN)_6^{4-}$ ion is produced. How many unpaired electrons does it contain?

Cyanide is a strong-field ligand, so $\Delta > PE$, which produces a low spin iron(II). The situation is shown in Figure b. The result is that the six electrons pair rather than occupy the higher energy set of orbitals to produce a complex with no unpaired electrons.

14.3 ISOMERS

When multiple types of ligands are attached to the same metal center, their arrangement about the metal strongly influences the properties of the complex. Complexes that differ only in the arrangement of the ligands around the metal are known as geometric isomers. This is a stereoisomer similar to those we encountered for organic compounds in Chapter 13. The chemical and physical properties of geometric isomers can be very different.

As shown in Figure 14.6, two ligands can be either *cis* (next to one another) or *trans* (opposite one another). Although the three *cis* structures shown in Figure 14.6a may look different, they are all the same isomer; each can be rotated such that it is superimposable with either of the other two. The same is true of the three *trans* structures shown in Figure 14.6b. There are only two isomers of a compound of this type, one *cis* isomer and one *trans* isomer.

There are only two ways in which three ligands can be situated in an octahedral geometry (Figure 14.7). One is said to be **meridional (mer)** because the three ligands lie on an arc of a circle (the meridian) going around the octahedron. The other is called **facial (fac)** because the three ligands define one of the faces of the octahedron (Figure 14.7c).

Example 14.3

- a) Draw all of the isomers of square planar $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

As in the case of octahedral complexes, the two chlorine atoms or the two ammonia molecules of a square planar complex can be either next to one another (*cis*) or opposite one another (*trans*), as shown in Figure 14.8. It may look like there are other ways to arrange the four groups around the platinum, but the other structures that can be drawn can all be arrived at by simply rotating one of the above two isomers.

- b) Draw the isomers of square planar $[\text{PtCl}_3(\text{NH}_3)]^{1-}$.

Only one structure can be drawn for $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{1-}$ because it does not matter which of the four positions is occupied by the one ammonia molecule.

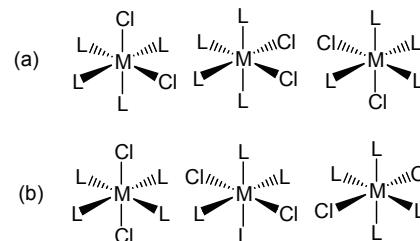


Figure 14.6 *cis* and *trans* isomers of an octahedral metal

a) The two chloride ions are *cis*. b) The two chloride ions are *trans*. L is used to represent unspecified ligands that are not chloride ions.

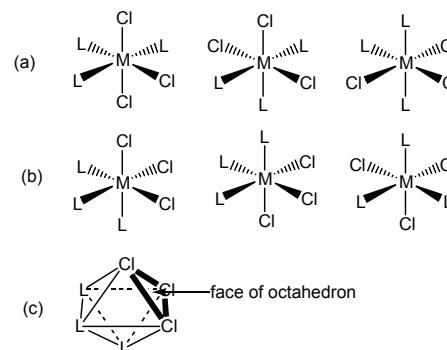


Figure 14.7 *fac* and *mer* isomers of an octahedral metal

a) The three chloride ions are meridional. b) The three chloride ions are facial. c) Three facial chloride ions define one of the eight faces of the octahedron. L represents unspecified ligands.

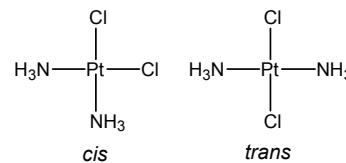


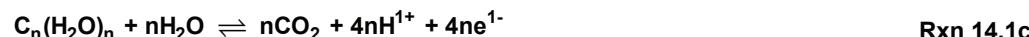
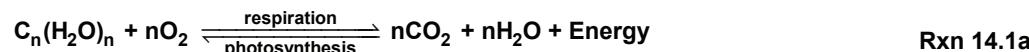
Figure 14.8 *cis* and *trans* isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

14.4 METALS IN BIOLOGY

Many main group elements, including Na, K, Ca, Mg, Se, and Si, and transition metals such as V, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, and Zn, are essential for biological function. These functions are both structural and metabolic. For example, the structural role of Ca^{2+} in teeth and bone is well recognized. In addition, proteins use metal ions for the formation and stabilization of their three-dimensional structures and to catalyze reactions that are not feasible in their absence. Two dramatic examples of the importance of metal ions in biology are the complementary processes of carbohydrate production in plants (photosynthesis) and the combustion of carbohydrates in animals (respiration), the topics of the this section.

PHOTOSYNTHESIS AND RESPIRATION

Plants extract energy from the sun to synthesize carbohydrates in a process called **photosynthesis** (synthesis using light), while animals burn the carbohydrates and extract the stored energy from exothermic combustion reactions in a process known as **respiration**. The reversible process, shown in Reaction 14.1a, is an electron transfer reaction, with each half-reaction (Reactions 14.1b and 14.1c) involving a four-electron transfer for each carbon atom in the carbohydrate molecule consumed or produced.



Metals play key roles in both processes. Four-electron transfer reactions involve high activation energies, so nature uses metals to catalyze the reactions.* Plants use a cluster of four *manganese* ions coordinated to proteins within the plant cells to break up the reaction into four one-electron processes, while animals use *iron* and *copper* ions to do the same for the reverse process. Chlorophyll uses a *magnesium* ion in the center of a porphyrin derivative to change the electronic structure of the porphyrin so that it absorbs red light, giving porphyrin its green color. The plant uses the energy of the red photons to carry out the photosynthesis reaction shown in Reaction 14.1a. Photosynthesis is the source not only of carbohydrates; it is also the source of all oxygen in the atmosphere today. *Without the light harvesting role of Mg^{2+} and the catalytic activity of the Mn cluster, animals such as humans would not exist.*

* As discussed in Section 9.8, catalysts decrease the activation energy by changing the nature of the transition state.

Animals also utilize metal-containing proteins to transport, store, and use the O₂ produced in photosynthesis. Heme is an iron(II) porphyrin (Figure 14.2b) that is the “active site” in *hemoglobin*. Hemoglobin is a protein found in red blood cells that transports oxygen from the lungs to the rest of the body, where it is used in respiration. The heme active site is shown in Figure 14.9. Fe²⁺ has six coordination sites, but the porphyrin ligand coordinates to only four. One of the two remaining sites is used to bind the heme unit to the polypeptide, represented by the ribbon. In *deoxyhemoglobin* (*without* O₂), the remaining site is unoccupied (Figure 14.9a). The resulting five-coordinate Fe²⁺ ion has square pyramidal coordination geometry (Figure 14.1d) in which the iron(II) ion is pulled out of the plane of the porphyrin. In lung tissue, the high concentration of O₂ favors the coordination of O₂ to the sixth Fe²⁺ coordination site. This gives a six-coordinate iron complex in which the iron is in the plane of the porphyrin ligand. The oxygen also hydrogen bonds to the protein, as shown in Figure 14.9b. When the *oxyhemoglobin* (*with* O₂) reaches oxygen-poor tissue, the oxygen is released.* The released oxygen is then used in the cell to produce energy by the reaction described in Equation 14.1.

Carbon monoxide poisoning is the result of the coordination of CO to hemoglobin, which destroys hemoglobin’s oxygen transport ability. CO is a strong-field ligand that binds to the heme irreversibly (does not come off), while O₂ binds reversibly (the oxygen is easily removed in the cell). Thus, when CO is in the lungs, it binds to the heme iron in place of O₂, and carbon monoxide asphyxiation results because the hemoglobin can no longer transport O₂ to the cells.

Hemoglobin, represented by a ribbon diagram in Figure 14.10, consists of approximately 600 amino acids in four heme-containing polypeptides held together by intermolecular forces. Although the iron porphyrin is the center of the oxygen transport process, the polypeptide chains play critical roles in stabilizing the binding and release of the four O₂ molecules. Changes in protein structure have profound effects on the ability of hemoglobin to carry O₂. For example, consider sickle-cell anemia, a hereditary condition affecting four in 1000 black people. In a person with sickle-cell anemia, two amino acids (glutamates), out of the 600 amino acids that comprise hemoglobin, are replaced with two other amino acids (valines, see Figure 14.11). The change results in a different charge on the protein because valine is neutral while glutamate carries a negative charge. The ability of the blood to transport oxygen is greatly reduced as a consequence of this very small change.

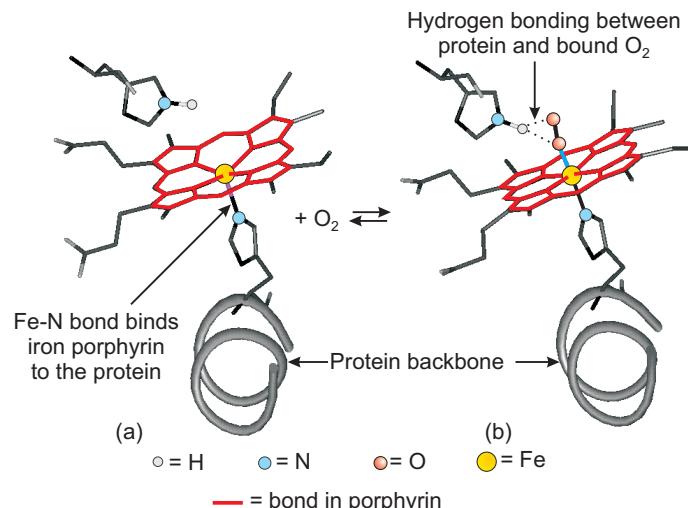


Figure 14.9 Active site of hemoglobin

- a) deoxyhemoglobin (hemoglobin without oxygen) and
b) oxyhemoglobin (hemoglobin with bound O₂)

* This is just what Le Châtelier’s principle predicts: the concentration of O₂ bound to iron increases when the concentration of O₂ increases (oxyhemoglobin \rightleftharpoons deoxyhemoglobin + O₂).

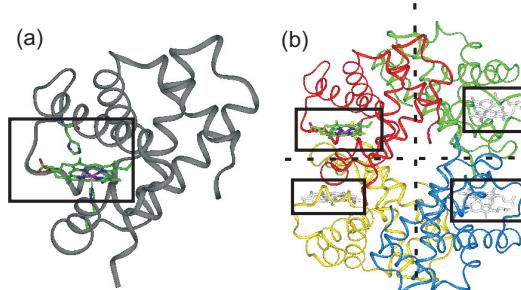


Figure 14.10 Hemoglobin structure

- a) Ribbon diagram of one quarter of the hemoglobin molecule, with the five-coordinate Fe(II) porphyrin outlined. The active site highlighted by the thick line is presented in more detail in Figure 14.9.
b) Ribbon diagram of the full hemoglobin molecule with four similar units. The porphyrin portion of each unit is outlined.

CISPLATIN

Metal ions, even many that are not essential to biological function, can be used for treatment of diseases. For example, complexes of gold are used to treat rheumatoid arthritis, and lithium is used to treat manic depression. The square planar complex *cis*-[Pt(NH₃)₂Cl₂] (also known as *cisplatin*) is an antitumor drug used to treat ovarian, testicular, and brain cancers. Its mode of action highlights the importance of geometric isomers in determining the properties of a complex and its reactivity toward *ligand substitution*.

The structures of *cis*-[Pt(NH₃)₂Cl₂] and *trans*-[Pt(NH₃)₂Cl₂] are shown in Figure 14.8. Although these two isomers differ only in the arrangement of the ligands around the platinum, they differ greatly in their ability to stop tumor growth. A look at the operation of cisplatin suggests the reason. Chloride ion is a weak Lewis base and is readily displaced from metal complexes. Even water is a stronger base than chloride ion. Thus, dissolving *cis*-[Pt(NH₃)₂Cl₂] in water results in the stepwise reactions shown in Figure 14.12. Notice that the chloride ligands are replaced by water, but the ammonia is a stronger base than water, so the ammonia molecules remain bonded to the platinum. This reaction is typical of a *ligand substitution reaction*, where one ligand is replaced by another. In a biological setting, functional groups on proteins and on DNA can act as ligands as well. Indeed, it is the bonding between the platinum in cisplatin and the lone pairs on two of the nitrogen atoms on a DNA strand of the cancer cell that is the main source of the antitumor activity.

The reactions represented in Figure 14.12 are written as dynamic equilibria. When the drug is administered into the blood stream, it is in an environment of relatively high chloride concentration ($\sim 0.1 \text{ M}$). Le Châtelier's principle tells us that a high chloride concentration will shift the equilibrium to the left, so most of the drug remains in its original state. However, inside the cell nucleus, the chloride concentration is much smaller ($\sim 0.003 \text{ M}$). Consequently, the equilibrium shown in Figure 14.12 shifts to the right. The resulting complex, in which both chlorides have been replaced with two water molecules, can then bind to the DNA, as depicted in Figure 14.13. Once bound, the DNA ligand is relatively unreactive.

The effect that the binding of platinum has on the shape of the DNA double helix is dramatic. The DNA double helix bends 30–40° at the site of binding. The bend is represented by α in Figure 14.13. Many cellular events are initiated with a reaction where a protein ‘reads’ a specific sequence on the DNA strand. This process is based almost entirely on the ability of the protein to conform to the shape of the double helix.

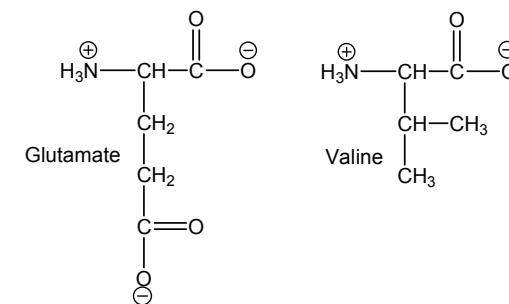


Figure 14.11 Amino acids involved in sickle-cell anemia

Two glutamates are replaced by two valines in people with sickle-cell anemia.

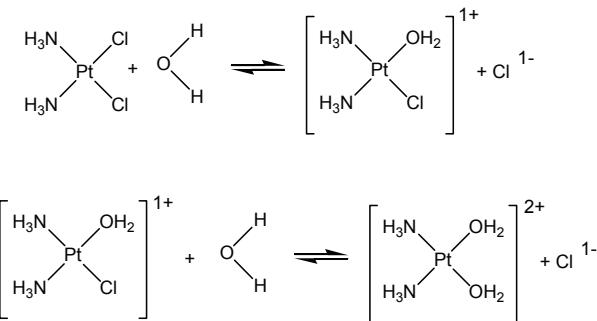


Figure 14.12 Replacement of chloride with water

Consequently, when the shape of the DNA double helix is changed (Figure 14.14), there is a dramatic effect on the processes that occur inside the cell. Because the platinum-bonded DNA strand has a different shape, some of the DNA-protein interactions are modified, thus prohibiting normal function of the protein. In the absence of normal protein-DNA interactions, the cell dies. The exact DNA-protein interactions are not yet fully understood, but the success of cisplatin as an antitumor drug appears to result from the change in shape of DNA upon binding of the drug.

The *trans* isomer (Figure 14.8) is much less effective as an antitumor agent. It also binds to DNA, but the two functional groups end up across from one another. This distorts the shape of DNA, but the distortions are different from those caused by the *cis* isomer. Whether this results in less disruption to protein-DNA interactions, or whether this type of shape change can be more easily “repaired” in the cell, the *trans* isomer of this complex is not as effective in killing tumor cells.

14.5 TRANSITION METALS AS CATALYSTS

The interaction of ligands with transition metals in coordination complexes can also be exploited to facilitate chemical reactions or to make useful materials. In Section 9.9, we indicated that a catalyst is a material that increases the rate of a reaction by lowering the activation energy. It does this by altering the path of the reaction to achieve a lower energy transition state. In many cases, the coordination of a ligand to a transition metal changes the reactivity of the ligand and thus creates new pathways through which the ligand can react. The catalyst itself is unchanged by the reaction. A catalyst can be classified as either heterogeneous or homogeneous, depending on whether it is in a different phase or the same phase as the reactants.

Heterogeneous catalysts are solids that catalyze solution or gas phase reactions on their surfaces. The adsorption of a ligand (reactant) to a metal catalyst weakens a bond in the reactant and makes it susceptible to further reaction. An important example of heterogeneous catalysis is the hydrogenation of alkenes, which has many practical applications, including the hydrogenation of food oils into solid fats such as margarine. The activation energy for this reaction is quite large because both the H-H bond and the C=C π bond of the alkene must be broken to form the transition state. Consequently, the reaction is slow unless the temperature is high, but increasing the temperature reduces the yield of the reaction because the reaction is exothermic (Section 9.11). However, in the

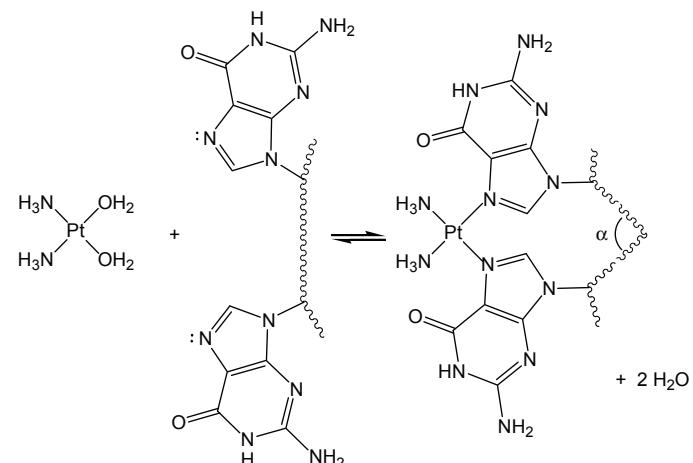


Figure 14.13 Cisplatin bound to two sites of a DNA strand
The DNA strand must bend (α) in order to accommodate the interaction with cisplatin.

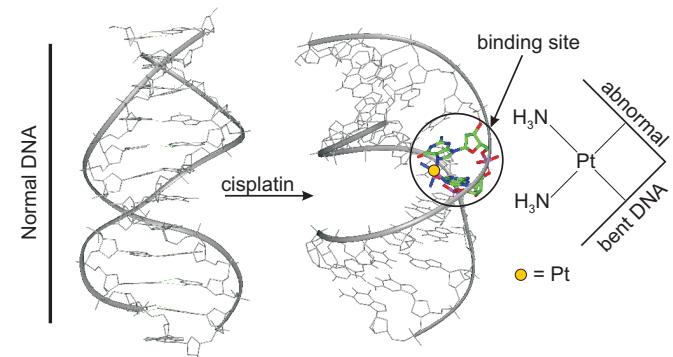


Figure 14.14 Changes in the double helix of DNA due to cisplatin binding

The region of cisplatin binding is outlined. The ribbon-like structure indicates that the DNA backbone distorts from the double helix.

presence of finely divided Ni, Pt, or Pd and a high pressure of H₂, the reaction proceeds rapidly even at ordinary temperatures. The mechanism for the reaction is shown in Figure 14.15. Hydrogen molecules approach the catalyst and interact with the surface (Figure 14.15a). The H-H bonds break, and the H atoms adsorb to the catalyst surface (Figure 14.15b), where they are free to migrate. The π bonds of ethene molecules are also broken when they interact with the surface (Figure 14.15c) as two Pt-C bonds are formed (Figure 14.15d). Migrating hydrogen atoms collide with the adsorbed ethene molecules and form C-H bonds, breaking a Pt-C and a Pt-H bond in the process (Figure 14.15e). A second collision with another migrating hydrogen atom results in the product (Figure 14.15f).

Controlling the emission products in gasoline engine exhaust is another use of heterogeneous catalysts. At the high operating temperatures of an automobile engine, nitrogen can react with oxygen to form NO and NO₂, which are responsible for the brown color of smog. If the car is incorrectly tuned, incomplete combustion may result in unused hydrocarbons and CO instead of CO₂ in the exhaust. To alleviate this problem, automobile manufacturers now install catalytic converters in the exhaust system. The **catalytic converter** is a heterogeneous catalyst that functions in much the same manner as the platinum surface described for the hydrogenation of ethene. The hot exhaust from the combustion of gasoline is passed over a mixture of Pt, Pd, and Rh. The mixture serves as a heterogeneous catalyst for the complete combustion of CO and unspent hydrocarbons to CO₂ and H₂O and for the decomposition of NO and NO₂ to N₂ and O₂. Tetraethyl lead, Pb(C₂H₅)₄, was once a common gasoline additive that was used to make ‘leaded’ gasoline burn ‘better’ (increase the octane rating). However, Pb atoms in the exhaust also adsorb to the catalyst’s surface, but they do not react. Instead, they remain on the surface, blocking active sites and ‘poisoning’ the catalyst. Therefore, only ‘unleaded’ gasoline is used in the US, which has the added benefit of discontinuing poisonous lead emission (PbO₂).

Homogeneous catalysts function in the same phase as the reactants, and a commercially important example is the transition metal-catalyzed polymerization of alkenes into polymers such as polyethylene* and polystyrene. This is a multibillion dollar industry in which millions of tons of polymers are produced annually. Consequently, even a small improvement in the functioning of a catalyst can reduce costs significantly.

