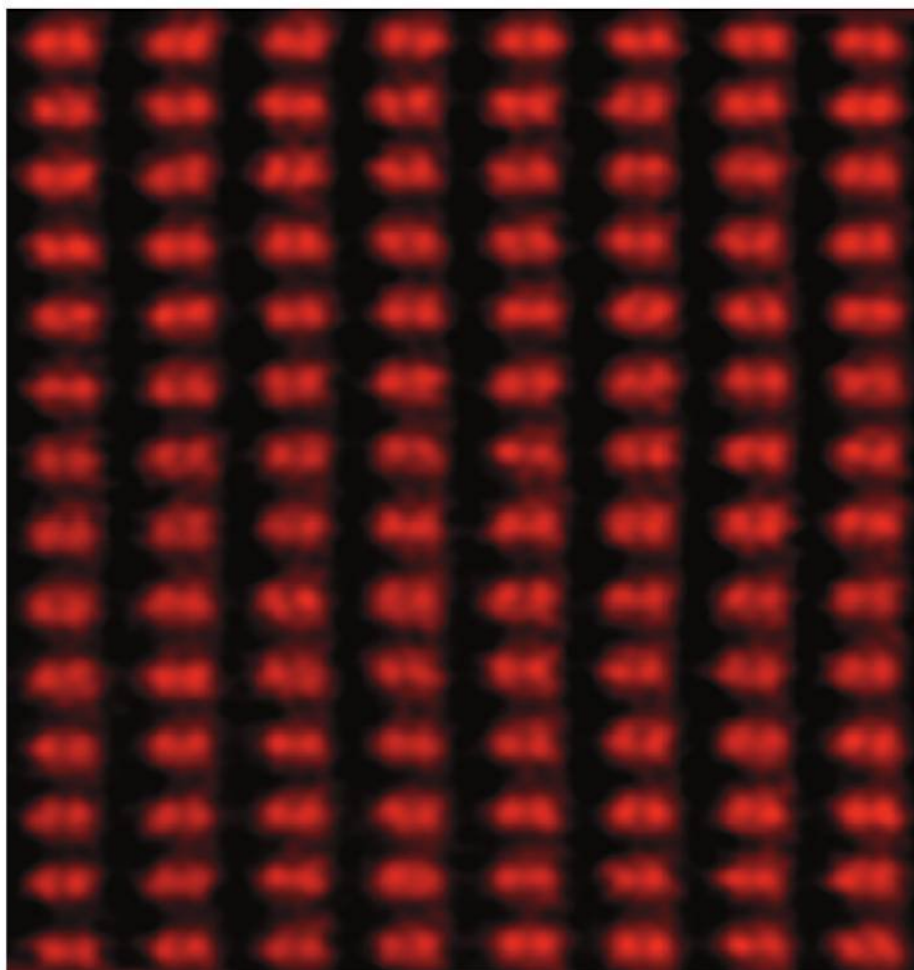# 2

Atoms and the Atomic Theory

CONTENTS

Image of silicon atoms that are only 78 pm apart; image produced by using a scanning transmission electron microscope (STEM). The hypothesis that all matter is made up of atoms has existed for more than 2000 years. It is only within the last few decades, however, that techniques have been developed that can render individual atoms visible.

We begin this chapter with a brief survey of early chemical discoveries, culminating in Dalton's atomic theory. This is followed by a description of the physical evidence leading to the modern picture of the *nuclear atom*, in which protons and neutrons are combined into a nucleus with electrons in space surrounding the nucleus. We will also introduce the periodic table as the primary means of organizing elements into groups with similar properties. Finally, we will introduce the concept

of the mole and the Avogadro constant, which are the principal tools for counting atoms and molecules and measuring amounts of substances. We will use these tools throughout the text.