The inorganic complex titanocene (Figure 14.16a) is a four-coordinate Ti(IV) complex with one chloride ion, two organic ligands (designated simply as L) that participate only indirectly in the reaction, and another organic ligand (C₂H₅ in Figure 14.16a) that serves as the foundation upon which the polymer forms. The fact that the titanium is in a high,

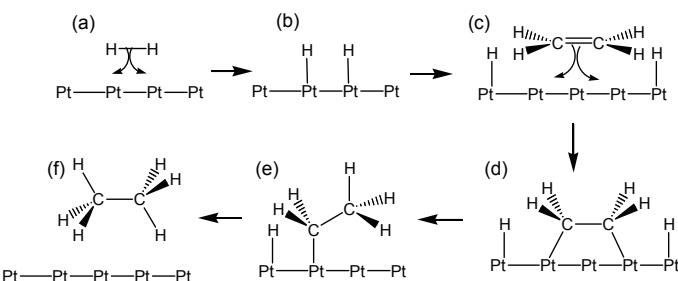


Figure 14.15 Hydrogenation of ethene using a platinum surface as a heterogeneous catalyst

* The accepted name for C₂H₄ is ethene. However, its older name, ethylene, is also in common use. Thus, the polymer formed from ethene units is called polyethylene.

positive oxidation state and is only four-coordinate makes it a good Lewis acid. As such, it is a good catalyst for the polymerization of alkenes, which are weak Lewis bases. Again, the activation energy for polymerization is reduced by first weakening the π bond of the alkene by coordination. As the ethene approaches the titanocene, the π electrons of the double bond are shared with the titanium, and the double bond weakens. Upon coordination, the titanium adopts a five-coordinate geometry, and the *original* Ti-C₂H₅ bond is weakened. As depicted by the curved arrows in Figure 14.16b, the π electrons on the ethene move to form a Ti-C σ bond. Simultaneously, the electrons that formed the original Ti-C bond move to form a C-C σ bond with the ethene (C₂H₄) to produce a coordinated C₄H₉ group. The resulting structure is shown in Figure 14.16c. It should be noted that the alkene is *inserted* into the original Ti-C bond. After the insertion, the titanocene reverts to a four-coordinate geometry and reacts with another ethene molecule, which inserts itself into the Ti-C bond in a similar manner to yield a coordinated C₆H₁₃ group. This process continues to cycle and, with each cycle, the length of the polymer chain increases by two CH₂ groups. As shown by the CH₂-CH₃ in bold in Figure 14.16, the initial organic group terminates the chain on the end away from the metal because insertion is always into the Ti-C bond.

14.6 TRANSITION METALS AS ELECTRONIC AND MAGNETIC MATERIALS

Transition metal complexes are also useful in a variety of materials applications such as electronic and magnetic materials. The reactivity of transition metal complexes is important for both their catalytic and biological function. However, the use of transition metal coordination complexes for materials applications requires systems in which the ligands are strongly coordinated and thus less reactive. Furthermore, to achieve such properties as conductivity or magnetism, we must focus on transition metal complexes in their crystalline form.

ELECTRONIC CONDUCTIVITY

Consider the square planar ion Pt(CN)₄²⁻, which is colorless in aqueous solution. As shown in Figure 14.17, the anions in crystalline K₂[Pt(CN)₄]·3H₂O stack face-to-face to form one-dimensional chains in the z-direction with Pt-Pt distances of 3.48 Å. The stacking of these square planar complexes aligns the z² orbitals of each platinum in the chain so that they can overlap in a σ -bonding fashion. Because the number of anions in a

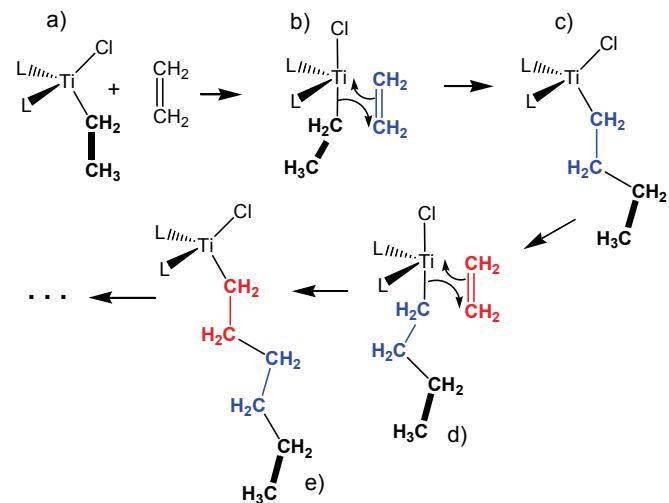


Figure 14.16 Polymerization of ethene to polyethylene by a titanium catalyst

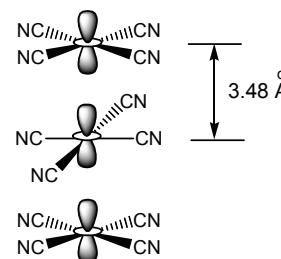


Figure 14.17 Linear chains formed from the face-to-face stacking of [Pt(CN)₄]²⁻ ions

Note that the [Pt(CN)₄]²⁻ units are staggered so that the cyanides of adjacent units are not directly under one another.

crystal is very large, the z^2 orbitals in the chain form a band. Subsequently, the z^2 orbitals are all filled in this ion, so the band is also filled, and the crystal is an insulator. However, this band can be partially oxidized by removing some of the electrons, either electrochemically or by reaction with bromine to form $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$. Complete oxidation of the platinum(II) to platinum(IV) would produce a compound with two bromide ions. The 0.3 subscript on the bromine indicates that only a partial oxidation has occurred. Figure 14.18 shows that the result of the oxidation is the removal of some of the electrons from the band formed from the z^2 orbitals. Because the result is a partially filled band, the material becomes metallic with a high degree of conductivity.

MAGNETIC MATERIALS

Magnetic materials are materials that can act as permanent magnets. The NO molecule has an unpaired electron and is paramagnetic (Section 3.4). Consequently, NO molecules are attracted by a magnetic field. However, they do not form permanent magnets because the spins of the isolated molecules do not align and thus cancel one another. Indeed, there are many atoms, ions, and molecules with unpaired electrons, but only a very few are magnetic materials. This is because there are two prerequisites for a magnetic material. First, the individual building blocks that make up the material must have nonzero spins, and, second, the material must have a three-dimensional crystal structure in which the spins of the atoms, ions, or molecules are aligned in an ordered fashion. Both of these requirements are satisfied by solid iron. Each iron atom has four unpaired electrons, and some of them align with their spins oriented in the same direction to produce a magnetic material (Figure 14.19a). This type of magnetic material is called a **ferromagnet**. However, without the three-dimensional crystal structure, the spins cannot stay aligned and a permanent magnet cannot form; consequently, molten iron is not magnetic.

The spins of adjacent atoms, ions, or molecules in a solid usually interact with one another so as to pair in much the same way that the electrons in a covalent bond pair. This is the situation depicted in Figure 14.19b, where the spins on neighboring units are opposed, so the material is not a permanent magnet. Materials in which adjacent spins are opposed are said to be **antiferromagnetic**. This is the most common occurrence and explains why the solids of most metals are not magnetic even though the individual atoms may be paramagnetic (have unpaired electrons).

The fact that the neighboring spins usually interact to yield materials with zero net

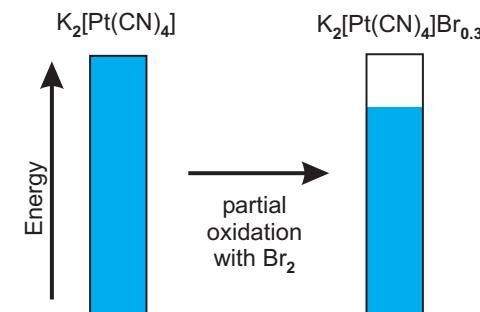


Figure 14.18 Band occupancy changes due to partial oxidation of platinum

The material with band structure (a) is an insulator, but partial oxidation produces structure (b), which is a conductor.

spin makes the synthesis of molecular magnets challenging. However, one method that has met with some success is to synthesize materials involving different ions with different spins. If the spins align as represented in Figure 14.19c, there is a net ‘up spin’, and the material is magnetic even though the neighboring spins are opposed. This type of magnetic material is called a **ferrimagnet**. Ferrimagnetic materials have been prepared from metal cyanide coordination complexes similar to the blue dye known as Prussian Blue. These materials are constructed starting with octahedral metal cyanide complexes $M(CN)_6$. While the carbon atoms of the cyanide ligand are coordinated to one metal, M, the nitrogen atoms of the cyanide ligands can also act as a Lewis base that can coordinate to another Lewis acidic transition metal, M'. The cyanide ligand *bridges* the two metals ($M:C\equiv N:M'$). The two metals are arranged into a crystalline solid with a face-centered cubic packing analogous to the sodium chloride structure. One such compound is $Cs_2Mn[V(CN)_6]$. The Mn(II) has five unpaired electrons, while the V(II) has only three. The structure of the material is represented in Figure 14.20. The cyanide bridge assures that there is an alternation of vanadium and manganese ions in all three directions (-Mn:N≡C:V:C≡N:Mn-) and imposes the required alternation of spins of different magnitudes.

14.7 CHAPTER SUMMARY AND OBJECTIVES

The bonding between a transition metal and its ligands can be described as a Lewis acid (metal)-Lewis base (ligand) interaction. The ligand *coordinates* (bonds) to the metal, and the geometry of the ligands about the metal is referred to as the metal’s *coordination geometry*; the number of ligands bound to the metal is the metal’s *coordination number*. Ligands forming more than one metal-ligand bond are said to be *bridging ligands* if the bonds are to two different metals or *chelating ligands* if they bond to only one metal.

The lone pairs on the ligands cause the energies of metal d orbitals directed along the bonding axes (z^2 and x^2-y^2 orbitals) to be higher than those directed between the axes (xy , xz , yz orbitals). The energy difference between the two sets of d orbitals is given the symbol Δ . The magnitude of Δ depends on the metal and the ligands. Ligands causing large Δ ’s are *strong-field ligands*, while those causing small Δ ’s are *weak-field ligands*. If Δ is larger than the pairing energy, the electrons pair before occupying the higher energy set of orbitals, and the metal is said to have a *low spin* configuration. If Δ is small, the electrons occupy the higher set of orbitals before pairing, and the metal has a *high spin*

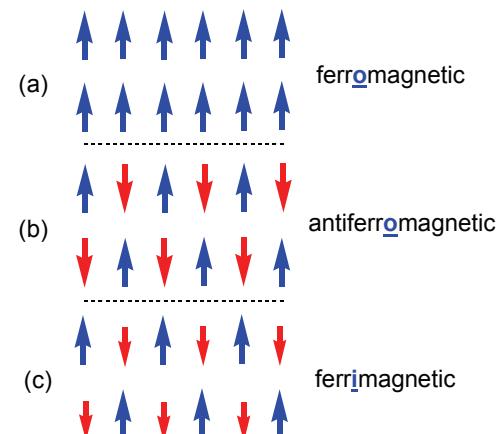


Figure 14.19 Electron spin and magnet type

a) Neighboring units have a net spin oriented in the same direction; the substance is magnetic. b) Adjacent units interact to produce opposing spins and a nonmagnetic material. c) Adjacent units have opposed spins, but the spins are of different magnitudes and the material is magnetic. The fact that the ↑ is longer than the ↓ is used to indicate the different magnitudes of the spin.

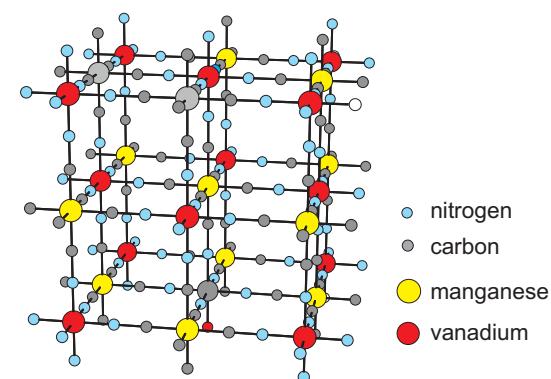


Figure 14.20 Structure of $Cs_2Mn[V(CN)_6]$

The cesium ion in the center of each cube is omitted for simplicity.

configuration. The color of transition metals can often be attributed to the metal absorbing a visible photon as an electron is promoted from the lower set of d orbitals to the higher set.

Square planar and octahedral complexes can exist as either *cis* or *trans* isomers, depending on whether two unique ligands are next to or opposite one another. In addition, octahedral complexes with three unique ligands can be either *mer* or *fac* isomers, depending on whether the unique ligands are situated on the meridian or face of the octahedron.

Metals are critical to the proper function of living organisms. A magnesium ion coordinated to a porphyrin derivative optimizes the absorption of visible light in photosynthesis, while manganese ions help the plant carry out the four-electron transfer reactions required for the production of carbohydrates from carbon dioxide. Hemoglobin uses an Fe^{2+} ion at the center of a porphyrin that is bound to a protein to bind oxygen in the lungs, where oxygen concentration is high. It then releases it in tissue, where the oxygen concentration is low.

Metals can also play key roles in drugs. Cisplatin, *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, is an antitumor drug that functions by binding to two sites of DNA. When bound to the platinum, the DNA double helix develops a kink. This change in secondary structure results in a modification of some of the DNA-protein interactions and prohibits the normal function of the protein, causing the cell to die.

Transition metals can serve as either heterogeneous or homogeneous catalysts. The catalyst lowers the activation energy of a reaction by weakening the bonds of one of the reactants. The catalytic converter is a heterogeneous catalyst that is used to rid automobile exhaust of pollutants. Titanocene is a homogeneous catalyst for the polymerization of alkenes. It functions by coordinating the alkene and weakening the C=C double bond.

The crystalline structure of $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ shows that the $\text{Pt}(\text{CN})_4^{2-}$ anions are stacked face-to-face and form linear chains in the solid. The interactions of the z^2 orbitals on the platinum atoms result in an electronic band. The band is full and $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ is an insulator. However, a partial oxidation transforms it into a metallic conductor.

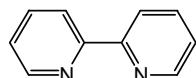
Magnetic materials require unpaired electrons and a three-dimensional crystal structure that aligns the spins of the electrons. Cyanide ion has been used to bridge metals with unpaired electrons to make magnets. The first magnetic materials that are permanent magnets above room temperature were prepared with cyanide-bridged vanadium and chromium.

After studying the material presented in this chapter, you should be able to:

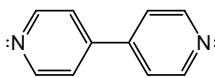
1. determine the coordination number of a metal (Section 14.1);
2. give an example of a ligand behaving as a Lewis base (Section 14.1);
3. distinguish between chelating and bridging ligands (Section 14.1);
4. predict the relative energies of d orbitals in octahedral complexes (Section 14.2);
5. distinguish between the properties of complexes of weak- and strong-field ligands (Section 14.2);
6. explain the origin of the color of many transition metal complexes and show how the color varies with the field strength of the ligand (Section 14.2);
7. explain the difference between high-spin and low-spin complexes and show how the spin depends upon Δ (Section 14.2);
8. identify and differentiate *cis* and *trans* isomers and *fac* and *mer* isomers (Section 14.3);
9. explain the relationship between photosynthesis and respiration (Section 14.4);
10. identify the heme portion in hemoglobin and explain its function (Section 14.4);
11. explain the role of cisplatin in the treatment of cancer (Section 14.4);
12. distinguish between homogenous and heterogeneous catalysis and give an example of each (Section 14.5);
13. explain how partial oxidation of a filled band can result in conductivity (Section 14.6); and
14. describe the prerequisites for a molecular magnet (Section 14.6).

14.8 EXERCISES

1. 2,2'- and 4,4'-bipyridine are bidentate ligands (see below). Can each be chelating, bridging, or both? Explain.



2,2'-bipyridine



4,4'-bipyridine

2. In Example 14.1, we used the fact that CoBr_2 is green while CoCl_2 is blue to determine the relative ligand field strengths of bromide and chloride ions. Explain why dissolving both of these substances in water results in a red solution. Which has a stronger ligand field, water or halide ion?
3. How many d electrons does Co^{2+} contain? What is the spin of Co^{2+} in a weak octahedral field? What is the spin of Co^{2+} in a strong octahedral field?
4. Draw all possible isomers of $\text{Co}(\text{NH}_3)_4\text{Cl}_2$. Draw all possible isomers of $\text{Co}(\text{NH}_3)_3\text{Cl}_3$.
5. What is the role of the magnesium ion in photosynthesis?
6. Draw the heme group and discuss its role in respiration.
7. Discuss the coordination chemistry of carbon monoxide poisoning.
8. Explain the function of cisplatin in treating cancer.
9. Explain how a partial reduction of an empty band results in conductivity.
10. Four- and five-coordinate transition metal complexes frequently function as homogeneous catalysts, but catalytic six-coordinate complexes are rare. Explain.

Appendix A

Stoichiometry of Elements and Compounds

A.1 INTRODUCTION

In this appendix, we will look at some of the quantitative relationships associated with the mass of elements and compounds. This subset of chemistry is called stoichiometry, a word derived from the Greek word “stoikheion”, meaning element. Before we begin, we need to say a few words about the approach that we will take to the calculations in this appendix.

A.2 THE CONVERSION FACTOR APPROACH TO CALCULATIONS

If someone told you that she was “six”, you might have a little trouble deciding what was meant. That person could be six years old, but if she were a college student, that would probably not be correct. She could weigh six tons or be six inches tall, but probably not. She is more likely six feet tall. The point is that there are two parts to a measurement or a piece of quantitative information; the “number” and the “unit”. Six inches, six feet and six meters all have the same number, but are clearly different lengths. In scientific measurements or calculations, we must pay attention to both the number and the unit.

In order to convert the height of six feet to inches, most of us would say “multiply by 12” to give an answer of 72 inches. Although the result is correct, we did not multiply by 12; we actually multiplied by 1! Here’s how:

We know the following equality: $12 \text{ in} = 1 \text{ ft}$

Divide both sides by 1 ft:

$$\frac{12 \text{ in}}{1 \text{ ft}} = \frac{1 \text{ ft}}{1 \text{ ft}} = 1$$

The fraction in the box is called a “conversion factor” and it is equal to 1. In converting six feet to inches, we actually performed the following operation:

$$6 \text{ ft} \times \frac{12 \text{ in}}{1 \text{ ft}} = 72 \text{ in}$$

In the above, the distance in feet is multiplied by a conversion factor to produce a distance in inches.

Notice that we did the operation on the numbers (six times twelve divided by one equals seventy-two) and on the units as well (feet times inches divided

by feet equals inches; feet “cancel out”). Both the number and the unit changed, but the height did not (going from six feet to 72 inches, the person did not grow or shrink). This is what we would expect upon multiplication by 1. Although this is a trivial example, we will use this same **conversion factor** or **factor label** approach for nearly all of the stoichiometric calculations in this book.

A.3 MOLAR MASSES AND ATOMIC WEIGHTS OF THE ELEMENTS

The number under the symbol of an element on the periodic table is the element’s atomic weight. It represents the “average atomic weight” or “average atomic mass” of the element because it is determined from the masses and abundance of the different isotopes of the element. Although there is a technical difference between weight and mass (weight depends on the gravitational force where you do the measurement), the two terms are often used interchangeably. We will use the term mass here, although your instructor may refer to “atomic weight”. The mass of a single atom is the element’s atomic weight expressed in units of amu, atomic mass units. The mass of a mole of atoms is the atomic weight expressed in units of grams/mol. The latter is referred to as the **molar mass** of the element. In this book, we use the symbol M_m to represent molar mass.

A.4 RELATING GRAMS, MOLES AND MOLAR MASS

Molar mass can also be used as a conversion factor. Using carbon as an example, the molar mass can be expressed as a fraction:

$$M_m = \frac{12.01 \text{ g}}{1 \text{ mol}}$$

The above is a conversion factor and is also equal to 1 because 12.01 grams of carbon and one mole of carbon are the same amount of carbon. The molar mass of an element can be used to convert between grams and moles.

Example 1

How many grams of sulfur are present in 0.250 moles of sulfur?

Solution:

The molar mass of sulfur from the periodic table is 32.07 g/mol. We start with the given information and apply the molar mass as a conversion factor.

$$0.250 \text{ moles} \times \frac{32.07 \text{ g}}{1 \text{ mol}} = 8.02 \text{ g}$$

Example 2

How many moles of copper are contained in 525 g of copper?

Solution:

The molar mass of copper from the periodic table is 63.55 g/mol. We again start with the given information and apply the molar mass as a conversion factor, but this time we use it in its reciprocal form (turn it “upside down”) with moles in the numerator and grams in the denominator such that grams cancel out.

$$525 \text{ g} \times \frac{1 \text{ mol}}{63.55 \text{ g}} = 8.26 \text{ mol}$$

Comment:

In examples 1 and 2, a conversion factor was applied, that changed the number and the unit, but not the amount of substance (which is what you would expect upon “multiplying by 1”). 525 g of copper and 8.26 moles of copper are the same amount of copper, expressed in two different units.

A.5 COUNTING INDIVIDUAL ATOMS

Avogadro’s number, which is $6.02 \times 10^{23} \text{ mol}^{-1}$, is the number of items present in a mole. Whether you are counting individual atoms, molecules, or trees, Avogadro’s number can be used to convert between the number of items and the number of moles of items; *i.e.*, it is just another conversion factor.

$$\frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{ mole of atoms}}$$

$$\frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mole of molecules}}$$

$$\frac{6.02 \times 10^{23} \text{ trees}}{1 \text{ mole of trees}}$$

Example 3

How many calcium atoms are in 2.25 moles of calcium?

Solution:

Start with the known information and apply Avogadro’s number as a conversion factor:

$$2.25 \text{ mol Ca} \times \frac{6.02 \times 10^{23} \text{ Ca atoms}}{1 \text{ mol Ca}} = 1.35 \times 10^{24} \text{ Ca atoms}$$

Example 4

How many calcium atoms are in 2.25 grams of calcium?

Solution:

Avogadro’s number tells us how many calcium atoms are in a mole of calcium, but the given information in this example is grams of calcium. Therefore, we must use the molar mass of calcium from the periodic table (40.08 g/mol) to convert grams to moles of calcium. We then apply Avogadro’s number to obtain the number of atoms.

$$2.25 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} \times \frac{6.02 \times 10^{23} \text{ Ca atoms}}{1 \text{ mol Ca}} = 3.38 \times 10^{22} \text{ Ca atoms}$$

Comment:

Here we have combined two separate calculations (grams to moles and moles to number of atoms) by stringing together two conversion factors. We could, of course, have done the two separate calculations on two separate lines.

Example 5

What is the mass of 1.00×10^{22} bromine atoms?

Solution:

We apply Avogadro’s number to determine the number of moles of bromine in the given number of atoms. Next we use, the molar mass of bromine (79.90 g/mol from the periodic table), to convert moles into grams.

$$1.00 \times 10^{22} \text{ Br atoms} \times \frac{1 \text{ mol Br}}{6.02 \times 10^{23} \text{ Br atoms}} \times \frac{79.90 \text{ g Br}}{1 \text{ mol Br}} = 1.33 \text{ g Br}$$

Comment:

Again, two separate calculations were combined in one step.

A.6 CHEMICAL FORMULAS OF COMPOUNDS

A compound is a pure substance that is made up of more than one element. Compounds can be *ionic* (CAMS Chapter 4) or *covalent* as described in (CAMS Chapter 5). Covalent compounds are said to be *molecular* because they exist as discrete molecules, but ionic compounds exist as extended three-dimensional arrays of ions and not as discrete molecules.

The molecular formula of a compound tells us how many atoms of each element are in one molecule. A carbon dioxide molecule, which has the formula CO_2 , contains one carbon atom and two oxygen atoms. This information is contained in the subscripts after each element. A molecule of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) has 12 carbon atoms, 22 hydrogen atoms and 11 oxygen atoms. The subscripts also indicate the ratios of the elements. A dozen CO_2 molecules have one dozen carbon atoms and two dozen oxygen atoms. A million CO_2 molecules have one million carbon atoms and two million oxygen atoms. A mole of CO_2 molecules (we usually just say “a mole of CO_2 ”) has one mole of carbon atoms and two moles of oxygen atoms. The atom ratio and the mole ratio of the elements are identical!

The chemical formula of an ionic compound does not tell us the number of atoms in a molecule because ionic substances are not molecular. However, it still gives the mole ratio of the elements. One mole of NaCl contains one mole of Na^{1+} ions and one mole of Cl^{1-} ions. Ionic compounds with polyatomic ions are somewhat more complicated. One mole of sodium sulfate, Na_2SO_4 , contains two moles of Na^{1+} ions and one mole of SO_4^{2-} ions or two moles of sodium, one mole of sulfur and four moles of oxygen. An additional complexity comes from the way we write formulas of compounds containing polyatomic ions. Iron (III) nitrate has the formula $\text{Fe}(\text{NO}_3)_3$. This tells us that for every iron(III) ion (Fe^{3+}), there are three nitrate ions (NO_3^{1-}). Each nitrate ion contains one nitrogen atom and three oxygen atoms. Therefore, one mole of iron(III) nitrate contains one mole of iron, three moles of nitrogen and nine moles of oxygen.

A.7 MOLAR MASSES, MOLECULAR WEIGHTS AND FORMULA WEIGHTS OF COMPOUNDS

The molar mass of a compound can be determined from its chemical formula and the periodic table. The number obtained is sometimes referred to as the *molecular weight* or the *formula weight*. Molecular weight refers to the weight or mass of one molecule, in units of amu. Formula weight refers to the same quantity, but can be applied to substances that are not molecular, e.g., NaCl . Thus, even though iron(III) nitrate is not molecular, we can still talk about the mass of one formula unit, that is, one iron, three nitrogens and nine oxygens. All three terms are often used interchangeably, although molar mass is technically the only one that is in units of grams/mole.

To calculate a molar mass, we simply sum up the contributions of each element or atom. For carbon dioxide, CO_2 , one carbon atom contributes 12.01 g/mol, the two oxygens together contribute $(2)(16.00) = 32.00$ g/mol. The molar mass is then $12.01 + 32.00 = 44.01$ g/mol.

The same procedure is followed, whether the compound is covalent or ionic, as shown in the following examples.

Example 6

Calculate the molar mass of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

Solution:

Find the molar mass of each element on the periodic table and sum up the contributions.

$$\begin{aligned} \text{Contribution from C: } (12 \text{ mol})(12.01 \text{ g/mol}) &= 144.12 \text{ g} \\ \text{Contribution from H: } (22 \text{ mol})(1.008 \text{ g/mol}) &= 22.18 \text{ g} \\ \text{Contribution from O: } (11 \text{ mol})(16.00 \text{ g/mol}) &= \underline{\underline{176.00 \text{ g}}} \\ \text{Total} &= 342.30 \text{ g/mol} \end{aligned}$$

Comment:

Notice that the molar mass of each element was multiplied by the number of times that element appeared in the chemical formula (as indicated by the subscripts in the formula).

Example 7

Calculate the molar mass of cobalt(II) phosphate, $\text{Co}_3(\text{PO}_4)_2$.

Solution:

Determine the contribution from each element and sum.

cobalt(II) phosphate :

Co: (3 mol)(58.93 g/mol)	=	176.79 g
P: (2 mol)(30.97 g/mol)	=	61.94 g
O: (8 mol)(16.00 g/mol)	=	<u>128.00 g</u>
Total	=	366.73 g/mol

Comment:

Even though the compound contains cobalt(II) ions, we use the molar mass of cobalt atoms. The difference in mass between a cobalt atom and a cobalt(II) ion is negligible, because the mass of an electron is so small compared to the mass of an atom.

A.8 RELATING GRAMS, MOLES AND MOLAR MASS OF COMPOUNDS

The molar mass of a compound can be used as a conversion factor in the same way as the molar mass of an element.

Example 8

How many grams of sucrose ($M_m = 342.30 \text{ g/mol}$) are present in 0.125 moles of sucrose?

Solution:

We start with the given information and apply the molar mass as a conversion factor.

$$0.125 \text{ mol} \times \frac{342.30 \text{ g}}{1 \text{ mol}} = 42.8 \text{ g}$$

Example 9

What is the mass of 2.50 moles of $\text{Mg}(\text{ClO}_4)_2$?

Solution:

In order to convert moles to grams, we need a molar mass from the chemical formula and the periodic table. Then we apply the molar mass as a conversion factor.

Magnesium perchlorate : $\text{Mg}(\text{ClO}_4)_2$

Molar mass :

Mg: (1 mol)(24.31 g/mol)	=	24.31 g
Cl: (2 mol)(35.45 g/mol)	=	70.90 g
O: (8 mol)(16.00 g/mol)	=	<u>128.00 g</u>
Total	=	223.21 g/mol

$$2.50 \text{ mol} \times \frac{223.21 \text{ g}}{1 \text{ mol}} = 558 \text{ g}$$

Comment:

This example involves putting together several individual skills that you have learned to solve a problem. Rarely does an experiment or problem in science require only one skill. Often new discoveries and new applications result from putting known information together in new ways!

A.9 PERCENT COMPOSITION OF COMPOUNDS

The method we have used to calculate molar masses gives us a simple way to figure out the percentage of each element in a compound. Let's use ammonium nitrate as an example. This compound has the formula NH_4NO_3 and its molar mass is:

N: (2 mol)(14.01 g/mol)	=	28.02 g
H: (4 mol)(1.008 g/mol)	=	4.03 g
O: (3 mol)(16.00 g/mol)	=	<u>48.00 g</u>
		Total = 80.05 g/mol

This calculation not only tells us the mass of a mole of the compound, but it also tells us how many grams of each element are in a mole of the compound. For instance, in every 80.05 grams of the compound, there are 28.02 grams of nitrogen. Taking the ratio of grams of nitrogen to total grams of compound, we find:

$$\frac{28.02 \text{ g}}{80.05 \text{ g}} = 0.3500$$

This number, 0.3500, is the mass fraction of nitrogen in the compound. This can easily be converted into a percent by multiplying by 100:

$$(0.3500)(100) = 35.00 \%$$

Ammonium nitrate is 35.00% nitrogen by mass.

The ratio of grams of nitrogen to total grams of compound can be used as a conversion factor, too. If we want to know how many grams of nitrogen there are in 275 grams of ammonium nitrate, we would do the following :

$$275 \text{ g } \text{NH}_4\text{NO}_3 \times \frac{28.02 \text{ g N}}{80.05 \text{ g } \text{NH}_4\text{NO}_3} = 96.3 \text{ g N}$$

Notice that grams of NH_4NO_3 cancel out in this calculation, leaving grams of N in the product. Also notice that the ratio 28.02/80.05 is identical to the ratio 96.3/275 (which is identical to 35/100 from the percent composition calculation). This technique is summed up in the following example.

Example 10

- a) What is the percent nitrogen in potassium nitrate (KNO_3)?

Solution:

Percent nitrogen can be found from the data in a molar mass calculation. First, we need the chemical formula of potassium nitrate.

Potassium nitrate : KNO_3

Molar mass:

K: (1 mol)(39.10 g/mol)	=	39.10 g
N: (1 mol)(14.01 g/mol)	=	14.01 g
O: (3 mol)(16.00 g/mol)	=	<u>48.00 g</u>
Total	=	101.11 g/mol

Percent nitrogen:

$$\frac{14.01 \text{ g N}}{101.11 \text{ g total}} \times 100\% = 13.86 \% \text{ N}$$

- b) How many grams of potassium are present in 137 g of KNO_3 ?

Solution:

The molar mass calculation tells us that, for every 101.11 g of compound, there are 39.10 g of K. Start with the given information and apply the ratio of grams of K to grams of compound as a conversion factor.

$$137 \text{ g } \text{KNO}_3 \times \frac{39.10 \text{ g K}}{101.11 \text{ g } \text{KNO}_3} = 53.0 \text{ g K}$$

- c) What mass of KNO_3 contains 125 g of potassium?

Solution:

The given quantity is 125 g of K. Clearly, we need more than 125 g of compound to give us 125 g of K, since the compound is only about 39% K. We can apply the same ratio as in part b, but turning it "upside down" to give us a result in units of grams of KNO_3 .

$$125 \text{ g K} \times \frac{101.11 \text{ g } \text{KNO}_3}{39.10 \text{ g K}} = 323 \text{ g } \text{KNO}_3$$

Comment:

We said that multiplication by a conversion factor is multiplication by 1. In this case, 101.11 g of KNO_3 is the same as "the amount of KNO_3 that contains 39.10 g of K". In other words, the numerator and denominator represent the same amount of compound. This gives the effect of multiplying by 1.

A.10 COUNTING ATOMS, IONS AND MOLECULES IN COMPOUNDS

We use Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$, to "count" the number of individual particles in a sample. The key in our calculations is to first find the number of moles of whatever item it is we wish to count, and then apply Avogadro's number to convert from moles to individual items. The following examples all involve multiple steps, each of which we have discussed separately.

Example 11

- a) How many water molecules are contained in 10.0 g of H_2O ?

Solution:

In order to "count" water molecules, we first find how many moles of water are present in 10.0 g ($M_m = 18.02 \text{ g/mol}$), and then apply Avogadro's number.

$$10.0 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times \frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 3.34 \times 10^{23} \text{ molecules}$$

b) How many hydrogen atoms are contained in 10.0 g of H₂O?

Solution to part b:

In order to “count” hydrogen atoms, we first find how many moles of hydrogen atoms are present in 10.0 g of water, and then apply Avogadro’s number.

$$10.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times \frac{6.02 \times 10^{23} \text{ H atom}}{1 \text{ mol H}} = 6.68 \times 10^{23} \text{ H atoms}$$

Comment:

Note that the two calculations are almost identical, the only difference being the term that converts moles of H₂O to moles of H in part b. This extra step was necessary because we are “counting” hydrogen atoms, not water molecules. The conversion factor comes directly from the chemical formula, where the subscript 2 (after the H) indicates that there are two hydrogen atoms per water molecule and two moles of hydrogen atoms per mole of water molecules. Note also that each calculation simply strings together a series of conversion factors. Each conversion factor is applied such that the term in the denominator “cancels out” the unit from the previous step. For example, the first conversion factor in each part is the molar mass of water simply turned “upside down” to put grams of water in the denominator.

Example 12

How many iron(III) ions are contained in 68.4 g of Fe₂(SO₄)₃?

Solution:

Many chemistry students find that the hardest part of a problem like this is figuring out where to start. Let’s use some stepwise logic to figure out what we need for each step, working backwards to see where we should start. In order to count iron(III) ions, we need moles of iron(III). We can get moles of iron(III) if we know how many moles of iron(III) sulfate we have. We can get the moles of iron(III) sulfate from the 68.4 g and the molar mass. The molar mass is obtained from the chemical formula.

Molar mass :

$$\begin{aligned} \text{Fe: } (2 \text{ mol})(55.85 \text{ g/mol}) &= 111.70 \text{ g} \\ \text{S: } (3 \text{ mol})(32.07 \text{ g/mol}) &= 96.21 \text{ g} \\ \text{O: } (12 \text{ mol})(16.00 \text{ g/mol}) &= 192.00 \text{ g} \\ \text{Total} &= 399.91 \text{ g/mol} \end{aligned}$$

$$68.4 \text{ g Fe}_2(\text{SO}_4)_3 \times \frac{1 \text{ mol Fe}_2(\text{SO}_4)_3}{399.91 \text{ g Fe}_2(\text{SO}_4)_3} \times \frac{2 \text{ mol Fe}^{3+}}{1 \text{ mol Fe}_2(\text{SO}_4)_3} \times \frac{6.02 \times 10^{23} \text{ Fe}^{3+} \text{ ions}}{\text{mol Fe}^{3+} \text{ ions}} \\ = 2.06 \times 10^{23} \text{ Fe}^{3+} \text{ ions}$$

Comment:

As is often the case, there are several steps required to solve the problem. Each individual step is not that hard; it is putting them together in the proper order that is the stumbling block for some students. Our approach was to use some logic, starting at the end and working back to the beginning, keeping track of everything needed along the way to solve the problem.

Example 13

How many grams of sucrose (C₁₂H₂₂O₁₁) contain 4.75 × 10²⁵ carbon atoms?

Solution:

We are given the number of carbon atoms and are asked to find the mass of sucrose that contains them. (Notice that this problem works in the reverse direction to Examples 11 and 12, where grams were given and individual atoms were sought.) In order to calculate grams of sucrose, we need moles of sucrose (342.30 g/mol from Example 6). Moles of sucrose can be found from the moles of carbon atoms and the subscripts in the chemical formula. Moles of carbon atoms can be found from the number of individual atoms and Avogadro’s number.

$$4.75 \times 10^{25} \text{ C atoms} \times \frac{1 \text{ mol C}}{6.02 \times 10^{23} \text{ C atoms}} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{12 \text{ mol C}} \times \frac{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \\ = 2.25 \times 10^3 \text{ g} = 2.25 \text{ kg C}_{12}\text{H}_{22}\text{O}_{11}$$

Comment:

As always, each conversion factor we apply has the effect of “canceling out” the units from the previous step.

A.11 EXERCISES

Basic skills / elements

1. Arrange each of the following sets of elements in order of increasing atomic mass.
 - a) phosphorus, sodium, iron, carbon
 - b) manganese, potassium, fluorine, copper
 - c) selenium, beryllium, arsenic, iron
 - d) chlorine, zinc, scandium, helium
2. How many moles of titanium are contained in 15.5 g of titanium?
3. How many grams of sodium are contained in 1.25 moles of sodium?
4. How many moles of vanadium does 6.02×10^{22} vanadium atoms represent?
5. How many grams of magnesium are contained in 0.52 moles of magnesium?
6. How many moles of cobalt are contained in 66 kg of cobalt?
7. How many nickel atoms are contained in 0.50 moles of nickel?
8. How many moles of carbon are contained in 2.85 g of carbon?
9. How many moles of nitrogen does 7.5×10^{21} nitrogen atoms represent?
10. How many moles of germanium are contained in 25 mg of germanium?
11. How many oxygen atoms are contained in 6.25 moles of oxygen atoms?
12. How many grams of chromium are contained in 2.5×10^{-4} moles of chromium?
13. How many krypton atoms are contained in 1.22 moles of krypton?
14. How many kilograms of phosphorus atoms are contained in 38 moles of phosphorus atoms?
15. How many moles of silicon does 8.8×10^{24} silicon atoms represent?

Combined skills / elements

16. How many lithium atoms are contained in 1.0 g of lithium?
17. What is the mass of 2.5×10^{21} argon atoms?
18. How many aluminum atoms are contained in 1.5 kg of aluminum.
19. What is the mass of 3.5×10^{25} iron atoms?
20. What is the mass, in grams, of 8.25×10^{23} silver atoms?
21. How many barium atoms are contained in 0.050 g of barium?

Basic skills / compounds

22. Calculate the molar mass of the following compounds:

a) hydrazine, N_2H_4	b) acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$
c) pyridine, $\text{C}_5\text{H}_5\text{N}$	d) succinic acid, $\text{C}_4\text{H}_6\text{O}_4$
e) TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$	f) calcium nitrate, $\text{Ca}(\text{NO}_3)_2$
g) potassium chromate, K_2CrO_4	
h) cobalt(II)citrate, $\text{Co}_3(\text{C}_6\text{H}_8\text{O}_7)_2$	
23. Use the following molar masses to answer these questions:
cobalt(II) iodide, CoI_2 : 312.74 g/mol
morphine, $\text{C}_{17}\text{H}_{19}\text{NO}_3$: 285.35 g/mol
 - a) How many moles of CoI_2 are contained in 10.0 g of CoI_2 ?
 - b) How many grams of morphine are contained in 2.0×10^{-5} moles of morphine?
 - c) How many moles of morphine are contained in 35 mg of morphine?
 - d) How many kilograms of CoI_2 are contained in 12.0 moles of CoI_2 ?
24. What is the % carbon in each of the following compounds:

a) CH_4	b) $\text{C}_6\text{H}_{12}\text{O}_6$	c) C_7H_8
------------------	--	---------------------------
25. How many grams of potassium are contained in 8.00 g of KCl ?
26. How many chloride ions are contained in 8.00 g of KCl ?
27. How many grams of sulfur are contained in 1.00 kg of thiophene, $\text{C}_4\text{H}_4\text{S}$ ($M_m = 84.14$ g/mol)?
28. How many sulfur atoms are contained in 3.55 g of $\text{C}_4\text{H}_4\text{S}$?
29. How many carbon atoms are contained in 3.55 g of $\text{C}_4\text{H}_4\text{S}$?
30. If you wanted to obtain 1.00×10^5 g of nitrogen, what mass of NH_3 would you need?
31. If you wanted to obtain 1.00×10^5 g of nitrogen, what mass of NH_4NO_3 would you need?
32. How many oxygen atoms are contained in 5.25 g of $\text{Fe}(\text{NO}_3)_3$?
33. How many carbon atoms are contained in 65 g of quinine, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$ ($M_m = 324.41$ g/mol)?
34. How many grams of carbon are contained in 65 g of quinine?

Answers:

1. a) C(12) < Na(23) < P(31) < Fe(56)
 b) F(19) < K(39) < Mn(55) < Cu(64)
 c) Be(9) < Fe(56) < As(75) < Se(79)
 d) He(4) < Cl(35) < Sc(45) < Zn(65)

2. 0.324 mol Ti

3. 28.8 g Na

4. 0.100 mol V

5. 13 g Mg

6. 1.1×10^3 mol Co

7. 3.0×10^{23} atoms of Ni

8. 0.237 mol C

9. 0.012 mol N (or 0.0062 mol N₂)

10. 3.4×10^{-4} mol Ge = 0.34 mmol Ge

11. 3.76×10^{24} atoms of O

12. 0.013 g Cr

13. 7.35×10^{23} atoms of Kr

14. 1.2 kg of P atoms

15. 15 mol Si

16. 8.7×10^{22} atoms of Li

17. 0.17 g Ar

18. 3.3×10^{25} atoms of Al

19. 3.2 kg Fe

20. 148 g Ag

21. 2.2×10^{20} atoms of Ba

22. a) 32.05 b) 60.34

 e) 227.1 f) 164.1

23. a) 0.0320 mol CoI₂

 c) 1.2×10^{-4} g morphine

24. a) 75.0% b) 40.0 %

25. 4.19 g K

26. 6.46×10^{22} Cl¹⁻ ions

27. 381 g S

28. 2.54×10^{22} atoms of S

29. 1.02×10^{23} atoms of C

30. 122 kg NH₃

31. 286 kg NH₄NO₃

32. 1.18×10^{23} atoms of O

33. 2.4×10^{24} atoms of C

34. 48 g C

c) 79.1 d) 118.1

g) 194.2 h) 560.9

b) 0.0057 mol morphine

d) 3.75 kg CoI₂

c) 91.3 %

Appendix B

Gases

B.1 GAS MOLECULES ACTING COLLECTIVELY

According to the Kinetic Molecular Theory (CAMS Section 7.2), gases are in constant random motion and the average kinetic energy is proportional to the absolute temperature. The kinetic energy of a molecule is $1/2 mv^2$, so the average speed of the molecules also depends on the absolute temperature. The average O₂ molecule moves at about 1,000 mph on a nice day.

However, it is the collective action of large numbers of molecules that we sense or measure as gases not the individual molecules. When you fan your face, you feel some wind, which is the effect of molecules in the air hitting your face. You cannot sense the individual molecules hitting your skin, for they are much too small, but you can feel their collective action.

The fact that a balloon expands when it is filled with a gas also shows how gas molecules act collectively. The molecules in the balloon are moving around with an average kinetic energy dictated by the temperature. When a molecule strikes the inside wall of the balloon, it exerts a force on the balloon and pushes it outward. The collective forces of all of the molecules inside the balloon pushing outward cause it to stay inflated. At the same time, the gas molecules in the outside air are striking the outer surface of the balloon exerting a force pushing inward. The size of the balloon adjusts until the force from the “strikes” on the outside balances the force from the “strikes” on the inside.

The collective force of all of the molecules pushing on the inside wall of the balloon results in pressure. The collective force per unit area or pressure of the gas depends on the number of collisions with the walls per second and the force of each collision. The common units are pounds per square inch, atmosphere (atm), the millimeter of mercury (mm Hg or torr) and the pascal, the SI unit of pressure (N/m²).