2-1   Early Chemical Discoveries and the Atomic Theory

Chemistry has been practiced for a very long time, even if its practitioners were much more interested in its applications than in its underlying principles. The blast furnace for extracting iron from iron ore appeared as early as A.D. 1300, and such important chemicals as sulfuric acid (oil of vitriol), nitric acid (aqua fortis), and sodium sulfate (Glauber's salt) were all well known and used several hundred years ago. Before the end of the eighteenth century, the principal gases of the atmosphere—nitrogen and oxygen—had been isolated, and natural laws had been proposed describing the physical behavior of gases. Yet chemistry cannot be said to have entered the modern age until the process of combustion was explained. In this section, we explore the direct link between the explanation of combustion and Dalton's atomic theory.
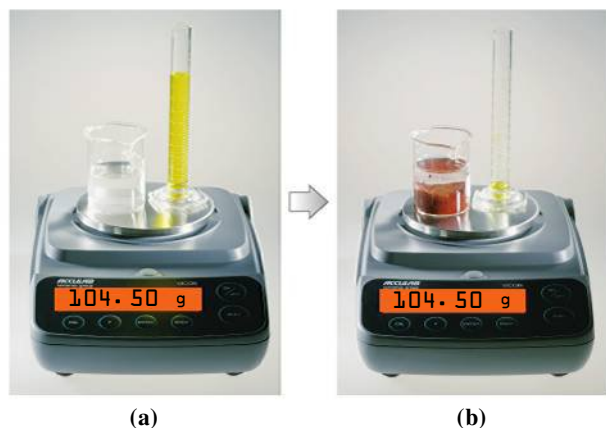
Law of Conservation of Mass

The process of combustion—burning—is so familiar that it is hard to realize what a difficult riddle it posed for early scientists. Some of the difficult-to-explain observations are described in Figure 2-1.

In 1774, Antoine Lavoisier (1743–1794) performed an experiment in which he heated a sealed glass vessel containing a sample of tin and some air. He found that the mass before heating (glass vessel + tin + air) and after heating (glass vessel + "tin calx" + remaining air) were the same. Through further experiments, he showed that the product of the reaction, tin calx (tin oxide), consisted of the original tin together with a portion of the air. Experiments like this proved to Lavoisier that oxygen from air is essential to combustion, and also led him to formulate the **law of conservation of mass**:

> The total mass of substances present after a chemical reaction is the same as the total mass of substances before the reaction.

This law is illustrated in Figure 2-2, where the reaction between silver nitrate and potassium chromate to give a red solid (silver chromate) is monitored by placing the reactants on a single-pan balance—the total mass does not change. Stated another way, the law of conservation of mass says that matter is neither created nor destroyed in a chemical reaction.

▲ FIGURE 2-1
Two combustion reactions
The apparent product of the combustion of the match—the ash—weighs *less* than the match. The product of the combustion of the magnesium ribbon (the "smoke") weighs *more* than the ribbon. Actually, in each case, the total mass remains unchanged. To understand this, you have to know that oxygen gas enters into both combustions and that water and carbon dioxide are also products of the combustion of the match.

(a)   **(b)**

◄ FIGURE 2-2
Mass is conserved during a chemical reaction
(a) Before the reaction, a beaker with a silver nitrate solution and a graduated cylinder with a potassium chromate solution are placed on a single-pan balance, which displays their combined mass—104.50 g. **(b)** When the solutions are mixed, a chemical reaction occurs that forms silver chromate (red precipitate) in a potassium nitrate solution. Note that the total mass—104.50 g—remains unchanged.

EXAMPLE 2-1   Applying the Law of Conservation of Mass

A 0.455 g sample of magnesium is allowed to burn in 2.315 g of oxygen gas. The sole product is magnesium oxide. After the reaction, no magnesium remains and the mass of unreacted oxygen is 2.015 g. What mass of magnesium oxide is produced?

Analyze

The total mass is unchanged. The total mass is the sum of the masses of the substances present initially. The mass of magnesium oxide is the total mass minus the mass of unreacted oxygen.

Solve

First, determine the total mass before the reaction.

$$\text{mass before reaction} = 0.455 \text{ g magnesium} + 2.315 \text{ g oxygen}$$
$$= 2.770 \text{ g mass before reaction}$$

The total mass after the reaction is the same as before the reaction.

$$2.770 \text{ g mass after reaction} = \text{? g magnesium oxide after reaction}$$
$$+ 2.015 \text{ g oxygen after reaction}$$
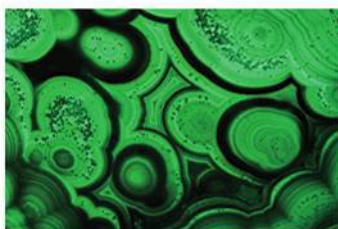
Solve for the mass of magnesium oxide.

$$\text{? g magnesium oxide after reaction} = 2.770 \text{ g mass after reaction}$$
$$- 2.015 \text{ g oxygen after reaction}$$
$$= 0.755 \text{ g magnesium oxide after reaction}$$

Assess

Here is another approach. The mass of oxygen that reacted is 2.315 g − 2.015 g = 0.300 g. Thus, 0.300 g oxygen combined with 0.455 g magnesium to give 0.300 g + 0.455 g = 0.755 g magnesium oxide.