B.2 RELATIONSHIP OF PRESSURE TO OTHER GAS PROPERTIES

Let's analyze what happens to the pressure of a gas as the temperature, the number of molecules and volume of the gas change. Imagine a cylinder with a movable piston. The gas molecules in the piston have kinetic energy (are moving) and are hitting the walls of the cylinder, the piston and each other.

If the temperature of the gas is increased, the molecules will move faster and will strike the piston more frequently and with more force. Consequently the pressure increases. If more molecules are added to the cylinder (moles of gas increase), the frequency of collisions and therefore the pressure increases. Finally, if we push the piston down and compress the gas to a smaller volume, the gas molecules have less distance to travel before they hit the piston, and they collide with the piston more frequently. Thus, a decrease in volume will result in an increase in pressure.

The relationships among the pressure, volume, number of moles, and temperature of a gas are summed up quantitatively in the *ideal gas law*:

$$PV = nRT$$

P is the pressure in atmospheres (atm), V the volume in liters (L), n the number of moles, T the absolute temperature in kelvins, and R is a constant called the ideal gas constant, which is 0.0821 L·atm·K⁻¹·mol⁻¹. However, when using SI units, P is expressed in pascals, V in m³, and R = 8.314 J·mol⁻¹·K⁻¹.

B.3 USING THE IDEAL GAS LAW

The ideal gas law contains four experimental quantities: pressure, volume, temperature, and number of moles. If we know three of the quantities, we can solve for the fourth. The first step is always to ensure that the units on the known quantities are consistent with our value of R. The following examples show how this can be done.

Example 1

What is the volume of 1.00 mole of gas at 1.00 atm and 0 °C?

Solution:

n is in mol and P in atm, but T is in °C, not K. To convert from °C to K, we add 273: 0 °C + 273 = 273 K = T. Next, rearrange the ideal gas law to solve for the unknown, which in this case is the volume.

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})}{1.00 \text{ atm}} = 22.4 \text{ L}$$

Comment:

The conditions 0 °C and 1.00 atm are often referred to as the Standard Temperature and Pressure (STP) for a gas. The volume at STP is 22.4 L, which is an experimental, not theoretical, number that students often remember from high school chemistry.

Example 2

An experiment yields 5.67 mL of CO₂(g) at 26 °C and 782 mm Hg.

How many grams of CO₂ is this?

Solution:

We are given V, T, and P, but none have the correct units for our value of R, so we convert each into the proper units.

$$V = 5.67 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.00567 \text{ L} \quad T = 26 \text{ °C} + 273 = 299 \text{ K}$$

$$P = 782 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}} = 1.03 \text{ atm}$$

Next, rearrange the ideal gas law to solve for n.

$$n = \frac{PV}{RT} = \frac{(1.03 \text{ atm})(0.00567 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(299 \text{ K})} = 2.38 \times 10^{-4} \text{ mol CO}_2$$

To find grams, apply the molar mass ($M_m = 44.01 \text{ g/mol}$) as a conversion factor as done in Appendix A,

$$2.38 \times 10^{-4} \text{ mol CO}_2 \times \frac{44.01 \text{ g CO}_2}{\text{mol CO}_2} = 0.0105 \text{ g CO}_2$$

Comment:

Notice that five and two-thirds mL of a gas seems like a very small amount in terms of mass! That is because we are used to weighing out solids and liquids, which are much denser than gases.

B.4 EXERCISES

1. What volume does 0.50 moles of CO₂ occupy at 725 mm Hg and 25 °C?
2. How many moles of He occupy a 2.50-L flask whose pressure is 945 mm Hg at 75 °C?
3. What is the pressure exerted by 28.8 g of N₂ contained in a 4.25 L-flask at 0 °C?
4. What volume does 5.8 moles of O₂ occupy at 285 mm Hg and -78 °C?
5. What is the temperature of 5.0 moles of N₂ contained in a 20.0 L-tank at a pressure of 7.5 atm?
6. What volume does 6.32 g of NH₃ occupy at 745 mm Hg and 25 °C?
7. How many moles of CH₄ occupy a 10.0-L tank whose pressure is 3.5 atm at 30 °C?
8. What volume does 0.45 g of Ar occupy at 1.25 atm and 27 °C?
9. What is the pressure exerted by 3.5 moles of H₂ contained in a 2.0-L tank at 27 °C?
10. What volume does 0.75 moles of N₂ occupy at 760 mm Hg and 0 °C?
11. What is the temperature of 7.65 g of He contained in a 6.25 L flask at a pressure of 1.75 atm?
12. How many moles of HCl gas occupy a 4.5 L tank whose pressure is 1875 mm Hg at 27 °C?
13. For this question, note that $M_m = \text{g/mol}$ and density, d = mass/volume.
 - a) What is the density of helium in g/L at 1.00 atm and 27 °C?
 - b) What is the density of nitrogen in g/L at 1.00 atm and 27 °C?

ANSWERS:

- | | | |
|------------------------|------------|----------------------|
| 1. 13 L | 6. 9.26 L | 11. 69.7 K = -203 °C |
| 2. 0.109 mol | 7. 1.4 mol | 12. 0.45 mol |
| 3. 5.42 atm | 8. 0.22 L | 13. a) 0.163 g/L |
| 4. 2.5×10^2 L | 9. 43 atm | 13. b) 1.14 g/L |
| 5. 365 K = 92 °C | 10. 17 L | |

Appendix C

Molarity

C.1 MOLARITY AND THE MOLE

The molar mass is the mass of a mole of a pure substance while the *molarity*, *M*, is the number of moles of a pure substance contained in a liter of a *solution*.

$$\text{molarity} = \frac{\text{moles}}{\text{liter}} = \frac{n}{V}$$

One liter of a solution that contains 0.1 moles of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is 0.1 M, or the solution is 0.1 molar in sugar. It can also be represented as: $[\text{C}_{12}\text{H}_{22}\text{O}_{11}] = 0.1 \text{ M}$, which is read as “the molar concentration of sugar is 0.1 molar.”

C.2 MOLARITY AS A CONVERSION FACTOR

Molarity is used to convert between moles of substance and liters of solution.

Example 1

How many moles of NaCl are in 325 mL of 0.25 M NaCl solution?

Solution:

We first convert mL to L, and then apply molarity as a conversion factor.

$$325 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.25 \text{ moles NaCl}}{1 \text{ L}} = 0.081 \text{ mol NaCl}$$

Example 2

How many mL of 5.0 M HCl contains 0.15 moles of HCl?

Solution:

Our known quantities are moles of HCl and molarity. We start with moles and apply molarity as a conversion factor. The final step is to convert liters to milliliters.

$$0.15 \text{ mol HCl} \times \frac{1 \text{ L}}{5.0 \text{ mol HCl}} \times \frac{10^3 \text{ mL}}{1 \text{ L}} = 30 \text{ mL}$$

Comment:

Note that our definition of molarity is turned upside down, and we were careful to write the units L and moles HCl in the numerator and denominator. Do not use M as the units of the conversion factor.

C.3 CONCENTRATIONS OF IONS

When ionic compounds dissolve, individual solvated ions are formed. (Recall that there are no molecules in ionic compounds.) When we refer to a 0.1 M NaCl solution, we mean that the solution has 0.1 moles of NaCl units in every liter. We can also determine the concentrations of the individual ions from the chemical formula. As discussed in Appendix A, the chemical formula relates moles of compound to moles of each element in the compound. In one mole of Na_2SO_4 there are two moles of Na^{1+} ions and one mole of SO_4^{2-} ions.

Example 3

a) What is the concentration of Na^{1+} ions in 0.25 M NaCl?

b) What is the total concentration of all ions in the above solution?

Solution:

Part a), knowing the molarity of the compound and the formula, we can easily see that for every mole of NaCl, there is one mole of Na^{1+} .

$$\frac{0.25 \text{ mol NaCl}}{1 \text{ L}} \times \frac{1 \text{ mol Na}^{1+}}{1 \text{ mol NaCl}} = \frac{0.25 \text{ mol Na}^{1+}}{1 \text{ L}} = 0.25 \text{ M Na}^{1+}$$

Part b), for every mole of NaCl, there is one mole of Na^{1+} ions and one mole of Cl^{1-} ions, which adds up to two moles total of ions. Again, start with the concentration of the compound and find the concentration of ions.

$$\frac{0.25 \text{ mol NaCl}}{1 \text{ L}} \times \frac{2 \text{ mol ions}}{1 \text{ mol NaCl}} = \frac{0.50 \text{ mol ions}}{1 \text{ L}} = 0.50 \text{ M ions}$$

Comment:

In each step, we have used the moles of ions per mole of compound as a conversion factor much like we did in Examples 11-13 in Appendix A. Notice that this conversion gets us directly to the molarity of the ions (moles of ions per liter).

Example 4

- What is the concentration of chloride ions in a 0.1 M CaCl2?
- What is the total concentration of ions in a 0.1 M solution of CaCl2?

Solution:

As in Example 3, we start with the solution concentration and apply a conversion factor that converts moles of compound to moles of individual ions. In CaCl2, the chemical formula tells us that there are two moles of Cl^- in every mole of compound, and three moles of total ions (1 mole Ca^{2+}, 2 moles Cl^-) in every mole of compound.

$$\frac{0.1 \text{ mol } \text{CaCl}_2}{1 \text{ L}} \times \frac{2 \text{ mol } \text{Cl}^-}{1 \text{ mol } \text{CaCl}_2} = \frac{0.2 \text{ mol } \text{Cl}^-}{1 \text{ L}} = 0.2 \text{ M Cl}^-$$

$$\frac{0.1 \text{ mol } \text{CaCl}_2}{1 \text{ L}} \times \frac{3 \text{ mol ions}}{1 \text{ mol } \text{CaCl}_2} = \frac{0.3 \text{ mol ions}}{1 \text{ L}} = 0.3 \text{ M ions}$$

Comment:

We have taken some care to write down the units in detail for each conversion, but once you understand chemical formulas and the fact that ionic compounds dissolve to form individual ions, you will be able to do these calculations in your head!

C.4 MAKING SOLUTIONS

One of the most common tasks in the chemistry laboratory is making solutions of desired concentrations. In this section, we will explore how to make solutions starting with a solid solute.

Example 5

How many grams of Na2CO3 ($M_m = 105.99 \text{ g/mol}$) are required to make 0.500 L of a 0.10 M Na2CO3 solution?

Solution:

We have a target volume and molarity for our solution, and so we can calculate the necessary moles of Na2CO3. We can then use the molar mass to calculate the necessary grams of Na2CO3.

$$0.500 \text{ L} \times \frac{0.10 \text{ mol}}{1 \text{ L}} \times \frac{106 \text{ g}}{1 \text{ mol}} = 5.3 \text{ g}$$

Example 6

What is the molar concentration of a 2.5 L of solution that contains 254 g of Na2CO3?

Solution:

In this problem, we have a known mass of solid and a molar mass, enough information to calculate moles of Na2CO3. We can then use the relationship between moles and volume to calculate molarity.

$$254 \text{ g} \times \frac{1 \text{ mol}}{106 \text{ g}} = 2.40 \text{ mol}$$

$$\text{concentration} = \frac{2.40 \text{ mol}}{2.5 \text{ L}} = 0.96 \text{ M}$$

Comment:

Note that Examples 5 and 6 start from opposite ends of the same type of calculation. In each case, we have enough information to calculate moles of Na2CO3. In Example 5, we had a target volume and molarity; in Example 6, we had a mass and a molar mass. Determining the amount of solute that is needed to make a desired solution or the concentration of a particular solution by knowing how it was made are two types of calculations that are performed routinely in the chemistry laboratory.

C.5 DILUTION OF SOLUTIONS

In the previous section, solution concentrations were related to the mass of the solute. That type of calculation is appropriate when the solutes come from a chemical supply house in solid form. Some compounds are supplied as concentrated solutions. HCl is a good example. Most HCl in the laboratory is

purchased as ‘concentrated hydrochloric acid’, which is often called a “stock solution”. The dilution of stock solutions to give new solutions of desired concentrations is another very common laboratory procedure. The quantitative aspects will be detailed here.

When calculating molarity and volume of diluted solutions, we can take a shortcut if we are simply diluting with pure solvent. (Be careful, this shortcut does not work for experiments where you dilute with another solution, see Example 9, or for reaction stoichiometry, see Appendix D.) The shortcut is based on the idea that in diluting a concentrated solution with pure solvent, you are not changing the number of moles of solute. The molarity changes of course, because the volume changes. Since the number of moles of solute in the concentrated stock solution (n_c) equals the number of moles of solute in the diluted solution (n_d), we can write that $n_c = n_d$.

Rearranging the relationship $M = n/V$, we find that $n = MV$, so:

$$M_c V_c = M_d V_d$$

The only restriction on the units of the volumes is that they must be the same.

Example 7

What is the concentration of the solution prepared by diluting 25 mL of 12 M HCl to 1.0 L with pure water?

Solution:

The volume of the concentrated solution (before dilution) is 25 mL, and its concentration is 12.0 M solution. The volume of the diluted solution is 1.0 L, but its concentration is unknown. Remember that the volumes must have the same units. Using our shortcut, we write:

$$(12 \text{ M}) (25 \text{ mL}) = M_d (1000 \text{ mL})$$

$$M_d = 0.30 \text{ M}$$

Comment:

Notice that, upon rearranging the equation to solve for M_d , the mL units cancel out. Whether we use 25 and 1000 mL or 0.025 and 1.0 L for the two volumes, the results are the same. Also, we write the final result as 0.30 M. We could have written it out the long way, 0.30 moles/liter.

Example 8

An experiment requires 250. mL of 0.25 M KCl. How many mL of a 1.5 M stock solution of KCl must be used to prepare this solution?

Solution:

We are given the volume and molarity of a dilute solution and are asked for the volume of a stock (concentrated) solution of known molarity.

$$(1.5 \text{ M}) V_c = (0.25 \text{ M}) (250. \text{ mL}) \quad \text{or} \quad V_c = 42 \text{ mL}$$

Comment:

We need to dilute 42 mL of the concentrated solution to 250. mL to give the desired solution.

Example 9

15 mL of a 12 M solution of HCl was diluted with 100. mL of a 0.50 M solution of HCl. What is the concentration of the resulting solution? Assume that the volumes are additive.

Solution:

Note here that we are not diluting a stock solution with pure solvent as was done in Examples 7 and 8. We will not be able to use our shortcut because both the 12.0 M and the 0.50 M solutions contribute some moles of HCl to the final solution. Instead, we add up the total number of moles of HCl and divide by the total volume.

The first solution contributes:

$$15 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{12.0 \text{ mol HCl}}{1 \text{ L}} = 0.18 \text{ mol HCl}$$

The second solution contributes:

$$100 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.50 \text{ mol HCl}}{1 \text{ L}} = 0.050 \text{ mol HCl}$$

The total number of moles of HCl in the final solution is:

$$0.18 + 0.050 = 0.23 \text{ moles}$$

The total volume is: $15 \text{ mL} + 100. \text{ mL} = 115 \text{ mL} = 0.115 \text{ L}$

The concentration of the final solution is:

$$\frac{0.23 \text{ moles}}{0.115 \text{ L}} = 2.0 \text{ M}$$

Comment:

We found the total number of moles contributed by both initial solutions by first finding the number of moles of HCl in each solution separately and adding them together. Because we are not using the shortcut, volumes had to be in liters, and the appropriate conversions were applied. This problem also points out that a small volume of a more concentrated solution (the first one) often contains more of the solute than a larger volume of a less concentrated solution.

C.6 EXERCISES

1. What is the concentration of NaCl when 25.0 g of NaCl is dissolved in water to make 450. mL of solution?
2. How many mL of a 5.0 M solution of HCl contains 0.10 moles of HCl?
3. How many moles of K₂SO₄ are contained 100. mL of a 1.35 M solution?
4. What is the concentration of K¹⁺ ions in 500. mL of a 0.125 M solution of K₂SO₄?
5. How many mL of a 0.10 M solution of NaCl contains 6.2×10^{-3} moles of NaCl?
6. How many grams of CaCl₂ are required to make 10.0 mL of 1.00 M CaCl₂ solution?
7. How many moles of Cl¹⁻ ions are contained in 250. mL of a 0.552 M solution of MgCl₂?
8. How many mL of a 0.80 M solution of Na₂CO₃ contains 0.20 moles of Na¹⁺ ions?
9. How many moles of Li₂CO₃ are contained in 25.0 mL of a 1.15 M solution?
10. An experiment calls for 1.00 L of a 0.150 M KCl solution. How many mL of a 4.00 M stock solution of KCl must be used to prepare this solution?
11. How many moles of Cl¹⁻ ions are contained in 18.5 mL of a 1.28 M solution of NaCl?
12. What is the concentration of K¹⁺ ions in 25.0 mL of a 1.00 M solution of KCl?
13. What is the concentration of NaCl when 5.75 g of NaCl is dissolved in water to make 1.86 L of solution?
14. How many grams of LiCl are required to make 125 mL of 0.100 M LiCl solution?
15. How many mL of a 1.25 M solution of KCl contains 2.35 g of KCl?
16. How many grams of LiCl are required to make 625 mL of 2.87 M LiCl solution?
17. 10.0 mL of a 3.25 M solution of HCl is diluted with 200 mL of a 0.100 M solution of HCl. What is the concentration of the resulting solution? Assume that the volumes are additive.
18. What is the concentration of the solution prepared by diluting 25 mL of a 0.50 M solution of HCl to 125 mL with pure water?
19. What is the concentration of the solution prepared by diluting 5.0 mL of a 6.25 M solution of HCl to 65 mL with pure water?
20. How many moles of Li¹⁺ ions are contained in 0.500 L of a 2.25 M solution of Li₂CO₃?
21. An experiment calls for 125 mL of a 0.625 M HCl solution. How many mL of a 12.0 M stock solution of HCl must be used to prepare this solution?
22. 12.5 mL of a 12.0 M stock solution of HCl is diluted with 85.0 mL of a 0.200 M solution of HCl. What is the concentration of the resulting solution? Assume that the volumes are additive.

ANSWERS:

- | | | | | |
|---------------------|----------------------|-----------------------|---------------------|--------------------|
| 1. 0.950 M | 6. 1.11 g | 11. 0.0237 mol | 16. 76.1 g | 21. 6.51 mL |
| 2. 20 mL | 7. 0.276 mol | 12. 1.00 M | 17. 0.250 M | 22. 1.71 M |
| 3. 0.135 mol | 8. 125 mL | 13. 0.0528 M | 18. 0.10 M | |
| 4. 0.250 M | 9. 0.0288 mol | 14. 0.530 g | 19. 0.48 M | |
| 5. 62 mL | 10. 37.5 mL | 15. 25.2 mL | 20. 2.25 mol | |

Appendix D

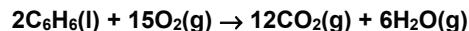
Reaction Stoichiometry

D.1 INTRODUCTION

In Appendix A, the stoichiometry of elements and compounds was presented. There, the relationships among grams, moles and number of atoms and molecules were reviewed. A similar relationship exists for chemical reactions, and we will now extend this concept of stoichiometry to reactions. In reaction stoichiometry, we are interested in the quantitative relationships between the amounts of reactants and products in a reaction. We will find, as we did in Appendix A, that the mole is the central character in these calculations.

D.2 QUANTITATIVE RELATIONSHIPS IN REACTIONS

Chemical reactions surround us. Chemists use shorthand notation to describe them in a sentence called a chemical equation. The chemical equation that describes the combustion of benzene is



This equation implies that for every two benzene molecules that react, 15 dioxygen molecules must also react and 12 carbon dioxide molecules and six water molecules will be produced. In other words, it tells us about the “stoichiometry”, or the amounts of reactants and products involved. The coefficients, or numbers in front of each chemical formula, tell us the relative number of molecules involved in the reaction. They also tell us the relative number of *moles* involved in the reaction. Two moles of benzene will react with 15 moles of dioxygen to form twelve moles of carbon dioxide and six moles of water. It is important to note that the equation does not give us any direct information about the number of grams of each reactant or product, only the moles. If we want to know about a measurable quantity like grams, we will have to do some conversions.

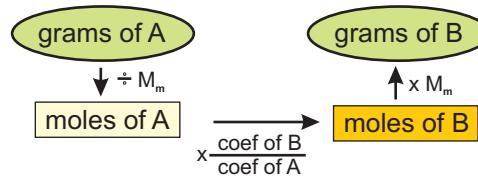
The first requirement for any stoichiometric calculation is a balanced equation. Once we have a balanced equation, the calculations will be performed by following three steps.

1. Convert the given quantitative information to moles. Experiments are always set up (thus chemistry problems are always written) such that number of moles of at least one reactant or product can be determined.
2. Use the balanced equation to convert from the moles of given substance to the moles of desired substance. Remember, we're given quantitative information on one reactant or product, we desire quantitative information on another. This is the heart of all stoichiometry problems.
3. Convert from moles of the desired compound to the appropriate quantity.

These three steps are purposely vague. In the three previous appendices, we have discussed the conversion of moles to grams for a solid, moles to pressure, volume and temperature for a gas, and moles to volume and molarity for a solution. As you might guess, there are several variations on this three-step theme. The following examples will show some of the variety.

D.3 REACTION STOICHIOMETRY INVOLVING GRAMS

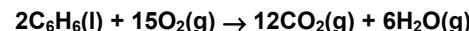
For calculations involving grams of reactants and products, our three-step scheme looks like this:



In the preceding diagram, A and B are products and/or reactants. The gram to mole conversion is achieved through application of the molar mass, the mole to mole conversion comes from the coefficients in the balanced equation.

Example 1

Consider the combustion of benzene:



What is the maximum mass of CO₂ (M_m = 44.0 g/mol) that can be produced from the combustion of 10.0 g of C₆H₆ (M_m = 78.1 g/mol)?

Solution:

The given information is grams of benzene. The desired information is grams of CO₂. The road map above tells us we must convert grams of benzene to moles, use the mole ratio from the equation to give moles of carbon dioxide, and then convert back to grams of carbon dioxide.

$$10.0 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.1 \text{ g C}_6\text{H}_6} = 0.128 \text{ mol C}_6\text{H}_6$$

$$0.128 \text{ mol C}_6\text{H}_6 \times \frac{12 \text{ mol CO}_2}{2 \text{ mol C}_6\text{H}_6} = 0.768 \text{ mol CO}_2$$

$$0.768 \text{ mol CO}_2 \times \frac{44.0 \text{ g CO}_2}{\text{mol CO}_2} = 33.8 \text{ g CO}_2$$

Comment:

As we have seen several times in the previous appendices, each individual step is not difficult. Putting the steps together in a logical manner is the challenge. In this example, we have done each of the three steps separately. However, we could have strung together the conversion factors to save ourselves some writing. We will do that in the next example.

Example 2

How many grams of O₂ (M_m = 32.0 g/mol) are required to completely react with 10.0 g of C₆H₆?

Solution:

The given information is the mass of benzene, the desired information is the mass of dioxygen. Start with the given information and apply conversion factors following the road map.

$$10.0 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.1 \text{ g C}_6\text{H}_6} \times \frac{15 \text{ mol O}_2}{2 \text{ mol C}_6\text{H}_6} \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 30.7 \text{ g O}_2$$

Comment:

Stoichiometry problems do not always relate reactants to products. Here is a situation where both the given and desired information deals with reactants. In this example, we have done our three step calculation by stringing together the three conversion factors appropriate to the three steps. Note that the order of operation can be determined by using the units because the units of the denominator of each conversion factor must be the same as the units of the previous numerator. Using the units to help is called the factor-label method.

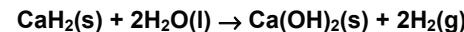
D.4 LIMITING REACTANTS

We know from experience that the amount of product that is formed depends on the amount of reactant that is consumed. You can drive a car only as long as it has gasoline. The gasoline is the limiting reactant because it dictates how much product (miles) can be achieved. The amount of gasoline determines not only how far you can go, but it also determines how much CO₂ and H₂O (the reaction products of the combustion of gasoline) can be made.

In any chemical reaction, the amount of products that are made is limited by the amount of reactants. When any one reactant runs out, the reaction stops. The reactant that runs out is called the *limiting reactant* or *limiting reagent*. Any reactants that do not run out are said to be in excess. In most chemical reactions, one or more of the reactants is in excess. In the gasoline combustion reaction, there is certainly more oxygen available than there is gasoline in the gas tank, and so the oxygen is in excess.

In calculating the amount of product formed in a reaction, we always have to identify the limiting reactant. In some cases it is obvious. In Example 1 above, we read that 10.0 g of C₆H₆ reacts with excess O₂. Clearly, C₆H₆ is the limiting reactant, and O₂ is the excess reactant. But consider the following example.

Calcium hydride reacts with water to form calcium hydroxide and hydrogen gas, *via* the following reaction



If 10.0 g of CaH₂ reacts with 9.00 g of H₂O, what mass of Ca(OH)₂ can be formed? We start by determining the limiting reactant, but we cannot tell which

reactant will limit the amount of product just by comparing the grams of each reactant, we must determine how much $\text{Ca}(\text{OH})_2$ we can make from each reactant. Based on the amount of CaH_2 we start with, we can make:

$$10.0 \text{ g } \text{CaH}_2 \times \frac{1 \text{ mol } \text{CaH}_2}{42.10 \text{ g } \text{CaH}_2} \times \frac{1 \text{ mol } \text{Ca}(\text{OH})_2}{1 \text{ mol } \text{CaH}_2} \times \frac{74.10 \text{ g } \text{Ca}(\text{OH})_2}{1 \text{ mol } \text{Ca}(\text{OH})_2} = 17.6 \text{ g } \text{Ca}(\text{OH})_2$$

Based on the amount of H_2O available, we can make:

$$9.0 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.0 \text{ g } \text{H}_2\text{O}} \times \frac{1 \text{ mol } \text{Ca}(\text{OH})_2}{2 \text{ mol } \text{H}_2\text{O}} \times \frac{74.10 \text{ g } \text{Ca}(\text{OH})_2}{1 \text{ mol } \text{Ca}(\text{OH})_2} = 18.5 \text{ g } \text{Ca}(\text{OH})_2$$

Even though we have enough water to make 18.5 g of $\text{Ca}(\text{OH})_2$, there is only enough calcium hydride to make 17.6 g. In this case, CaH_2 is the limiting reactant, H_2O is in excess, and 17.6 g of $\text{Ca}(\text{OH})_2$ would be produced.

Let's determine how much of the excess reactant remains. CaH_2 is the limiting reactant and all amounts are calculated from it, and so we must now determine how much water reacts with the CaH_2 .

$$10.0 \text{ g } \text{CaH}_2 \times \frac{1 \text{ mol } \text{CaH}_2}{42.10 \text{ g } \text{CaH}_2} \times \frac{2 \text{ mol } \text{H}_2\text{O}}{1 \text{ mol } \text{CaH}_2} \times \frac{18.0 \text{ g } \text{H}_2\text{O}}{1 \text{ mol } \text{H}_2\text{O}} = 8.56 \text{ g } \text{H}_2\text{O}$$

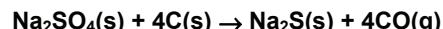
The above is how much water reacts, we now determine how much remains by subtracting the amount that reacts from the initial amount.

$$9.00 - 8.56 = 0.44 \text{ g } \text{H}_2\text{O} \text{ remains}$$

Let's summarize limiting reactants with another example.

Example 3

25.0 g of Na_2SO_4 is added to 7.00 g of carbon and allowed to react according to the following equation:



- What is the limiting reactant?
- How many grams of Na_2S can be formed?
- How many grams of the excess reactant will be leftover?

Solution:

Perform the three-step calculation twice, starting from the information given for each reactant.

$$25.0 \text{ g } \text{Na}_2\text{SO}_4 \times \frac{1 \text{ mol } \text{Na}_2\text{SO}_4}{142.05 \text{ g } \text{Na}_2\text{SO}_4} \times \frac{1 \text{ mol } \text{Na}_2\text{S}}{1 \text{ mol } \text{Na}_2\text{SO}_4} \times \frac{78.05 \text{ g } \text{Na}_2\text{S}}{1 \text{ mol } \text{Na}_2\text{S}} = 13.7 \text{ g } \text{Na}_2\text{S}$$

$$7.00 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{1 \text{ mol } \text{Na}_2\text{S}}{4 \text{ mol C}} \times \frac{78.05 \text{ g } \text{Na}_2\text{S}}{1 \text{ mol } \text{Na}_2\text{S}} = 11.4 \text{ g } \text{Na}_2\text{S}$$

Comparing the two calculations leads us to conclude that C is the limiting reactant and Na_2SO_4 is in excess. 11.4 g of Na_2S can be produced. Next, find the amount of excess reactant that reacts.

$$7.00 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{1 \text{ mol } \text{Na}_2\text{SO}_4}{4 \text{ mol C}} \times \frac{142.05 \text{ g } \text{Na}_2\text{SO}_4}{1 \text{ mol } \text{Na}_2\text{SO}_4} = 20.8 \text{ g } \text{Na}_2\text{SO}_4$$

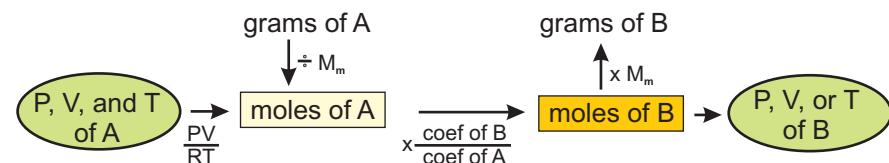
The amount remaining is given by the difference

$$25.0 \text{ g initially} - 20.8 \text{ g consumed} = 4.2 \text{ g of } \text{Na}_2\text{SO}_4 \text{ remain}$$

D.5 REACTIONS INVOLVING GASES

Examples 1 and 2 dealt with the combustion of benzene. In each, a known amount of benzene was burned, and we calculated the mass of CO_2 or O_2 produced. However, the measurable quantities of gases are pressure, volume and temperature, not mass. In this section, we use the treatment presented in Appendix B to introduce these quantities into our stoichiometric calculations.

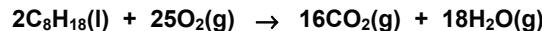
If there is known quantitative information about the pressure, volume and temperature of a gas, we can calculate the moles of that gas, using $PV = nRT$. We can use this relationship in the first or last step of our calculation. We summarize this through the following road map or flowchart:



Notice that this flowchart is identical to the one that appeared earlier in this appendix, except that the use of P,V, and T information for a gas has been added as an entry into the scheme at the left and as a result from the scheme at the right. The following examples show how the ideal gas law can be used in reaction stoichiometry calculations.

Example 4

Octane combusts via the following chemical reaction:



How many liters of CO_2 , collected at a pressure of 1.00 atm and a temperature of 25 °C, can be produced by the combustion of 35.0 kg of octane (the amount held by a typical car gasoline tank)?

Solution:

We first must recognize this as a reaction stoichiometry problem. We know the mass and therefore the number of moles of octane. We desire the volume of the carbon dioxide, so $PV = nRT$ will be our third step. It is somewhat complicated to use the ideal gas law as a conversion factor, so we will string together the first two steps, and then do the third step separately, solving for volume.

$$35 \text{ kg C}_8\text{H}_{18} \times \frac{10^3 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114 \text{ g C}_8\text{H}_{18}} \times \frac{16 \text{ mol CO}_2}{2 \text{ mol C}_8\text{H}_{18}} = 2.45 \times 10^3 \text{ mol CO}_2$$

Next apply the ideal gas law, $PV = nRT$.

$$V = \frac{nRT}{P} = \frac{(2.45 \times 10^3 \text{ mol})(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1.00 \text{ atm}} = 5.99 \times 10^4 \text{ L}$$

Comment:

Burning a tank of gasoline generates enough carbon dioxide at 1.00 atm and 25 °C to fill a 16 ft × 16 ft room with an 8 ft ceiling.

Example 5

The following reaction is used to quickly inflate some car airbags:



How many grams of NaN_3 must be used if you wish to fill a 20.0 L airbag with dinitrogen to a pressure of 1.25 atm at 25 °C?

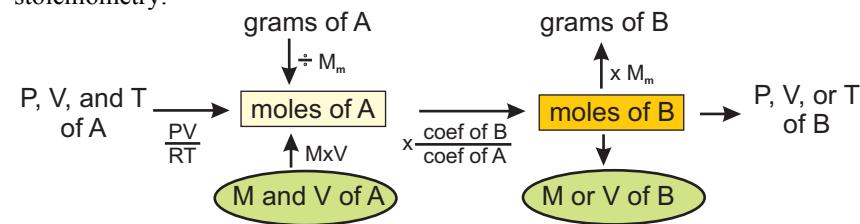
Solution:

In this problem the known information involves a gaseous product (a pressure, volume and temperature are all given) and information on the reactant is desired. This time, the first of the three steps involves the ideal gas law, with the second and third steps being simple application of conversion factors.

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{(1.25 \text{ atm})(20.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 1.02 \text{ mol N}_2 \\ 1.02 \text{ mol N}_2 &\times \frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \times \frac{65.0 \text{ g NaN}_3}{1 \text{ mol NaN}_3} = 44.2 \text{ g NaN}_3 \end{aligned}$$

D.6 REACTIONS INVOLVING SOLUTIONS

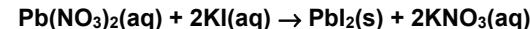
In the previous sections, we have discussed the quantitative relationships between reactants and products in a reaction. In all cases, the heart of the problem was the mole ratio, and the only difference in the problems lies in how we get to the mole ratio and what we do after we have applied it. We will now consider our last conversion to and from moles. If a reactant or product is dissolved in solution, the moles of that compound are related to the molarity and the solution volume, $M = n/V$. (See Appendix C if you do not remember this relationship.) We can add this route to our road map of reaction stoichiometry.



The following examples show how solution data can be manipulated along with masses and data on gases to give information on reaction stoichiometry.

Example 6

The Pb^{2+} ions from water soluble $\text{Pb}(\text{NO}_3)_2$ can be precipitated by the addition of KI , forming insoluble PbI_2 :



If 25.0 mL of 0.375 M $\text{Pb}(\text{NO}_3)_2$ is reacted with excess KI , how many grams of PbI_2 will be produced?

Solution:

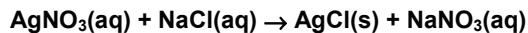
The moles of $\text{Pb}(\text{NO}_3)_2$ can be found since the volume and molarity of the solution are known. We convert the volume to liters then apply

molarity to determine moles. The final two steps of the calculation are the mole to mole conversion from the balanced equation, and the conversion from moles of PbI_2 to grams, using the molar mass of 461.0 g/mol.

$$25.0 \text{ mL} \times \frac{0.375 \text{ mol } \text{Pb}(\text{NO}_3)_2}{1000 \text{ mL}} \times \frac{1 \text{ mol } \text{PbI}_2}{1 \text{ mol } \text{Pb}(\text{NO}_3)_2} \times \frac{461.0 \text{ g } \text{PbI}_2}{1 \text{ mol } \text{PbI}_2} = 4.32 \text{ g } \text{PbI}_2$$

Example 7

The silver ions in AgNO_3 solution can be precipitated by the addition of aqueous NaCl :



When 35.0 mL of a AgNO_3 solution of unknown concentration is reacted with excess NaCl solution, 8.53 g of AgCl is formed. What is the concentration of the AgNO_3 solution?

Solution:

In this problem, there is some information about the AgNO_3 solution and some information about the solid AgCl . After rereading the problem, it should become clear that the desired quantity is molarity of the AgNO_3 solution. Thus, we need to start at the other end, with the mass of AgCl . You should also recognize that whenever mass data is presented along with either a molar mass or a chemical formula (from which we can get a molar mass), we have an entry into our road map. Here, we will do the first two steps of the calculation in the usual manner, and then use the $M = n/V$ relationship as our third step.

$$8.53 \text{ g } \text{AgCl} \times \frac{1 \text{ mol } \text{AgCl}}{143.35 \text{ g } \text{AgCl}} \times \frac{1 \text{ mol } \text{AgNO}_3}{1 \text{ mol } \text{AgCl}} = 0.0595 \text{ mol } \text{AgNO}_3$$

$$M = \frac{n}{V} = \frac{0.0595 \text{ mol}}{0.0350 \text{ L}} = 1.70 \text{ mol/L} = 1.70 \text{ M}$$

Comment:

The first two steps are as we have done many times now. The third step, using the molarity relationship, may at first seem a little unusual. Molarity is always the ratio of moles of a substance to the volume in liters. The first two steps tell us that there are 0.0595 moles of AgNO_3 contained in the 35.0 mL of solution. We simply take the ratio of these two numbers, first converting 35.0 mL to 0.0350 L, since molarity is moles per liter. Note that the experiment did not have to be done on a 1 L scale in order to calculate the molarity!

Example 8

Potassium permanganate solutions can react with acidic hydrogen peroxide solutions via the following balanced equation in water:



When 15.0 mL of 0.0200 M KMnO_4 reacts with excess H_2O_2 and HCl , how many liters of O_2 , collected at a total pressure of 1.00 atm and a temperature of 27 °C, will be formed?

Solution:

The volume and molarity data on KMnO_4 allow us to enter into the road map. The desired information is volume of O_2 . We start by converting mL to L, and then proceed through the first two of the three steps in the calculation to find moles of O_2 . We will do the third step, manipulation of $PV = nRT$, separately.

$$15.0 \text{ mL} \times \frac{0.0200 \text{ mol } \text{KMnO}_4}{1000 \text{ mL}} \times \frac{5 \text{ mol } \text{O}_2}{2 \text{ mol } \text{KMnO}_4} = 7.50 \times 10^{-4} \text{ mol } \text{O}_2$$

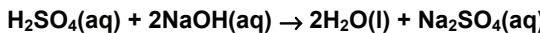
$$V = \frac{nRT}{P} = \frac{(7.50 \times 10^{-4} \text{ mol})(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(300 \text{ K})}{1.00 \text{ atm}} = 0.0185 \text{ L}$$

Comment:

As you can see, there are many possible routes along our road map for solving stoichiometry problems.

Example 9

How many mL of a 0.250 M NaOH solution are required to completely react with 40.0 mL of a 0.150 M H_2SO_4 solution. The overall reaction is:



Solution:

We see that there is enough information to calculate moles of H_2SO_4 . We desire information on NaOH . Start with the volume of 0.0400 L of H_2SO_4 solution and proceed as usual.

$$0.0400 \text{ L} \times \frac{0.150 \text{ mol } \text{H}_2\text{SO}_4}{1 \text{ L}} \times \frac{2 \text{ mol } \text{NaOH}}{1 \text{ mol } \text{H}_2\text{SO}_4} \times \frac{1 \text{ L}}{0.250 \text{ mol } \text{NaOH}} \times \frac{10^3 \text{ L}}{\text{mL}} = 48.0 \text{ mL}$$

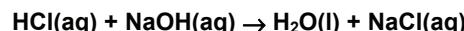
Comment:

The mL to L conversion was done at the beginning and the end of the

problem since the volume information is in mL, but the concentration (molarity) is, of course, in moles per liter. Both molarities were used as conversion factors; 0.150 M converted volume of solution to moles of H₂SO₄, 0.250 M was “turned upside down” to convert moles of NaOH to liters of solution.

Example 10

Aqueous HCl and NaOH react in the following manner:



When 30.0 mL of 0.100 M HCl are mixed with 20.0 mL of 0.125 M NaOH, what is concentration of the excess reagent?

Solution:

This is a limiting reactant problem. At first glance, it would appear quite different than the limiting reactant problems we saw earlier. However, upon careful reading of the experiment, we see that we have quantitative information on both reactants, enough to calculate moles of both. The desired quantity the concentration of the excess reactant. In essence, we are reacting an acid and a base, and need to determine which reactant is limiting, and find how much of the excess reactant is leftover, as was done in Example 3 above. In order to determine the limiting reactant, we calculate how much product can be made from each reactant. It doesn't matter which product we choose. Let's pick water.

$$30 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}} = 0.0030 \text{ mol H}_2\text{O}$$

$$20 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.125 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol NaOH}} = 0.0025 \text{ mol H}_2\text{O}$$

Fewer moles of water can be made from the NaOH, so NaOH is the limiting reactant, HCl is the excess reactant. Notice that it was not necessary to go all the way through and calculate the grams of water. Clearly, if we multiply each result by 18.02 g/mol (the molar mass of H₂O), the conclusion is the same, NaOH is limiting. In order to calculate molarity of HCl, we need the number of moles of HCl which were leftover, and the total solution volume.

Moles of HCl at the start:

$$30 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L}} = 0.0030 \text{ mol HCl}$$

The number of moles of HCl consumed is based on the amount of limiting reactant consumed:

$$20 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.125 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 0.0025 \text{ mol HCl react}$$

Moles of HCl remaining:

$$0.0030 - 0.0025 = 0.0005 \text{ moles of HCl remain}$$

Concentration of HCl at the end

$$\frac{\text{moles of HCl}}{\text{total volume}} = \frac{0.0005 \text{ mol HCl}}{0.050 \text{ L}} = 0.010 \text{ M}$$

Comment:

This problem is actually very similar to the limiting reactant problems we did before. The difference is that, instead of finding the grams of the leftover reactant, we had to find the concentration, which involved a calculation of the number of moles of the leftover reactant.

D.7 EXERCISES

Use the following molar masses to do the following problems:

$$\text{C}_4\text{H}_8 : 56.10 \text{ g/mol} \quad \text{C}_4\text{H}_9\text{OH} : 74.12 \text{ g/mol}$$

$$\text{Fe}_2\text{O}_3 : 159.70 \text{ g/mol} \quad \text{Al}_2\text{O}_3 : 101.96 \text{ g/mol}$$

$$\text{V}_2\text{O}_5 : 181.88 \text{ g/mol} \quad \text{NH}_4\text{VO}_3 : 116.98 \text{ g/mol}$$

$$\text{NH}_3 : 17.03 \text{ g/mol} \quad \text{V}_2\text{O}_3 : 149.88 \text{ g/mol}$$

$$\text{Cu}_2\text{S} : 159.17 \text{ g/mol} \quad \text{CuO} : 79.55 \text{ g/mol}$$

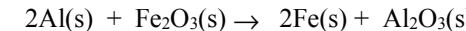
$$\text{Cu}_2\text{O} : 95.55 \text{ g/mol} \quad \text{AgCl} : 143.4 \text{ g/mol}$$

1. In the presence of acids, water can react with alkenes to form alcohols:



If 250 g of C₄H₈ reacts with excess H₂O, how many grams of C₄H₉OH can be produced?

2. Aluminum reacts with iron(III) oxide in the “thermite reaction”:



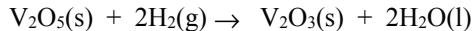
- a) If 10.0 g of Al reacts with excess Fe₂O₃, how many grams of Al₂O₃ can be produced?
- b) If 25.0 g of Al reacts with 10.0 g of Fe₂O₃, how many grams of Al₂O₃ can be produced?
- c) In the experiment in part b, what is the mass of the excess reactant remaining after complete reaction?

3. Vanadium(V) oxide reacts with ammonia and water as follows:



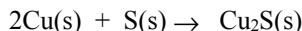
- a) If 50.0 g of V_2O_5 is reacted with excess ammonia and water, how many grams of NH_4VO_3 can be produced?
- b) How many grams of NH_3 are required to completely react with 50.0 g of V_2O_5 ?