PRACTICE EXAMPLE A: A 0.382 g sample of magnesium is allowed to react with 2.652 g of nitrogen gas. The sole product is magnesium nitride. After the reaction, the mass of unreacted nitrogen is 2.505 g. What mass of magnesium nitride is produced?

PRACTICE EXAMPLE B: A 7.12 g sample of magnesium is heated with 1.80 g of bromine. All the bromine is used up, and 2.07 g of magnesium bromide is the only product. What mass of magnesium remains *unreacted*?

(a)

🔍   **2-1**   **CONCEPT ASSESSMENT**

Jan Baptista van Helmont (1579–1644) weighed a young willow tree and the soil in which the tree was planted. Five years later he found that the mass of soil had decreased by only 0.057 kg, while that of the tree had increased by 75 kg. During that period he had added only water to the bucket in which the tree was planted. Helmont concluded that essentially all the mass gained by the tree had come from the water. Was this a valid conclusion? Explain.

(b)

▲ The mineral malachite **(a)** and the green patina on a copper roof **(b)** are both basic copper carbonate, just like the basic copper carbonate prepared by Proust in 1799.

Law of Constant Composition

In 1799, Joseph Proust (1754–1826) reported, "One hundred pounds of copper, dissolved in sulfuric or nitric acids and precipitated by the carbonates of soda or potash, invariably gives 180 pounds of green carbonate."* This and similar observations became the basis of the **law of constant composition**, or the **law of definite proportions**:

All samples of a compound have the same composition—the same proportions by mass of the constituent elements.

To see how the law of constant composition works, consider the compound water. Water is made up of two atoms of hydrogen (H) for every atom of oxygen (O), a fact that can be represented symbolically by a *chemical formula*, the familiar H_2O.

*The substance Proust produced is actually a more complex substance called *basic* copper carbonate. Proust's results were valid because, like all compounds, basic copper carbonate has a constant composition.

The two samples described below have the same proportions of the two elements, expressed as percentages by mass. To determine the percent by mass of hydrogen, for example, simply divide the mass of hydrogen by the sample mass and multiply by 100%. For each sample, you will obtain the same result: 11.19% H.

Sample A and Its Composition		Sample B and Its Composition	
10.000 g		27.000 g	
1.119 g H	% H = 11.19	3.021 g H	% H = 11.19
8.881 g O	% O = 88.81	23.979 g O	% O = 88.81

EXAMPLE 2-2   Using the Law of Constant Composition

In Example 2-1 we found that when 0.455 g of magnesium reacted with 2.315 g of oxygen, 0.755 g of magnesium oxide was obtained. Determine the mass of magnesium contained in a 0.500 g sample of magnesium oxide.

Analyze

We know that 0.755 g of magnesium oxide contains 0.455 g of magnesium. According to the law of constant composition, the mass ratio 0.455 g magnesium/0.755 g magnesium oxide should exist in all samples of magnesium oxide.

Solve

Application of the law of constant composition gives

$$\frac{0.455 \text{ g magnesium}}{0.755 \text{ g magnesium oxide}} = \frac{? \text{ g magnesium}}{0.500 \text{ g magnesium oxide}}$$

Solving the expression above, we obtain

$$? \text{ g magnesium} = 0.500 \text{ g magnesium oxide} \times \frac{0.455 \text{ g magnesium}}{0.755 \text{ g magnesium oxide}}$$

$$= 0.301 \text{ g magnesium}$$

Assess

You can also work this problem by using mass percentages. If 0.755 g of magnesium oxide contains 0.455 g of magnesium, then magnesium oxide is $(0.455 \text{ g}/0.755 \text{ g}) \times 100\% = 60.3\%$ magnesium by mass and $(100\% - 60.3\%) = 39.7\%$ oxygen by mass. Thus, a 0.500 g sample of magnesium oxide must contain $0.500 \text{ g} \times 60.3\% = 0.301$ g of magnesium and $0.500 \text{ g} \times 39.7\% = 0.199$ g of oxygen.

PRACTICE EXAMPLE A: What masses of magnesium and oxygen must be combined to make exactly 2.000 g of magnesium oxide?

PRACTICE EXAMPLE B: What substances are present, and what are their masses, after the reaction of 10.00 g of magnesium and 10.00 g of oxygen?