4. Vanadium(III) oxide can be made by reduction of vanadium(V) oxide with hydrogen:



- a) How many liters of H_2 , measured at 1.00 atm and 30 °C, are required to completely react with 75.0 g of V_2O_5 ?
- b) If 10.0 g of V_2O_5 reacts with 1.65 L of H_2 , measured at 1.00 atm and 30 °C, how many grams of V_2O_3 can be produced?

5. Copper(I) sulfide is prepared by heating copper and sulfur in the absence of air:



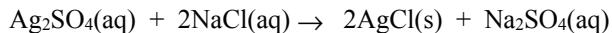
- a) How many grams of Cu_2S can be produced from the reaction of 25.0 g of Cu with excess S?
- b) How many grams of sulfur are required to form 75.0 g of Cu_2S ?
- c) If a mixture of 135 g of Cu and 45 g of S is allowed to react, how many grams of Cu_2S could be produced?
- d) How many grams of the excess reactant remain in the experiment in part c?

6. Copper(I) oxide can be prepared by thermal decomposition of copper(II) oxide:



- a) How many grams of Cu_2O can be produced upon the decomposition of 450 g of CuO ?
- b) How many liters of O_2 , collected at 1.00 atm and 27 °C, can be produced by the decomposition of 450 g of CuO ?

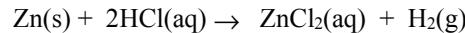
7. The silver ions in aqueous silver sulfate can be precipitated by addition of excess chloride:



- a) How many grams of silver chloride can be formed when 35.0 mL of a 0.100 M Ag_2SO_4 solution is reacted with excess sodium chloride solution?

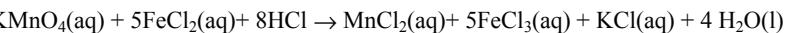
- b) If 22.7 mL of a silver sulfate solution of unknown concentration yields 0.985 g of AgCl upon reaction with excess sodium chloride solution, what is the concentration of the silver sulfate solution?

8. Zn metal reacts with hydrochloric acid to produce hydrogen gas and zinc(II) chloride:



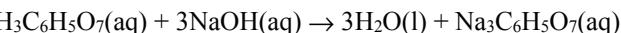
- a) If 15.0 g of Zn are added to excess $\text{HCl}(\text{aq})$, how many liters of $\text{H}_2(\text{g})$, collected at 27 °C and 725 mm Hg, are produced?
- b) If excess Zn is added to 25.0 mL of 0.025 M $\text{HCl}(\text{aq})$, how many liters $\text{H}_2(\text{g})$, collected at 27 °C and 725 mm Hg, can be produced?

9. Potassium permanganate and iron(II) chloride undergo an electron transfer reaction in acid solution:



How many mL of 0.150 M $\text{FeCl}_2(\text{aq})$ are needed to completely react with 13.7 mL of 0.110 M KMnO_4 ?

10. Citric acid reacts with sodium hydroxide in a proton transfer reaction:



- a) How many mL of 0.125 M $\text{NaOH}(\text{aq})$ are required to completely react with 25.0 mL of 0.0695 M citric acid?
- b) If 37.5 mL of 1.25 M $\text{NaOH}(\text{aq})$ is needed to completely react with 22.5 mL of a citric acid solution, what is the concentration of the citric acid solution?

ANSWERS:

1. 330 g
2. a) 18.9 g b) 6.38 g c) 21.6 g
3. a) 64.3 g b) 9.34 g
4. a) 20.5 L b) 4.97 g
5. a) 31.3 g b) 15.1 g c) 169 g
d) 11 g
6. a) 405 g b) 34.8 L
7. a) 1.00 g b) 0.151 M
8. a) 5.92 L b) 8.07 mL
9. 50.2 mL
10. a) 41.7 mL b) 0.694 M

Appendix E

Fundamental Constants

ENERGY

1 joule (J)	= $1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$
1 calorie (cal)	= 4.184 J
1 V	= 96.485 kJ/mol

FORCE

1 newton (N)	= $1 \text{ kg} \cdot \text{m/s}^2$
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LENGTH

1 meter (m)	= 39.37 inches (in)
1 inch	= 2.54 centimeters (cm) - exact
1 Å	= $1 \times 10^{-10} \text{ m}$

MASS

1 kilogram (kg)	= 2.205 pounds (lb)
1 lb	= 453.6 grams (g)
1 amu	= $1.661 \times 10^{-24} \text{ g}$

PRESSURE

1 atm	= 760 mm Hg (torr)
	= $1.01325 \times 10^5 \text{ Pa}$

VOLUME

$$1 \text{ liter (L)} = 1000 \text{ mL} = 1000 \text{ cm}^3$$

PHYSICAL CONSTANTS

Avogadro's number	$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$
Electronic Charge	$e = 1.6022 \times 10^{-19} \text{ C}$
Electron rest mass	$m_e = 9.1094 \times 10^{-31} \text{ kg}$
Faraday constant	$\mathcal{F} = 9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}$
Gas constant	$0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $1.9872 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Neutron rest mass	$m_n = 1.675 \times 10^{-27} \text{ kg}$
Planck's constant	$h = 6.6261 \times 10^{-34} \text{ J} \cdot \text{s}$
Proton rest mass	$m_p = 1.6726 \times 10^{-27} \text{ kg}$
Speed of light (vacuum)	$c = 2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1}$

TEMPERATURE

$$\begin{aligned} 0 \text{ K} &= -273.15 \text{ }^\circ\text{C} (\text{Celsius}) = -459.67 \text{ }^\circ\text{F} (\text{Fahrenheit}) \\ \text{ }^\circ\text{F} &= (\frac{9}{5}) \text{ }^\circ\text{C} + 32 & \text{ }^\circ\text{C} &= (\frac{5}{9})(\text{ }^\circ\text{F} - 32) \\ \text{K} &= \text{ }^\circ\text{C} + 273.15 \end{aligned}$$

SI PREFIXES

10^9	giga (G)	10^6	mega (M)
10^3	kilo (k)	10^{-1}	deci (d)
10^{-2}	centi (c)	10^{-3}	milli (m)
10^{-6}	micro (μ)	10^{-9}	nano (n)
10^{-12}	pico (p)		

Glossary

A

Absolute (or Kelvin) temperature scale is used for the temperature in all calculations involving T. The unit is the kelvin (K). The average kinetic energy of the molecules in a system is directly proportional to its temperature in kelvins.

Absolute zero is 0 K, which is -273.16 °C. It is the temperature at which molecules have no kinetic energy.

Absorbance is a measure of the amount of light absorbed by a substance. The absorbance of a solution depends upon both the concentration and the molar absorptivity of the absorbing substance at the wavelength of the light, and the distance through the solution that the light travels. See Beer's Law.

Absorption of a photon increases the energy of an atom or a molecule by the energy of the photon ($h\nu$). A photon can be absorbed only if its energy matches the energy difference between two energy levels in the atom or molecule.

An **absorption spectrum** presents the absorbance of a substance as a function of the wavelength or frequency of light.

The **acceptor orbital** is the orbital on an oxidizing agent that accepts the transferred electrons in a redox reaction.

The **acid dissociation or ionization constant** is the equilibrium constant for the reaction of an acid with water: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{1+} + \text{A}^{1-}$.

An **acidic salt** is a salt in which the acidity of the cation is greater than the basicity of the anion.

An **acidic solution** is one with $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$. As a result, $\text{pH} < 7.0$ at 25 °C for acidic solutions.

The **activation energy** is the energy of the transition state relative to that of the reactants or products. It is the minimum energy that the reactants must have in order for a reaction to occur.

An **active electrode** is one that is a participant in a reaction. For example, a copper electrode in a $\text{Cu}^{2+} + 2\text{e}^{1-} \rightarrow \text{Cu}$ half-cell is active because copper metal participates in the reaction.

The **activity** is the ratio of the concentration of a substance to its concentration in the standard state. It is unitless. The activities of pure solids and liquids are unity. The activity of a gas equals the partial pressure of the gas in atmospheres divided by 1 atm, while the activity of a solute equals its molar concentration divided by 1 M.

Addition polymers are formed by addition reactions.

An **addition reaction** is a reaction in which two reactants combine to form a single product.

Adhesive forces are forces between different molecules (compare with cohesive force).

An **alcohol** is a compound with the general formula R-OH, where R is a generic group of atoms and OH is the hydroxyl group.

An **alkali metal** is an element that belongs to Group 1A.

An **alkaline earth metal** is an element that belongs to Group 2A.

An **alkane** is a saturated hydrocarbon, *i.e.*, a hydrocarbon that contains no multiple bonds.

An **alkene** is a hydrocarbon that contains carbon-carbon double bonds.

An **alkyl group** is an organic group formed by removing one hydrogen atom from an alkane.

Allotropes are different crystalline forms of the same element that have different properties. Graphite and diamond are allotropes of carbon.

Alpha decay is the emission of an alpha particle. It is common among the heavy isotopes because it is the best way to reduce mass.

An **alpha particle** is a helium nucleus.

An **amide** is an amine attached to a carbonyl.

An **amine** is an ammonia molecule in which one or more of the hydrogen atoms have been replaced with other groups.

An **amino acid** is a compound that contains both amine and carboxylic acid functional groups.

Amorphous solids have ordered arrangements of particles over short distances only. This is referred to as local order.

The **ampere (A)** is the SI unit for electrical current. $1 \text{ A} = 1\text{C/s}$.

An **amphiprotic** substance is able to function as either an acid or a base.

An **analyte** is a substance that is being analyzed.

The **angstrom (Å)** is 10^{-10} m. It is commonly used for bond lengths because most bond lengths are between 1 and 2 Å.

Angular momentum (L) is a property of a rotating object. It is equal to the mass of the object times its velocity times its distance from the center of rotation; *i.e.*, $L = mvr$.

The **angular momentum quantum number (l)** is an integer between 0 and n-1 that defines the shape of an atomic orbital.

An **anion** is a negatively charged ion.

The **anode compartment or electrode** is where oxidation occurs in an electrochemical cell.

Antibonding interactions occur in molecular orbitals when the atomic orbitals on adjacent atoms used to construct the molecular orbital have opposite phases.

An **antibonding MO** is one in which the number of antibonding interactions exceeds the number of bonding interactions.

An **antiferromagnetic** substance is not magnetic because all of its electron spins are paired.

An **Arrhenius acid** is a substance that contains H atoms and produces H^{1+} ions in water.

An **Arrhenius base** is a substance that contains OH and produces OH^{-} ions in water.

The **Arrhenius equation** relates a rate constant to the temperature and activation energy of the reaction: $k = Ae^{-E_a/RT}$ or $\ln k = \ln A - E_a/RT$

An **Arrhenius plot** is a plot of $\ln k$ (rate constant) versus $1/T$. The slope is $-E_a/R$ and the intercept is $\ln A$ (the pre-exponential).

Atoms are the building blocks of matter. Elements consist of only one type of atom.

Atomic mass or atomic weight is the average mass of the atoms of an element relative to that of carbon-12, which is assigned a relative mass of exactly 12.

The **atomic mass unit (amu)** is a unit of mass that is $1/12$ the mass of a single atom of carbon-12.

The **atomic number (Z)** is the number of protons in the nucleus. It identifies the atom.

The **atomization energy (ΔH_{atom})** is the energy required to break all of the bonds in a molecule in the gas phase to produce the atoms.

Autoionization of water is the reaction of water with itself: $2H_2O \rightarrow H_3O^{1+} + OH^{-}$.

Avogadro's law states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Avogadro's number is 6.02×10^{23} . It is the number of items in a mole.

B

The **band gap** is the energy separation between the valence and conduction bands of a metallic or covalent solid.

The **band or belt of stability** is the region of a plot of the number of neutrons versus the number of protons in a nucleus in which the stable nuclei fall.

Band theory is an extension of mo theory to metals. A very large number of atomic orbitals in a metal combine to form a very large number of molecular orbitals. The resulting molecular orbitals are so close in energy that they form an energy band.

A **barometer** is a device used to determine atmospheric (or barometric) pressure.

A **base pair** consists of two complementary, N-containing bases whose structures maximize H-bonding between them. Guanine and cytosine are base pairs as are adenine and thymine. Base pairs hold the two strands of DNA together.

A **basic salt** is one in which the basicity of the anion exceeds the acidity of the cation.

Basic solutions are solutions in which $[H_3O^{1+}] < [OH^{-}]$. A basic solution has a pH > 7.0 at 25 °C.

A **battery** is a galvanic cell or a collection of galvanic cells. Batteries harness the free energy changes in redox reactions.

Beer's Law: The absorbance (A) of a solution equals the product of its molar absorptivity (ϵ), its molar concentration (c), and the path length (l) of the cell in which its absorbance is measured; $A = \epsilon clc$.

Belt of stability See band of stability.

Beta decay is the ejection from the nucleus of an electron produced by the decay of a neutron. β -decay reduces the neutron/proton ratio, so it is common among nuclei that lie above the band of stability.

A **beta particle (β)** is a high energy electron.

A **bimolecular** process is one that involves two molecules.

Binary compounds are composed of only two elements; Al_2O_3 is a binary compound because it contains only Al and O.

The **binding energy** is the energy that holds the nucleus together. It is related to the mass defect by $\Delta E = \Delta mc^2$.

Blackbody radiation is the light emitted by a solid when it is heated.

A **body-centered cubic (bcc)** unit cell is one in which the particles that lie on the corners are also in the body center.

The **boiling point** is the temperature at which the vapor pressure equals the external pressure. If the external pressure is 1 atm, then the temperature is called the **normal boiling point**.

Boiling point elevation (ΔT_b) is the increase in the boiling point caused by the addition of a non-volatile solute to a solvent.

The **boiling point elevation constant** (k_b) is the proportionality constant that relates the boiling point elevation of a solution to its colligative molality. $\Delta t_b = k_b m_c$.

The **bond angle** is the angle formed by two bonds to an atom.

The **bond dipole** is a measure of bond polarity. It is represented by an arrow pointing from the less electronegative atom toward the more electronegative atom.

The **bond energy** or **bond dissociation energy** is the amount of energy required to break one mole of bonds *in the gas phase*.

The **bond length** is the distance between two bound nuclei.

The **bond order** is the number of shared pairs in a bond. As the bond order increases, the length of the bond decreases and its strength increases. The bond order in a diatomic molecule is also equal to $1/2$ the difference between the number of its bonding and antibonding electrons.

The **bonding electrons** are the shared electrons in a covalent bond.

A **bonding interaction** occurs in a molecular orbital when the phases of the atomic orbitals of two adjacent atoms are the same.

A **bonding MO** is a molecular orbital in which the number of bonding interactions exceeds the number of antibonding interactions.

Boyle's law states that the pressure-volume product of a fixed amount of gas at constant temperature is constant. $PV = k(n,T)$.

A **branched chain hydrocarbon** contains a chain of carbons atoms in which at least one carbon is bound to three or four other carbon atoms.

A **Bronsted acid** is a proton donor.

A **Bronsted base** is a proton acceptor.

A **buffer** is a solution that contains a weak acid and its conjugate base in appreciable and comparable amounts. Buffers reduce pH changes brought about by the addition of strong acids and bases.

The **buffer capacity** is the amount of strong acid or base on which a buffer can act.

The **buffer range** is the pH range over which a buffer can function.

A **bulk property** is a property of a material (such as a pure solid or liquid) as opposed to individual atoms or molecules. Bulk properties are different than the atomic or molecular properties of its components due to the interactions between the components.

C

The **calorie (cal)** is the heat required to raise 1 g of water 1 °C. 1 cal = 4.184 J. The dietary calorie (Cal) is actually a kilocalorie (kcal).

A **calorimeter** is a piece of equipment used to determine the amount of heat released or absorbed during a reaction.

A **carbonyl** contains the C=O group.

A **carboxyl group** is the combination of a carbonyl (C=O) and a hydroxyl (O-H) group. Molecules with carboxyl groups are called carboxylic acids (RCOOH), and the deprotonated ions are called carboxylates (RCOO⁻¹).

A **catalyst** is a substance that speeds up a reaction but is unchanged by it.

The **cathode compartment or electrode** is where reduction occurs in an electrochemical cell.

A **cathode ray** is light emitted from the cathode (negative electrode) of a gas discharge tube.

A **cation** is a positively charged ion.

The **cell potential** is the potential difference between the cathode and anode of an electrochemical cell.

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}}$$

The **Celsius (or centigrade) scale** is the temperature scale based on the freezing (0 °C) and boiling points (100 °C) of water.

A **chain reaction** is a reaction in which a product initiates more reaction.

Charles' law states that the volume of a fixed amount of gas at constant pressure is proportional to its absolute temperature. $V = k(n,P)T$

A **chemical property** is a property of a substance that requires the substance to change into another substance. Hydrogen and oxygen react to produce water is a chemical property of hydrogen.

Chemistry is that branch of science that deals with matter and the changes it undergoes.

A **cis** configuration is one in which two groups are on the same side of a bond or atom.

Cohesive forces are forces between like molecules (compare with adhesive force).

The **colligative concentration** is the concentration of all solute particles in a solution. The colligative concentration of a solute equals its concentration times its van't Hoff factor.

Colligative properties are those properties of a solution that depend upon the concentration, but not the identity, of the solute particles.

The **collision frequency** is the number of collisions per unit volume per unit time, which normally has units of (moles of collisions)/(liters·s).

Combustion is a reaction with oxygen.

A **common ion** is an ion that appears in an equilibrium but has at least two sources.

A **complex ion** is an ion in which a central metal is surrounded by molecular or anionic ligands.

A **compound** is a pure substance that consists of more than one element.

The **concentration** of a solute is the amount of solute divided by the volume in which it is contained.

A **concentration cell** is an electrochemical cell in which the two compartments differ only in their concentrations. The cell potential depends upon the concentration difference.

Condensation is the process of converting a vapor into its liquid.

Condensation polymers are formed by condensation reactions.

A **condensation reaction** is a reaction in which two reactants combine to form two products (one of which is often a small molecule such as water or an alcohol).

The **conduction band** is the lowest energy unfilled band in a solid that has no partially filled bands. Electrons in a conduction band are free to move throughout the metal due to the presence of unfilled orbitals. Thus, electrons can conduct electricity only when they are in the conduction band.

A **conductor** is a substance that conducts electricity at all temperatures. Its conduction decreases slightly with increasing temperature.

A **conjugate acid-base pair** is a Brønsted acid and base that differ by one proton only.

Connectivity is the manner in which the atoms in a molecule are connected.

Constitutional isomers are compounds with the same formula but different connectivities.

A **continuous chain hydrocarbon** is a chain of carbon atoms in which no carbon is bound to more than two other carbon atoms.

A **continuous spectrum** is a spectrum in which all wavelengths of light in the region are present. Thus, they merge into one another continuously. A rainbow is a continuous spectrum of visible light.

A **coordinate covalent bond** is a bond in which both bonding electrons are contributed by the same atom. The bonds formed in Lewis acid-base reactions are coordinate covalent because both bonding electrons always come from the base.

The **coordination number** of a particle is the number of its nearest neighbors in a crystal or in a compound.

Core electrons are the tightly bound electrons that are unaffected by chemical reactions. They reside in filled sublevels and form a spherical shell of negative charge around the nucleus that affects the amount of nuclear charge that the outermost electrons experience.

Corrosion is the natural oxidation of a metal.

The **coulomb (C)** is the SI unit of electrical charge. The charge on one electron is 1.602×10^{-19} C.

Coulomb's law states that two charged particles experience a force that is proportional to the product of their charges and varies inversely with the dielectric of the medium and the square of the distance that separates them. Negative forces are attractive, while positive forces are repulsive.

A **counter ion** is an ion that accompanies a desired ion

in order to maintain the electrical neutrality of the compound that contains the desired ion. Counter ions are spectator ions in net chemical equations.

A **covalent bond** results when electrons are shared. It can be viewed as the attraction of the bonding electrons for the bound nuclei.

The **covalent radius** of an atom X is equal to one-half of the distance between the X atoms in X_2 .

The **critical mass** is the minimum mass of a radioactive material required to maintain a chain reaction.

The **critical point** is the temperature and pressure beyond which the liquid cannot exist. Substances beyond their critical point are supercritical fluids.

The **critical pressure** is the pressure required to liquefy a gas at its critical temperature.

The **critical temperature** is the highest temperature at which a gas can be liquefied.

A **crystal orbital** is to a crystal what a molecular orbital is to a molecule.

Crystalline solids are solids with well defined and ordered repeat units. The order, which exists throughout the crystal, is said to be long range order.

D

Degrees of freedom are the basic set of motions (translations, rotations, and vibrations) that a molecule undergoes. The kinetic energy of a molecule is distributed amongst its degrees of freedom. A molecule with N atoms has $3N$ degrees of freedom.

Delocalized electrons or bonds are spread over several atoms.

Density is the mass to volume ratio of a substance or solution. $d = m/V$

The **density of states** is the number of allowed energy states in a region of energy.

Deposition is the process in which a vapor is converted into its solid.

A **detergent** is a substance that has both a hydrophobic region that interacts well with nonpolar molecules such as grease, and a hydrophilic region that interacts well with polar molecules such as water.

Diamagnetism is the tendency of certain atoms not to be attracted by a magnetic field. It is an atomic property associated with atoms that have no unpaired electrons.

Diatomc molecules contain two and only two atoms.

The **dielectric constant** (ϵ) is a number that relates the ability of a medium to shield two charged particles from one another. A medium with a high dielectric constant shields the charges better than one with a low constant.

A **dipole** consists of two electrical poles, one positive and one negative. Bonds dipoles arise between atoms of different electronegativities. A molecular dipole is the vector sum of its bond dipoles.

Dipole-dipole or dipolar forces are the inter-molecular forces that result from the interaction of the oppositely charged poles of two polar molecules.

Dispersion forces are forces between molecules that result from the interaction of temporary or induced dipoles. Dispersion forces increase approximately with molecular size.

The **dissociation constant** is the equilibrium constant for the dissociation of a complex ion into its component ions and/or molecules. Also see acid dissociation constant.

The **dissociation or bond energy** is the energy required to break one mole of bonds in the gas phase.

Dissolution is the process in which an ionic substance dissolves in water to produce ions.

A **donor orbital** is the orbital on the reducing agent that contains the electrons to be transferred in a redox reaction.

The **double helix** is the structure adopted by DNA. It consists of a pair of intertwined polynucleotide strands held together by hydrogen bonding between base pairs.

Dynamic equilibria are attained when two competing processes occur at equal rates. Contrast to a static equilibrium where the competing processes stop.

E

Effective nuclear charge (Z_{eff}) is the nuclear charge experienced by an electron in an atom. It is less than the nuclear charge due to shielding by the other electrons.

An **electrical current** is the rate at which charge flows through a circuit. A current of one ampere is a rate of one Coulomb of charge per second.

An **electrochemical cell** is a device used to extract the free energy change of a spontaneous redox reaction (see Galvanic cells) or to inject the energy required to drive a redox reaction that is not spontaneous (see electrolytic cells).

Electrochemistry is the combination of electrical conduction through a circuit and electron transfer reactions.

An **electrode** is a metal that provides a surface at which electrons can be transferred between an electrical circuit and a reactant in a redox reaction.

Electrodes are active if they participate in the reaction and passive if they do not.

Electrolysis is a non-spontaneous redox reaction that is driven uphill in free energy by the application of an external electrical potential.

An **electrolyte** is a material that produces ions when dissolved in water. Electrolytes can be weak or strong depending upon the extent to which they produce ions. Substances that dissolve in water as molecules rather than ions are called non-electrolytes.

An **electrolytic cell** is an electrochemical cell that converts electrical potential energy into chemical potential energy. See electrolysis.

Electrolytic conduction is conduction of electricity through a solution as a result of the migration of ions in the solution.

Electromagnetic radiation is an electric and a magnetic field oscillating perpendicular to one another that travels through space in the form of radio waves, microwaves, infrared waves, visible light, ultraviolet light, etc.

An **electron** is the basic quantity of negative charge. It carries a charge of -1.602×10^{-19} C and has a mass of 5×10^{-4} amu.

Electron capture is the capture of a core electron by the nucleus. It converts a proton into a neutron.

The **electron configuration** of an atom is a listing of the sublevels that are occupied and the number of electrons in them.

Electron density is the probability of finding an electron in a particular region of space. The electron density is high in regions where the probability of finding an electron is high.

Electronegativity (χ) is a relative measure of the ability of an atom to attract bonding electrons to itself. Atoms with high electronegativities have unfilled orbitals that are low in energy.

An **electronic transition** is the changing of the energy of an electron from one quantum state to another.

An **element** is a pure substance that cannot be broken down into a simpler substance by chemical means.

The **elemental composition** of a compound is a listing of the relative masses, usually expressed as percents, of the elements in the compound.

An **elementary reaction** is a reaction that occurs in one step.

Emission is the ejection of a photon by an atom or a molecule. The energy of the atom or molecule decreases by the energy of the photon ($h\nu$).

An **empirical or simplest formula** is a chemical formula that indicates only the smallest whole number ratio of the atoms present in the compound.

Enantiomers are two molecules that are non-superimposable mirror images of one another.

An **endothermic** process absorbs heat.

The **end point** is the point at which an indicator changes color. The end point should be nearly the same as the equivalence point.

Energetics is a combination of thermodynamics and kinetics.

Energy is the capacity to do work or to transfer heat.

An **energy band** is a region of allowed energy in a metal in which there is no separation between adjacent energy levels.

The **energy of interaction** is the energy of two interacting particles relative to the energy of the

two particles when they are not interacting. Energies of interaction in chemistry result from the electrostatic interactions.

The **enthalpy or heat of combustion** is the heat absorbed when one mole of a substance reacts with oxygen. Heats of combustion are negative because they are exothermic.

The **enthalpy or heat of reaction** is the heat absorbed by a reaction run at constant temperature and pressure. A negative heat of reaction simply means that the heat is given off not absorbed.

Entropy is the thermodynamic measure the number of ways in which a system can distribute its energy. It is often related to the disorder in the system.

An **enzyme** is a biological compound (usually a protein) that acts as a catalyst.

The **equilibrium constant (K)** is the value of the reaction quotient (Q) when equilibrium activities are used.

The **equivalence point** is the point in a titration at which stoichiometric amounts of reactants are present.

Esters are compounds with the general formula RCOOR', *i.e.*, two groups connected by a carboxyl group.

Esterification is a condensation reaction between a carboxylic acid and an alcohol to produce an ester and water.

Evaporation is the conversion of a liquid to its vapor.

An **excited state** is an allowed state that is not the lowest energy state.

An **exothermic** process gives off heat.

Exponential decay is a decrease in concentration that goes as e^{-x} . First order reactions undergo exponential decay: $[A] = [A]_0 e^{-kT}$.

An **extensive property** is one that depends upon the amount of material. Mass and volume are extensive properties. Also see intensive property.

An **extensive reaction** is one with a large equilibrium constant. If a reaction is extensive, then the equilibrium concentration of least one of the reactants will be very small.

F

A **face centered cubic (fcc)** unit cell is one in which the atoms that are located in the corners are also found in the centers of the faces.

The **factor label method** is a method that uses the labels (units) of the factors to determine the order and manner in which the factors should be used to convert one quantity into another.

Family See group.

The **Faraday (\mathcal{F})** is the charge of one mole of electrons. $1\mathcal{F} = 96,485 \text{ C/mol}$.

A **fatty acid** is a carboxylic acid with a long hydrocarbon chain.

The **Fermi level** the highest occupied energy level in a band.

A **ferrimagnet** is a magnetic material whose particles have opposing but unequal spins.

A **ferromagnet** is a magnetic material whose particles have aligned spins.

Ferromagnetism is a bulk magnetism in a material (such as iron) resulting from the alignment of the spins of adjacent atoms in the same direction.

The **first law of thermodynamics** states that energy is neither created nor destroyed in any process.

Fission is the process in which a heavy nucleus splits into lighter nuclei.

Formal charge is the charge an atom would have if the bonds were completely covalent, *i.e.*, if its bonding electrons were assigned equally between the atoms in each bond.

The **formation constant** (K_f) is the equilibrium constant for the formation of a complex ion. For example, $\text{Ag}^{1+} + 2\text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^{1+}$.

Free energy is the energy that is required to drive a non-spontaneous process. The negative of the free energy is the amount of work that can be extracted from a spontaneous process.

The **freezing point depression** (ΔT_f) is the decrease in the freezing point of a liquid caused by the addition of a non-volatile solute.

The **frequency** of a light wave is the number of oscillations per second that the wave undergoes.

A **functional group** is a group of connected atoms within a molecule that has a specific reactivity.

Fusion is the state change from a solid to a liquid or the combination of two lighter nuclei to produce a heavier one.

G

A **galvanic cell** is a spontaneous electrochemical cell. Galvanic cells convert chemical potential energy into electrical potential energy.

Geometric isomers are stereoisomers that differ because two groups can be on the same side (*cis* isomer) or on the opposite side (*trans* isomer) of some structural feature.

Gibbs free energy (ΔG) is the change in free energy at constant temperature and pressure.

The **ground state** is the state of an atom or molecule that has the lowest energy.

A **group (or family)** is a vertical column in the periodic table. The elements in a group have similar properties

H

A **half-cell** is that portion of an electrochemical cell in which one half-reaction takes place.

The **half-life** ($t_{1/2}$) is the time required for one-half of a reactant to disappear.

A **half-reaction** is half of a redox reaction. They represent the electron gain or loss by showing the electrons explicitly. $\text{Ox} + n\text{e}^{-} \rightarrow \text{Red}$ is the general form of a reduction half-reaction.

A **halogen** is an element that belongs to Group 7A. The common halogens are fluorine, chlorine, bromine, and iodine. The elemental halogens are diatomic.

Hard water contains Mg^{2+} and Ca^{2+} , which form insoluble salts with soaps.

Heat (q) is that form of energy that is transferred as a result of a temperature difference. By definition, q is the heat absorbed by the system, and $-q$ is the heat released by the system.

The **heat capacity** (C) of an object is the amount of heat required to raise the temperature of the object by 1 °C or 1 K.

Heat of combustion (ΔH_{comb}) is the heat absorbed when one mole of a substance reacts with oxygen.

Heat of formation (ΔH_f) is the enthalpy change resulting when one mole of a substance is formed from its elements in their standard states.

Heat of fusion (ΔH_{fus}) is the heat required to melt one mole of a substance at its melting point.

Heat of sublimation (ΔH_{sub}) is the heat required to convert one mole of a solid into its gas.

Heat of vaporization (ΔH_{vap}) is the amount of heat required to convert one mole of a liquid into its gas.

The **Henderson-Hasselbalch equation** is used to calculate the pH of a buffer solution.

$$\text{pH} = \text{pK}_a + \log(\frac{n_b}{n_a})$$

Hess' law of heat summation states that if a process can be expressed as the sum of several steps, then the enthalpy change of the process is the sum of the enthalpy changes of the steps.

A **heterogeneous catalyst** is in a different phase than the reactants. Typically it is a solid for gas or solution reactions.

A **heterogeneous mixture** is one whose composition varies as in a mixture of water and oil.

A **high spin metal** is one in which the splitting of the d orbitals is small enough that the d electrons remain unpaired in the higher energy set rather than pairing in the lower energy set.

Homo is the abbreviation for the highest occupied molecular orbital.

A **homogeneous catalyst** is in the same phase as the reactants.

A **homogeneous mixture** is a mixture whose composition is the same throughout, *i.e.*, one in which the concentration of each component is the same regardless of the volume that is sampled. Homogeneous mixtures are called solutions.

A **homonuclear diatomic molecule** is one in which the two atoms are the same.

Hund's rule states that the number of electrons with identical spin is maximized when filling the orbitals of a sublevel.

A **hybrid orbital** is an orbital constructed by mixing two atomic orbitals on the same atom. They are used to explain bonding in the valence bond model.

Hybridization is the process by which hybrid orbitals are produced from atomic orbitals.

A **hydrate** is a compound with a characteristic number of water molecules associated with it.

Hydration is the process in which a solute particle interacts with the surrounding water molecules.

A **hydrocarbon** is a compound that contains only carbon and hydrogen.

Hydrogenation is the addition of hydrogen to a compound.

The **hydrogen bond** is an especially strong dipolar interaction that occurs in compounds containing a hydrogen atom attached to N, O, or F.

The **hydronium ion (H_3O^{1+})** is the conjugate acid of water. Therefore, it is the strongest acid that can be present in aqueous solutions.

A **hydrophilic** molecule interacts well with water.

A **hydrophobic** molecule is excluded from water because it does not interact well with water.

The **hydrophobic effect** is the tendency of water to exclude hydrophobic molecules by establishing an ice-like structure around them.

A **hypothesis** is a proposed explanation of an observation. If a hypothesis proves successful in explaining many other experiments, it becomes a theory, but if it fails to explain a test, it is discarded or modified.

I

An **ideal gas** is a hypothetical gas composed of molecules that do not interact with one another.

The **ideal gas law** is the relationship between the pressure (P), volume (V), temperature (T) and number of moles (n) of an ideal gas. $PV = nRT$.

Ideal gases obey the ideal gas law at all T and P, while real gases deviate at high P and low T.

An **indicator** is a compound that changes color within a small pH range. The pH at which the indicator changes color is called the end point.

An **induced dipole** is a molecular dipole in one molecule caused by the asymmetric charge distribution in a neighboring molecule.

The **instantaneous rate** of a reaction is the rate at a specified time. It is equal to the slope of the concentration vs. time plot at the specified time.

An **insulator** is a substance that does not conduct electricity at reasonable temperatures because its band gap is too large.

An **integrated rate law** expresses the concentration of a reactant as a function of time.

An **intensive property** is independent of sample size. Color and density are intensive properties.

An **intermediate** in a chemical reaction is a substance that is formed and then consumed in the reaction. Intermediates do not appear in the net chemical equation for the reaction.

Intermolecular interactions are between different molecules. Dipolar and dispersion forces are intermolecular interactions.

Intramolecular interactions are within a molecule. Chemical bonds are intramolecular interactions.

An **ion** is a charged chemical species.

The **ion product (Q_{ip})** is the reaction quotient for the reaction in which a solid dissolves as its ions in solution. $Q_{ip} = K_{sp}$ at equilibrium.

The **ion product constant of water (K_w)** is the equilibrium constant for the reaction $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{1+} + \text{OH}^{1-}$. $K_w = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$, which has a value of 1.0×10^{-14} at 25°C .

An **ionic bond** is an electrostatic (Coulombic) force between oppositely charged ions.

The **ionic radius** of an ion is determined from the distances between it and adjacent ions in an ionic crystal. The distance between the two adjacent ions equals the sum of their ionic radii.

The **ionization energy** is the energy required to remove an electron from an atom or molecule.

Ionizing radiation is high energy radiation that can remove electrons from a substance. X-rays are ionizing radiation.

Two substances are **isoelectronic** if they have the same number of electrons.

Isomers are different molecules with the same formula.

Isotopes are atoms with the same atomic number but different mass numbers, *i.e.*, isotopes have the same number of protons but different numbers of neutrons.

J

The **joule (J)** is the SI unit of energy.

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$$

K

Kaolinite clays are composed of silicate and aluminosilicate layers (aluminosilicates). They are the main component of china clay.

The **kelvin (K)** is the SI unit of temperature. $K = {}^\circ\text{C} + 273.15$.

Kinetics is the study of reaction rates and mechanisms.

Kinetic energy ($KE = \frac{1}{2}mv^2$) is energy of motion. Anything in motion has the capacity to do work on another object by simply colliding with it.

Kinetic-molecular theory is the model used to explain the ideal gas law. One of its postulates is that the average kinetic energy of the molecules in a gas is directly proportional to the absolute temperature of the gas.

The **kinetic region** of a reaction is the period of the reaction in which concentrations are changing.

L

A **crystal lattice** is the arrangement of the particles in a crystal. Each particle lies on a lattice site.

A **law** is a statement that summarizes many observations.

The **law of combining volumes** states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

The **law of conservation of energy** is stated by the first law of thermodynamics; $\Delta E_{\text{univ}} = 0$.

The **law of conservation of mass** states that the total mass of reactants and products remains constant during a chemical reaction; *i.e.*, mass is neither created nor destroyed in a chemical reaction.

The **law of definite or constant proportions** states that the elements of a compound are always present in definite proportions by mass.

The **law of multiple proportions** states that the masses of one element that combine with a fixed mass of another element in different compounds of the same elements are in a ratio of small whole numbers.

Le Châtelier's principle states that a system at equilibrium will respond to a stress in such a way as to minimize the effect of the stress.

A **level** or shell is an allowed energy designated by the principal quantum number n .

The **leveling effect** of a solvent requires that no acid in a solvent can be stronger than the conjugate acid of the solvent and no base can be stronger than the conjugate base of the solvent. Thus, hydronium ion is the strongest acid that can exist in water and hydroxide ion is the strongest base.

A **Lewis acid** is a substance with a low lying, empty orbital that can be used to form a covalent bond to a Lewis base. Lewis acidic sites are characterized by less than four electron regions.

A **Lewis acid-base reaction** is the conversion of a lone pair on a Lewis base and the empty orbital on a Lewis acid into a covalent bond between the acid and the base.

A **Lewis base** is a substance with a lone pair that can be shared with a Lewis acid to form a covalent bond between the acid and the base.

A **Lewis structure** is a representation of a molecule that shows all of the valence electrons. The non-bonding electrons are represented as dots, but the bonding pairs are usually shown as lines.

The **Lewis symbol** shows the atom's valence electrons as dots in four regions around an atom.

A **ligand** is a molecule or ion that is attached to a metal.

The **ligand field splitting energy (Δ)** is the energy difference between the sets of d-orbitals in an atom. It results from the electrostatic field of the ligands, *i.e.*, the ligand field.

The **limiting reactant** is that reactant whose amount limits the amount of product that can be obtained in a reaction, *i.e.*, the reactant that is totally consumed.

A **line spectrum** is a spectrum in which only certain wavelengths (lines) are present. Atomic spectra are line spectra.

A **liquid junction** is a device that allows ion migration between the electrodes of an electro-chemical cell to complete the electrical circuit.

A **load** is a device in a galvanic cell that utilizes the free energy given off by the transferred electrons.

A **lone pair** is a pair of nonbonding valence electrons.

A **low-spin metal** is a metal in which the d electrons pair in the lower energy set of orbitals before occupying the higher energy set.

The **lumo** is the lowest unoccupied molecular orbital.

M

The **magnetic quantum number (m_l)** is an integer between $-l$ and $+l$ that specifies the directional character of an atomic orbital.

A **main group element** is an element in one of the groups designated as 'A' in the periodic table. Other elements are either transition or inner transition elements.

A **manometer** is a device used to determine the pressure of a gas.

The **mass fraction** of a substance in a mixture is the mass of the substance divided by the mass of the mixture. Mass fractions represent the fraction of the whole, so they are less than one. However, they can be expressed as fractions of 100, in which case they are called mass percents.

The **mass defect (Δm)** is the difference between the mass of a nucleus and the sum of the masses of its neutrons and protons.

Mass-energy is a term used to show that mass and energy are interchangeable ($E = mc^2$).

The **mass number (A)** is the number of protons plus the number of neutrons in the nucleus.

The **mechanical surroundings** is that portion of the surroundings that exchanges energy with the system in the form of work.

The **melting point** is the temperature at which the solid and liquid states are in equilibrium.

A **meniscus** is the curved shape of the top of a liquid.

A **metal** is a material that is shiny, malleable, and a good conductor of electricity. Elements that are metals lie on the left side of the periodic chart and represent about 80% of the elements.

A **metallic bond** is one delocalized over the entire metal. The large number of atoms involved in a typical metallic bond is so large that the bonding electrons occupy bands of energy.

Metalloids have properties intermediate between the metals and nonmetals. The eight metalloids are shiny and brittle. They are not good conductors of heat or electricity (they are semiconductors).

A **micelle** is spherical arrangement of detergent molecules in which the heads form a polar outer shell and the tails form a hydrophobic liquid center.

Micro (μ) is the SI prefix for 10^{-6} , a millionth.

Milli (m) is the SI prefix for 10^{-3} , a thousandth.

Two liquids are **miscible** if they are soluble in one another in all proportions.

The **molality (m)** of a solute is the number of moles of solute present in 1 kg of solvent.

The **molar absorptivity (ϵ)** is the absorbance of a 1 M solution in a 1 cm cell.

The **molarity (M)** of a solute is the number of moles of solute present in a liter of solution.

The **molar mass (M_m)** is the mass of one mole of substance. It is equal to the atomic or molecular mass (weight) expressed in grams.

The **mole (mol)** is 6.02×10^{23} items. It is the number of molecules or atoms in a sample of a compound or element that has a mass equal to its molecular or atomic mass expressed in grams.

The **mole fraction (X)** of a substance in a mixture is the number of moles of that substance divided by the number of moles of all components of the mixture.

A **molecular dipole** is equal to the product of the charges on the two poles of a polar molecule and the distance between them. It is represented by an arrow pointing from the center of positive charge toward the center of negative charge.

The **molecular formula** of a compound shows the actual numbers of atoms present in the molecule. Contrast with the simplest or empirical formula that shows only the smallest integers that are in the same ratio as in the molecular formula.

Molecularity is the number of reacting molecules in an elementary reaction.

The **molecular mass or weight** is the relative mass of a molecule relative to the mass of a carbon-12 atom.

Molecular orbital theory is a bonding theory in which bonds are formed from the combination of several atomic orbitals on several atoms.

Molecular weight See molecular mass

A **molecule** is an independent particle that consists of two or more chemically bound atoms.

A **monatomic ion** is derived from a single atom.

A **monomer** is a single unit building block that can be bound to other monomers to form larger molecules. Linking two monomers produces a dimer, linking three produces a trimer, and linking many produces a polymer.

N

Nano (n) is the SI prefix for 10^{-9} , a billionth.

Nanotechnology is science and engineering of systems on the nanoscale (1-50 nm).

The **Nernst equation** relates a cell's potential to its standard potential and its reaction quotient.

$$\mathcal{E}_{\text{cell}} = \mathcal{E}^{\circ} - \left(\frac{RT}{nF} \right) \ln Q$$

A **net chemical equation** shows only those substances that are changed during the reaction.

In a **network covalent solid**, all of the atoms are bound covalently with no discernable molecules.

A **neutral salt** is a compound in which the acid and base strengths of the cation and anion are equal.

In **neutral solutions**, $[\text{H}_3\text{O}^{+}] = [\text{OH}^{-}]$. The pH of a neutral solution is 7.0 at 25 °C.

In **neutralization reactions**, an acid reacts with a base to produce water and a salt.

A **neutron** is a subatomic particle found in the nucleus. It has no charge and a mass of ~1 amu.

A **noble gas** is an element that belongs to Group 8A. The noble gases are helium, neon, argon, krypton, xenon, and radon.

A **nodal plane** is a plane of zero electron density that lies between regions of opposite algebraic sign in an orbital. A p orbital and a π orbital each contain a single nodal plane.

A **nonbonding MO** has an equal number of bonding and antibonding interactions.

A **nonelectrolyte** is a substance whose aqueous solution does not conduct electricity. Electricity is not conducted because the electrolyte produces no ions in solution.

Non-ionizing radiation, such as visible light, does not have sufficient energy to ionize matter.