2-2   CONCEPT ASSESSMENT

When 4.15 g magnesium and 82.6 g bromine react, (1) all the magnesium is used up, (2) some bromine remains unreacted, and (3) magnesium bromide is the only product. With this information alone, is it possible to deduce the mass of magnesium bromide produced? Explain.

Dalton's Atomic Theory

From 1803 to 1808, John Dalton, an English schoolteacher, used the two fundamental laws of chemical combination just described as the basis of an atomic theory. His theory involved three assumptions:

1. Each chemical element is composed of minute, indivisible particles called atoms. Atoms can be neither created nor destroyed during a chemical change.

▲ John Dalton (1766–1844), developer of the atomic theory. Dalton has not been considered a particularly good experimenter, perhaps because of his color blindness (a condition sometimes called daltonism). However, he did skillfully use the data of others in formulating his atomic theory. (The Granger Collection)

KEEP IN MIND

that all we know is that the second oxide is twice as rich in oxygen as the first. If the first is CO, the possibilities for the second are CO_2, C_2O_4, C_3O_6, and so on. (See also Exercise 18.)

▲ FIGURE 2-3
Molecules CO and CO_2 illustrating the law of multiple proportions
The mass of carbon is the same in the two molecules, but the mass of oxygen in CO_2 is twice the mass of oxygen in CO. Thus, in accordance with the law of multiple proportions, the masses of oxygen in the two compounds, relative to a fixed mass of carbon, are in a ratio of small whole numbers, 2:1.

2. All atoms of an element are alike in mass (weight) and other properties, but the atoms of one element are different from those of all other elements.

3. In each of their compounds, different elements combine in a simple numerical ratio, for example, one atom of A to one of B (AB), or one atom of A to two of B (AB_2).

If atoms of an element are indestructible (assumption 1), then the *same* atoms must be present after a chemical reaction as before. The total mass remains unchanged. Dalton's theory explains the law of conservation of mass. If all atoms of an element are alike in mass (assumption 2) and if atoms unite in *fixed* numerical ratios (assumption 3), the percent composition of a compound must have a unique value, regardless of the origin of the sample analyzed. Dalton's theory also explains the law of constant composition.

Like all good theories, Dalton's atomic theory led to a prediction—the **law of multiple proportions**.

> If two elements form more than a single compound, the masses of one element combined with a fixed mass of the second are in the ratio of small whole numbers.

To illustrate, consider two oxides of carbon (an oxide is a combination of an element with oxygen). In one oxide, 1.000 g of carbon is combined with 1.333 g of oxygen, and in the other, with 2.667 g of oxygen. We see that the second oxide is richer in oxygen; in fact, it contains twice as much oxygen as the first, 2.667 g/1.333 g = 2.00. We now know that the first oxide corresponds to the formula CO and the second, CO_2 (Fig. 2-3).

The characteristic relative masses of the atoms of the various elements became known as atomic weights, and throughout the nineteenth century, chemists worked at establishing reliable values of relative atomic weights. Mostly, however, chemists directed their attention to discovering new elements, synthesizing new compounds, developing techniques for analyzing materials, and in general, building up a vast body of chemical knowledge. Efforts to unravel the structure of the atom became the focus of physicists, as we see in the next several sections.

2-2 Electrons and Other Discoveries in Atomic Physics

Fortunately, we can acquire a qualitative understanding of atomic structure without having to retrace all the discoveries that preceded atomic physics. We do, however, need a few key ideas about the interrelated phenomena of electricity and magnetism, which we briefly discuss here. Electricity and magnetism were used in the experiments that led to the current theory of atomic structure.

Certain objects display a property called electric charge, which can be either positive (+) or negative (−). Positive and negative charges attract each other, while two positive or two negative charges repel each other. As we learn in this section, all objects of matter are made up of charged particles. An object having equal numbers of positively and negatively charged particles carries no net charge and is electrically neutral. If the number of positive charges exceeds the number of negative charges, the object has a net positive charge. If negative charges exceed positive charges, the object has a net negative charge. Sometimes when one substance is rubbed against another, as in combing hair, net electric charges build up on the objects, implying that rubbing separates
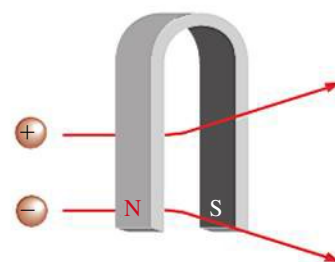
(a)   **(b)**
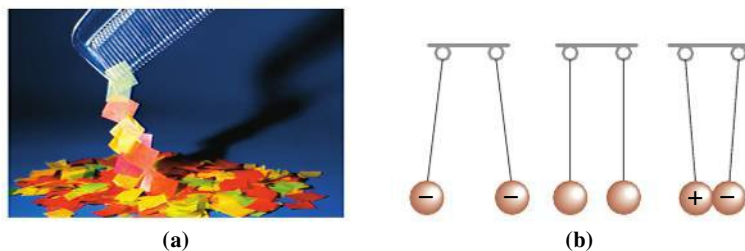
▲ FIGURE 2-4
Forces between electrically charged objects
(a) Electrostatically charged comb. If you comb your hair on a dry day, a static charge develops on the comb and causes bits of paper to be attracted to the comb. **(b)** Both objects on the left carry a negative electric charge. Objects with like charge repel each other. The objects in the center lack any electric charge and exert no forces on each other. The objects on the right carry opposite charges—one positive and one negative—and attract each other.

some positive and negative charges (Fig. 2-4). Moreover, when a stationary (static) positive charge builds up in one place, a negative charge of equal size appears somewhere else; charge is balanced.

Figure 2-5 shows how charged particles behave when they move through the field of a magnet. They are deflected from their straight-line path into a curved path in a plane perpendicular to the field. Think of the field or region of influence of the magnet as represented by a series of invisible "lines of force" running from the north pole to the south pole of the magnet.

The Discovery of Electrons

CRT, the abbreviation for cathode-ray tube, was once a familiar acronym. Before liquid crystal display (LCD) was available, the CRT was the heart of computer monitors and TV sets. The first cathode-ray tube was made by Michael Faraday (1791–1867) about 150 years ago. When he passed electricity through glass tubes from which most of the air had been evacuated, Faraday discovered **cathode rays**, a type of radiation emitted by the negative terminal, or *cathode*. The radiation crossed the evacuated tube to the positive terminal, or *anode*. Later scientists found that cathode rays travel in straight lines and have properties that are independent of the cathode material (that is, whether it is iron, platinum, and so on). The construction of a CRT is shown in Figure 2-6. The cathode rays produced in the CRT are invisible, and they can be detected only by the light emitted by materials that they strike. These materials, called *phosphors*, are painted on the end of the CRT so that the path of the cathode rays can be revealed. (*Fluorescence* is the term used to describe the emission of light by a phosphor when it is struck by
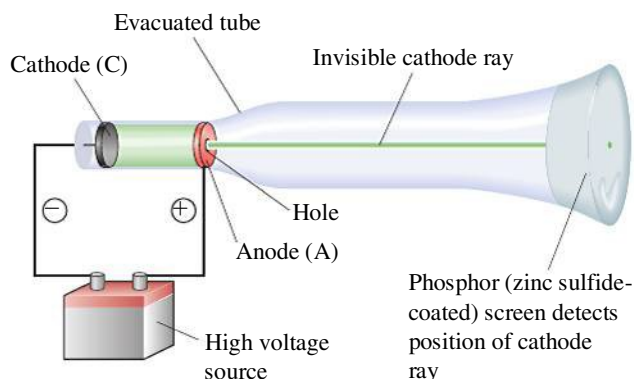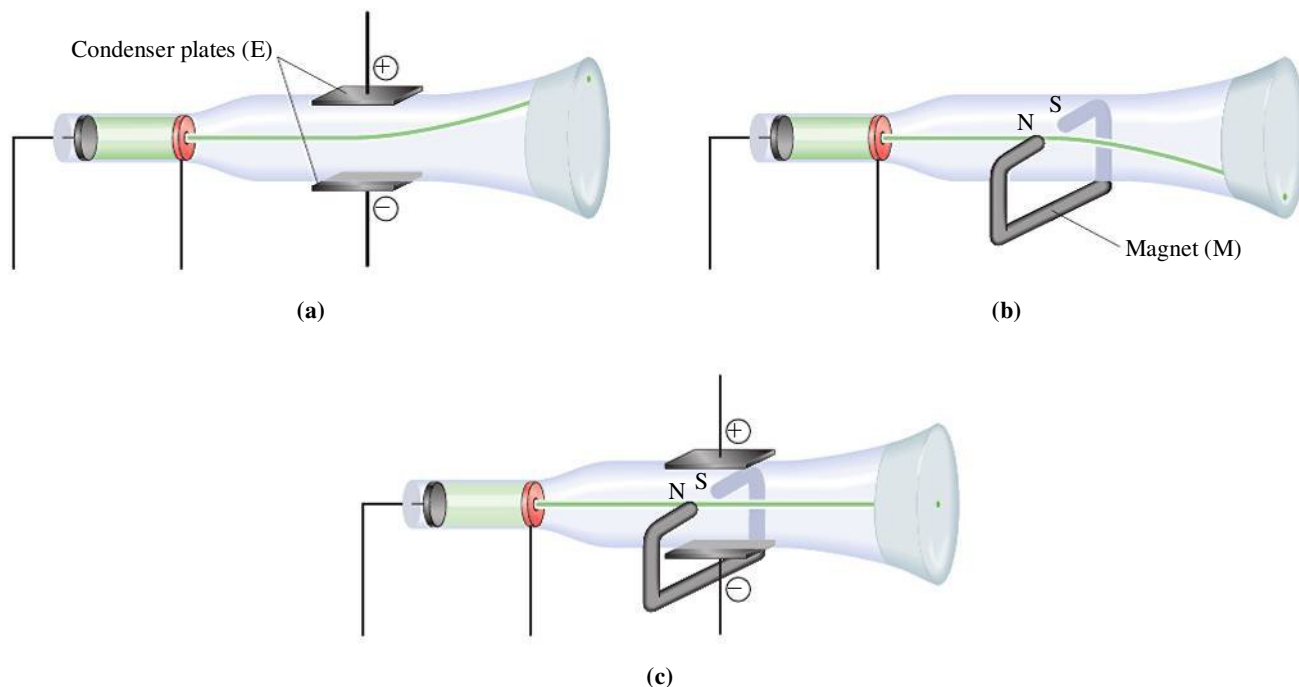