Nonmetals are elements on the right side of the periodic table. They can be gases, liquids, or solids and are dull, brittle, and poor conductors of electricity. Nonmetals react with one another to form covalent compounds or with metals to form ionic compounds.

The **normal boiling point** is the temperature at which the vapor pressure of a liquid is 1 atm.

The **nuclear binding energy** is the energy required to break one mole of nuclei into their constituent nucleons.

Nuclear chemistry or radiochemistry is the study of reactions that involve changes in the nucleus.

Nuclear fission is the splitting of a heavier nucleus into lighter nuclei.

Nuclear fusion is the combination of two lighter nuclei into a heavier one.

Nucleons are the particles found in the nucleus. Protons and neutrons are nucleons.

A **nucleotide** is a unit of a nucleic acid that consists of a phosphate, a sugar, and an N-containing base. Nucleic acids are polymers built with nucleotides.

The atomic **nucleus** contains all of the positive charge, virtually all of the mass, but occupies almost none of the volume of an atom.

Nylon is a polyamide produced in the reaction of a diamine and a diester.

O

The **octet rule** states that atoms in molecules strive to obtain an octet (eight) of valence electrons by sharing the bonding electrons with other atoms.

An **orbital** is a solution to the wave equation. Electrons reside in atomic or molecular orbitals, and bonding results from the interaction of atomic orbitals of different atoms.

An **organic compound** is one that is based on carbon.

Osmosis is the net movement of solvent molecules from a dilute solution into a more concentrated one through a semipermeable membrane, *i.e.*, one that allows only solvent molecules to pass.

Osmotic pressure is the pressure caused at a semipermeable membrane bounded by solutions of different concentration. It results because solute particles cannot pass through the membrane but solvent molecules can.

Overpotential is the amount by which the applied potential for electrolysis must be increased above that predicted from half-cell potentials to carry out the electrolysis at a reasonable rate. Overpotentials are due to high activation energies.

An **oxidant** is an oxidizing agent.

Oxidation is the loss of electrons or increase in oxidation state that accompanies electron transfer.

The **oxidation state** of an atom is the charge it would have if its bonds were assumed to be ionic, *i.e.*, if its bonding electrons were assigned to the more electronegative atom in each bond.

An **oxidizing agent** is a substance that promotes oxidation in other substances. The oxidizing agent is reduced by the electron transfer.

An **oxoacid** is a Brønsted acid in which the proton is attached to an oxygen atom.

An **oxoanion** has a central atom surrounded by oxygen atoms. The central atom is usually in a high oxidation state because it is surrounded by the very electronegative oxygen atoms.

P

Packing efficiency is the fraction of the volume of the unit cell that is occupied by particles.

Paramagnetism is the tendency of certain atoms to be attracted by a magnetic field. It is an atomic property that is related to the number of unpaired electrons on the atom.

Partial ionic character See percent ionic character.

The **partial pressure** of a gas is the pressure exerted by the gas in a mixture of gases. The total pressure exerted by a mixture is the sum of the partial pressures of all of the components of the mixture.

Parts per billion (ppb) is the number of grams of solute in 10^9 g of solution.

Parts per million (ppm) is the number of grams of solute in 10^6 g of solution.

Parts per thousand (ppt) is the number of grams of solute in 1000 g of solution.

The **pascal (Pa)** is the SI unit of pressure.

$$1\text{ Pa} = 1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2} = 9.9 \times 10^{-6} \text{ atm}$$

A **passive electrode** is one that does not participate in the half-reaction. For example, a platinum electrode in a $2\text{H}^{1+} + 2\text{e}^{-} \rightarrow \text{H}_2$ half-cell is passive.

The **Pauli Exclusion Principle** states that no two electrons in an atom can have the same set of quantum numbers.

A **peptide** is an amide produced from the reaction of two amino acids.

The **percent ionic character** is a measure of the charge separation in a bond, which results from electronegativity differences between the bound atoms. A bond is considered to be ionic if it has over 50% ionic character.

The **percent yield** is the fraction of the theoretical yield, expressed as a percent, that is actually isolated in a chemical reaction.

A **period** in the periodic table is a horizontal row. The properties of the elements in a period vary gradually across the period.

The **periodic law** states that the elements exhibit a periodicity in the chemical and physical properties when they are arranged in the order of their atomic numbers.

The **periodic table or chart** is an arrangement of the elements into rows (periods) and columns (groups) such that the elements in the same group have similar properties.

pH is the negative base 10 logarithm of the hydronium ion concentration in a solution.

$$\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$$

A **phase diagram** shows the state of a substance as a function of its temperature and pressure.

A **photon** is a quantum of energy in the form of electromagnetic radiation.

Photosynthesis is the process in which plants use solar energy to convert CO_2 and H_2O into carbohydrates.

A **physical property** is one that is independent of other substances. Melting point, boiling point, color, and hardness are some physical properties.

A **pi (π) bond** is formed from the side-on interaction of two p orbitals. Pi bonds have nodal planes that contain the internuclear axis.

The **pK_a** of an acid is the negative base 10 logarithm of the acid dissociation constant. $\text{pK}_a = -\log K_a$

Planck's constant (h) is the proportionality constant that relates the frequency of a photon to its energy. $h = 6.626 \times 10^{-34} \text{ J/s}$

A **polar covalent bond** is a covalent bond in which the

bonding electrons are NOT shared equally. Thus, the bonds are between atoms of different electronegativities.

Polar molecules have asymmetric charge distributions. The result is a molecular dipole.

The **polarizability** of an atom or molecule is a measure of the ease with which its electron cloud can be deformed.

A **polyamide** is a condensation polymer that contains many amide linkages. Nylons and peptides are polyamides.

A **polyatomic ion** is an ion, such as CO_3^{2-} , in which two or more atoms are covalently bound.

A **polyene** is an organic compound with many double bonds.

A **polymer** is a large molecule consisting of many single unit building blocks called mers.

A **polypeptide** is a polyamide produced from the reaction of many amino acids.

Polyprotic acid acids have more than one acidic proton. Examples: H_2SO_4 is a diprotic acid and H_3PO_4 is a triprotic acid.

Polyunsaturated organic compounds contain many C-C multiple bonds.

A **positron** is an elementary particle with the mass of an electron and a positive charge. It is the antimatter analog of the electron.

Positron decay is the emission of a positron from the nucleus. Positron decay increases the neutron/proton ratio, so it is common in nuclei that lie below the band of stability.

Potential energy is energy due to position. In chemistry, potential energy arises from the interaction of charged particles, and the closer they are, the stronger they interact.

A **precipitate** is a solid formed when two solutions are mixed, or the act of forming the solid. Thus, AgCl precipitates and is a precipitate when it does.

The **precision** of a number is given by the number of significant figures to which it is reported. 1.00 m is more precise than 1.0 m .

A **pre-exponential** precedes an exponential. Typically used in the Arrhenius equation: $k = A \exp\{-E/RT\}$, where A is the pre-exponential.

Pressure (P) is force per unit area: $P = F/A$.

Pressure-volume or PV work is done when the volume of a gas changes against an external pressure.

The **principal quantum number (n)** specifies the energy level of an electron in an atom.

A **protein** is a large polypeptide.

A **proton** is a subatomic particle found in the nucleus. It carries a +1 charge and has a mass of ~1 amu.

A **proton acceptor** is called a Brønsted base.

A **proton donor** is called a Brønsted acid.

A **purely covalent bond** is a covalent bond in which the bonding electrons are shared equally. Thus, the bonds between atoms of the same electronegativity are purely covalent.

Q

A **qualitative observation** is one that does not involve numbers.

A **quantitative observation** is one that does involve numbers.

A **quantity** in the factor label method is an amount and is characterized by a single unit. For example, 3 m is a quantity, but 3 m/s is a factor.

A **quantum** is a packet of energy.

A **quantum number** is a number (usually an integer) that designates an allowed state. All atomic and molecular states (e.g., electronic, vibrational, rotational, and nuclear) are described by quantum numbers.

R

A **radioactive** nucleus is unstable and disintegrates spontaneously to another nucleus by emitting or capturing particles.

Radioactive dating is the determination of the age of a material from the amount of material involved in the radioactive decay of one of its components.

Radiochemistry See nuclear chemistry.

Radioisotopes are radioactive nuclei.

The **rate of change** of a quantity is the rate at which it changes as a function of the change in another quantity.

A **rate constant (k)** is the proportionality constant between the concentrations of the components (usually reactants) of a reaction and the rate of reaction.

The **rate-determining step (RDS)** is the elementary reaction in a mechanism that is so much slower than the other elementary reactions that it dictates the rate of the overall reaction.

The **rate law** expresses the rate of a reaction as a function of the concentrations of the substances (usually reactants) involved in the reaction.

The **rate of disappearance** is the rate at which a reactant reacts.

The **rate of formation or appearance** is the rate at which a product is produced.

The **rate of reaction** is the rate at which a product is produced or a reactant reacts divided by its coefficient in the chemical equation.

A **reactant order** is the exponent of the concentration of a reactant in the rate equation for a reaction.

The **reaction coordinate** is the combination of intermolecular distance, bond length and bond angle changes required to convert reactant molecules into product molecules.

A **reaction mechanism** is a series of elementary processes that leads to the overall reaction.

The **reaction order** is the sum of all of the reactant orders in a reaction.

The **reaction quotient (Q)** is expressed as the activities of the products divided by the activities of the reactants. Each activity is raised to an exponent equal to the coefficient of the substance in the balanced equation. When the activities are equilibrium activities, the reaction quotient is called the equilibrium constant.

A **redox couple** is the oxidized and reduced forms of the species involved in a half-reaction. For example, Cu^{2+}/Cu is a redox couple.

The **redox electrons** are the electrons that are transferred in a redox reaction.

Redox reactions involve an electron transfer from a reductant to an oxidant.

A **reducing agent or reductant** is a substance that promotes reduction in another material. It is oxidized in the process.

Reduction is the gain of electrons, which results in a decrease in oxidation state of the species being reduced.

A **residue** in a protein is one of the amino acids making up the protein.

A **resonance structure** is a Lewis structure of a molecule that differs from another Lewis structure only in the placement of electrons.

Respiration is the process whereby animals extract energy from carbohydrates.

Rotational degrees of freedom are spinning motions about an axis through the center of mass of the molecule. Linear molecules have two rotational degrees of freedom, and nonlinear molecules have three.

S

Salts are ionic compounds formed in an Arrhenius acid-base reaction. The anion of a salt is supplied by the acid, and the cation by the base.

A **salt bridge** is a liquid junction that consists of a saturated solution of a strong electrolyte, such as KCl. Ions enter and leave the bridge so as to maintain electrical neutrality in the two half-cells of an electrochemical cell.

Saturated carbons are involved in four sigma bonds.

Science is that branch of knowledge that is gained by the application of the scientific method.

The **Schrödinger equation** relates the energy of an electron to its wavefunction.

The **scientific method** is used to further scientific knowledge. It involves observation, hypothesis formulation, prediction, and testing.

The **second law of thermodynamics** states that the entropy of the universe increases in all spontaneous processes.

A **semiconductor** is a substance whose electrical conductivity increases with temperature. Semiconductors are characterized by small but nonzero band gaps.

A **semipermeable membrane** allows the passage of solvent molecules but not of solute particles.

Shell See level.

Shielding is the amount by which the nuclear charge experienced by an electron is reduced by interference from other electrons. Core electrons shield valence electrons much better than do other valence electrons because most of the electron density and charge of the core electrons lies between the valence electrons and the nucleus.

Sigma bonds are formed from the interaction of s orbitals or the end-on interaction of p or d orbitals. The electron density in a sigma bond contains the internuclear axis.

Significant figures are used to express the precision of a measurement or result.

In a **simple cubic (sc)** unit cell, the particles are found only at the corners.

The **simplest or empirical formula** is a chemical formula whose subscripts indicate only the smallest whole numbers that are in the same ratio as the actual numbers of atoms present in the molecule.

Smectic clays are also called swelling clays, they consist of a layer of aluminate octahedra sandwiched between two layers of silicate tetrahedra.

Soaps are similar to detergents except the polar head is a COO^{1-} (carboxylate) group because soaps are the salts of fatty acids.

The **solubility** of a solute is the maximum amount of the solute that can dissolve in a solvent at a given temperature.

The **solubility product constant (K_{sp})** is the equilibrium constant for the dissolution of a salt in water.

A **solute** is a component of a solution that is not the solvent.

A **solution** is a homogeneous mixture.

Solvation is the process in which the solvent molecules interact with solute particles.

The **solvent** is the substance responsible for the phase of a solution. If one of the components of a solution is a liquid, then the liquid is considered the solvent.

An **sp hybrid orbital** is one of the two orbitals obtained by mixing one s and one p orbital on an atom. The two sp hybrids are separated by 180° .

An **sp² hybrid orbital** is one of the three orbitals obtained by mixing one s and two p orbitals on an atom. The three sp² hybrids lie in plane and are separated by 120° .

An **sp³ hybrid orbital** one of the four orbitals obtained by mixing one s and three p orbitals on an atom. The four sp³ hybrids point toward the corners of a tetrahedron and are separated by 109° .

The **specific heat (s)** of a substance is the amount of heat required to raise the temperature of 1 g of the substance by 1 $^\circ\text{C}$.

Spectator ions are ions in solution that do not undergo reaction. When KCl(aq) is added to $\text{AgNO}_3(\text{aq})$, the Ag^{1+} and Cl^{1-} ions react, but the K^{1+} and NO_3^{1-} ions are spectator ions. Spectator ions are brought into solution as counter ions to the ions that do react.

A **spectrum** is a display of radiant energy arranged in order of it frequency or wavelength.

The **spin quantum number (m_s)** of an electron is $+1/2$ or $-1/2$. It indicates the direction of the magnetic field produced by the electron.

A **spontaneous** process is one that takes place without intervention. $\Delta S_{\text{univ}} > 0$ for all spontaneous

processes, or $\Delta G < 0$ for spontaneous processes at constant temperature and pressure.

The **standard cell potential (E°)** is the cell potential when all reactants and products are in their standard states.

The **standard enthalpy or heat of reaction (ΔH°)** is the enthalpy change for a reaction when it is carried out with all reactants and products in their standard states.

The **standard heat or enthalpy of formation (ΔH_f°)** is the heat absorbed when one mole of a substance is formed from its elements in their standard states.

The **standard hydrogen electrode (SHE)** is a half-cell containing 1 M H^{1+} and 1 atm H_2 . It is used as the reference for standard reduction potentials. The standard reduction potential of the SHE is assigned a value of exactly 0 V.

The **standard reduction potential** of a redox couple is a measure of the free energy of the redox electrons relative to those in a reference couple such as the H^{1+}/H_2 couple. The more positive the standard reduction potential, the lower is the energy of the electrons.

A **standard solution** is a solution of known concentration that is used to determine an unknown concentration.

The **standard state** is a reference state used to compare thermodynamic quantities. It is 1 atm pressure for a gas, a concentration of 1 M for a solute, and the pure substance for a solid or a liquid.

A **state function** is a quantity that depends only upon the initial and final states.

A **stereocenter** in organic chemistry is a carbon atom that has four different groups attached to it.

Stereoisomers have the same connectivities but different spatial arrangements of their atoms.

The **steric factor** in kinetics represents the probability that a collision between the particles in an elementary process have the correct orientation to react.

The **stoichiometric factor** or **link** is the conversion factor in a stoichiometric calculation that converts from one substance into another. It is the ratio of subscripts in a chemical formula or the coefficients in a balanced chemical equation.

Stoichiometry is the study of the conversion from one chemical species into a chemically equivalent amount of another. The conversion is made through the use of chemical formulas or balanced chemical equations.

A **straight** or **continuous chain** is a chain of atoms in which no atom is bound to more than two other atoms in the chain.

A **strong acid** is an acid that reacts extensively with water, *i.e.*, one whose acid dissociation (ionization) constant is much greater than one. Aqueous solutions of strong acids are represented by H_3O^{1+} .

A **strong base** is a base that reacts extensively with water to produce OH^{1-} .

The **sublevel** of an electron is specified by the n and l quantum numbers. It dictates the energy, size, and shape of its orbitals.

Sublimation is the process in which a solid is converted into its vapor.

A **supercritical fluid** is the phase of matter beyond the critical point. It has some properties of the liquid and the gas, but it is neither.

The **surface tension** of a liquid is the energy required to increase its surface area by a fixed amount.

Surroundings See thermodynamic surroundings.

System See thermodynamic system.

T

Temperature is a measure of the average kinetic energy of the molecules in a system.

A **termolecular** process involves three molecules.

The **theoretical yield** is the amount of product predicted from the amount of limiting reactant and the stoichiometry of the reaction.

A **theory** is an explanation of many observations.

Thermal energy is the kinetic energy of a molecule, ion, or atom. Thermal energy depends only upon the temperature.

The **thermal surroundings** is that portion of the surroundings that exchanges heat with the system.

A **thermochemical equation** is a chemical equation that includes a thermodynamic quantity, usually ΔH or ΔG .

Thermochemistry is that branch of thermodynamics that deals with energy change in chemical reactions.

Thermodynamics is the study of energy and its transformations.

The **thermodynamic region** of a reaction is after equilibrium has been established.

The **thermodynamic surroundings** is that part of the universe that exchanges energy with the system.

A **thermodynamic system** is that part of the universe that is under investigation.

The **thermodynamic universe** is the system and its surroundings.

A **thermonuclear** reaction is a nuclear reaction that requires a large input of energy for initiation. Fusion reactions are thermonuclear.

The **third law of thermodynamics** states that the entropy of a perfect crystal at 0K is zero.

The **titrant** is the solution whose volume is determined in a titration.

In a **titration**, the volume of one solution of known concentration (the titrant) that is required to react with another solution (the analyte) is determined in order to find the concentration of the analyte.

A **titration curve** is a plot of the pH of the solution versus the volume of titrant.

The **torr** is a unit of pressure. A pressure of 1 torr supports a column of Hg to a height of 1 mm.

A **trans** configuration is one in which two groups are on opposite sides of a bond or atom.

A **transition element** or **metal** is an element (metal) in the d-block (B groups) of the periodic table.

The **transition state** is the highest energy species through which the reactants must pass in order to make the transition to the products.

Translational degrees of freedom are the straight-line motions of a particle. All straight line motion can be expressed as a sum of x, y, and z components, so all molecules have three translational degrees of freedom.

The **triple point** is the temperature and pressure at which the solid, liquid, and vapor states of a substance are in equilibrium.

U

The **uncertainty principle** states that it is impossible to know both the position and speed of subatomic particles to high accuracy. In order to measure one more accurately, you must lose accuracy in the other.

A **unimolecular** process involves only one particle.

A **unit cell** is the simplest arrangement of particles that generates the entire lattice when translated in all three dimensions.

Unsaturated carbon atoms are involved in less than four sigma bonds.

V

The **valence band** is the highest energy filled band containing the valence electrons of a metal.

In **valence bond theory**, bonds arise from the overlap of orbitals on adjacent atoms. The orbitals can be either atomic or hybridized.

Valence electrons are those outermost electrons that dictate the properties of the atom and are involved in chemical bonding. They reside in the outermost s sublevel and any unfilled sublevels.

Valence-shell electron-pair repulsion (VSEPR) theory is used to explain molecular shapes in terms of electron regions adopting the spatial orientation that minimizes the electron-electron repulsions between them.

The **Van't Hoff factor (*i*)** relates the colligative concentration to the concentration of the solute. For example, $m_c = im$.

The **van der Waals radius** is one-half of the distance between identical, nonbonded atoms in a crystal. Atoms that are closer than the sum of their van der Waals radii are assumed to be interacting.

Vaporization is the process by which a liquid is converted into its vapor.

The **vapor pressure** of a liquid is the pressure of its vapor in equilibrium with the liquid at a given temperature.

Vapor pressure lowering (ΔP) is amount by which the vapor pressure of a solvent is reduced by the addition of a volatile solute.

Vibrational degrees of freedom of a molecule are the relative motions of its atoms that result in small oscillating changes in bond lengths and angles.

Viscosity is the resistance of a liquid to flow.

Void space is unoccupied space.

The **volt** is the SI unit of electrical potential.
 $1 \text{ V} = 1 \text{ J}\cdot\text{C}^{-1}$.

W

The **wave function** of an electron is a function that contains all of the information about the electron.

The **wavelength (λ)** is the distance between two corresponding points on a wave.

Wave-particle duality is a term used to indicate that photons (light) and very small particles, such as electrons, behave as both particles and waves.

A **weak acid** is an acid that does not react extensively with water, *i.e.*, it is an acid with a dissociation constant that is much less than one.

A **weak base** is a substance that reacts only slightly with water to produce hydroxide ions.

A **weak electrolyte** is a substance whose aqueous solution conducts only a small current of electricity because only a small fraction of weak electrolyte molecules produce ions in water.

Work (*w*) is a force through a distance, $w = fd$. Thus, something must move, and there must be a resistance to the movement in order for work to be done. By definition, the symbol *w* is the work done ON the system, and *-w* is the work done BY the system.

X

X-ray diffraction is a technique in which x-rays are scattered from atoms in the solid to determine the distances between the atoms and ions in the crystal.

Z

Zeolites are aluminosilicates built from tetrahedral AlO_4 and SiO_4 units bridged by oxygen atoms. They are filled with channels and pores, which provide many uses for the material.

Useful tables

Select a table in the bookmark panel to navigate to it.

- Acid-Base Table (Table 12.3)
- Bond Energies and Bond Lengths (Table 5.3)
- Electronegativites (Table 5.1)
- Polyatomic Ions (Table 4.1)
- Prefixes for covalent compounds (Table 5.2)
- Roots for Simple Organic Compounds (Table 13.1)
- Solubility Rules for Ionic Compounds in Water (Table 10.4)
- Standard Reduction Potentials (Table 11.1)