▲ FIGURE 2-5
Effect of a magnetic field on charged particles
When charged particles travel through a magnetic field so that their path is perpendicular to the field, they are deflected by the field. Negatively charged particles are deflected in one direction, and positively charged particles in the opposite direction. Several phenomena described in this section depend on this behavior.

◀ FIGURE 2-6
A cathode-ray tube
The high-voltage source of electricity creates a negative charge on the electrode at the left (cathode) and a positive charge on the electrode at the right (anode). Cathode rays pass from the cathode (C) to the anode (A), which is perforated to allow the passage of a narrow beam of cathode rays. The rays are visible only through the green fluorescence that they produce on the zinc sulfide–coated screen at the end of the tube. They are invisible in other parts of the tube.

(a)

(b)

(c)

▲ FIGURE 2-7
Cathode rays and their properties
(a) Deflection of cathode rays in an electric field. The beam of cathode rays is deflected as it travels from left to right in the field of the electrically charged condenser plates (E). The deflection corresponds to that expected of negatively charged particles.
(b) Deflection of cathode rays in a magnetic field. The beam of cathode rays is deflected as it travels from left to right in the field of the magnet (M). The deflection corresponds to that expected of negatively charged particles. **(c)** Determining the mass-to-charge ratio, m/e, for cathode rays. The cathode-ray beam strikes the end screen undeflected if the forces exerted on it by the electric and magnetic fields are counterbalanced. By knowing the strengths of the electric and magnetic fields, together with other data, a value of m/e can be obtained. Precise measurements yield a value of -5.6857×10^{-9} g per coulomb. (Because cathode rays carry a negative charge, the sign of the mass-to-charge ratio is also negative.)

energetic radiation.) Another significant observation about cathode rays is that they are deflected by electric and magnetic fields in the manner expected for negatively charged particles (Fig. 2-7a, b).

In 1897, by the method outlined in Figure 2-7(c), J. J. Thomson (1856–1940) established the ratio of mass (m) to electric charge (e) for cathode rays, that is, m/e. Also, Thomson concluded that cathode rays are negatively charged *fundamental* particles of matter found in all atoms. (The properties of cathode rays are *independent* of the composition of the cathode.) Cathode rays subsequently became known as **electrons**, a term first proposed by George Stoney in 1874.

Robert Millikan (1868–1953) determined the electronic charge e through a series of oil-drop experiments (1906–1914), described in Figure 2-8. The currently accepted value of the electronic charge e, expressed in coulombs to five significant figures, is -1.6022×10^{-19} C. By combining this value with an accurate value of the mass-to-charge ratio for an electron, we find that the mass of an electron is 9.1094×10^{-28} g.

Once the electron was seen to be a fundamental particle of matter found in all atoms, atomic physicists began to speculate on how these particles were incorporated into atoms. The commonly accepted model was that proposed by J. J. Thomson. Thomson thought that the positive charge necessary to counterbalance the negative charges of electrons in a neutral atom was in the form of

▶ The coulomb (C) is the SI unit of electric charge (see also Appendix B).
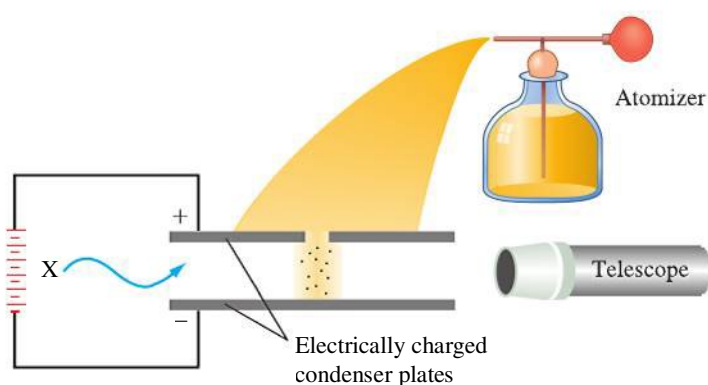
◀ FIGURE 2-8
Millikan's oil-drop experiment
Ions (charged atoms or molecules) are produced by energetic radiation, such as X-rays (X). Some of these ions become attached to oil droplets, giving them a net charge. The fall of a droplet in the electric field between the condenser plates is speeded up or slowed down, depending on the magnitude and sign of the charge on the droplet. By analyzing data from a large number of droplets, Millikan concluded that the magnitude of the charge, q, on a droplet is an *integral* multiple of the electric charge, e. That is, $q = ne$ (where $n = 1, 2, 3, \ldots$).

a nebulous cloud. Electrons, he suggested, floated in a diffuse cloud of positive charge (rather like a lump of gelatin with electron "fruit" embedded in it). This model became known as the plum-pudding model because of its similarity to a popular English dessert. The plum-pudding model is illustrated in Figure 2-9 for a neutral atom and for atomic species, called *ions*, which carry a net charge.

X-Rays and Radioactivity

Cathode-ray research had many important spin-offs. In particular, two natural phenomena of immense theoretical and practical significance were discovered in the course of other investigations.

In 1895, Wilhelm Roentgen (1845–1923) noticed that when cathode-ray tubes were operating, certain materials *outside* the tubes glowed or fluoresced. He showed that this fluorescence was caused by radiation emitted by the cathode-ray tubes. Because of the unknown nature of this radiation, Roentgen coined the term *X-ray*. We now recognize the X-ray as a form of high-energy electromagnetic radiation, which is discussed in Chapter 8.

Antoine Henri Becquerel (1852–1908) associated X-rays with fluorescence and wondered if naturally fluorescent materials produce X-rays. To test this idea, he wrapped a photographic plate with black paper, placed a coin on the paper, covered the coin with a uranium-containing fluorescent material, and exposed the entire assembly to sunlight. When he developed the film, a clear image of the coin could be seen. The fluorescent material had emitted radiation (presumably X-rays) that penetrated the paper and exposed the film. On one occasion, because the sky was overcast, Becquerel placed the experimental assembly inside a desk drawer for a few days while waiting for the weather to clear. On resuming the experiment, Becquerel decided to replace the original photographic film, expecting that it may have become slightly exposed. He developed the original film and found that instead of the expected feeble image, there was a very sharp one. The film had become strongly exposed because the uranium-containing material had emitted radiation continuously, even when it was not fluorescing. Becquerel had discovered **radioactivity**.

Ernest Rutherford (1871–1937) identified two types of radiation from radioactive materials, alpha (α) and beta (β). **Alpha particles** carry two fundamental units of positive charge and have essentially the same mass as helium atoms. In fact, alpha particles are identical to He^{2+} ions. **Beta particles** are negatively charged particles produced by changes occurring within the nuclei of radioactive atoms and have the same properties as electrons. A third form of radiation, which is not affected by electric or magnetic fields, was discovered in 1900 by Paul Villard. This radiation, called **gamma rays** (γ),

Helium atom
He

Helium ion
He^+

Helium ion
He^{2+}
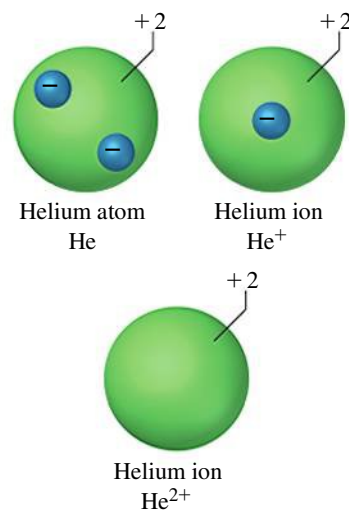
▲ FIGURE 2-9
The plum-pudding atomic model
According to this model, a helium atom would have a $+2$ cloud of positive charge and two electrons (-2). If a helium atom loses one electron, it becomes charged and is called an *ion*. This ion, referred to as He^+, has a net charge of $1+$. If the helium atom loses both electrons, the He^{2+} ion forms.
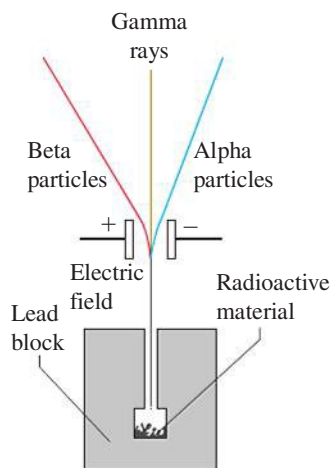
▲ FIGURE 2-10
Three types of radiation from radioactive materials
The radioactive material is enclosed in a lead block. All the radiation except that passing through the narrow opening is absorbed by the lead. When the escaping radiation is passed through an electric field, it splits into three beams. One beam is undeflected—these are gamma (γ) rays. A second beam is attracted to the negatively charged plate. These are the positively charged alpha (α) particles. The third beam, of negatively charged beta (β) particles, is deflected toward the positive plate.

is not made up of particles; it is electromagnetic radiation of extremely high penetrating power. These three forms of radioactivity are illustrated in Figure 2-10.

By the early 1900s, additional radioactive elements were discovered, principally by Marie and Pierre Curie. Rutherford and Frederick Soddy made another profound finding: The chemical properties of a radioactive element *change* as it undergoes radioactive decay. This observation suggests that radioactivity involves fundamental changes at the *subatomic* level—in radioactive decay, one element is changed into another, a process known as *transmutation*.

2-3 The Nuclear Atom

In 1909, Rutherford, with his assistant Hans Geiger, began a line of research using α particles as probes to study the inner structure of atoms. Based on Thomson's plum-pudding model, Rutherford expected that most particles in a beam of α particles would pass through thin sections of matter largely undeflected, but that some α particles would be slightly scattered or deflected as they encountered electrons. By studying these scattering patterns, he hoped to deduce something about the distribution of electrons in atoms.

The apparatus used for these studies is pictured in Figure 2-11. Alpha particles were detected by the flashes of light they produced when they struck a zinc sulfide screen mounted on the end of a telescope. When Geiger and Ernst Marsden, a student, bombarded very thin foils of gold with α particles, they observed the following:

- The majority of α particles penetrated the foil undeflected.
- Some α particles experienced slight deflections.
- A few (about 1 in every 20,000) suffered rather serious deflections as they penetrated the foil.
- A similar number did not pass through the foil at all, but bounced back in the direction from which they had come.

The large-angle scattering greatly puzzled Rutherford. As he commented some years later, this observation was "about as credible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you." By 1911, though, Rutherford had an explanation. He based his explanation on a model of the atom known as the *nuclear atom* and having these features:

1. Most of the mass and all of the positive charge of an atom are centered in a very small region called the *nucleus*. The remainder of the atom is mostly *empty space.*
2. The magnitude of the positive charge is different for different atoms and is approximately one-half the atomic weight of the element.
3. There are as many electrons outside the nucleus as there are units of positive charge on the nucleus. The atom as a whole is electrically neutral.

▶ Perhaps because he found it tedious to sit in the dark and count spots of light on a zinc sulfide screen, Geiger was motivated to develop an automatic radiation detector. The result was the well-known Geiger counter.

▶ FIGURE 2-11
The scattering of α particles by metal foil
The telescope travels in a circular track around an evacuated chamber containing the metal foil. Most α particles pass through the metal foil undeflected, but some are deflected through large angles.

(a) **(b)**
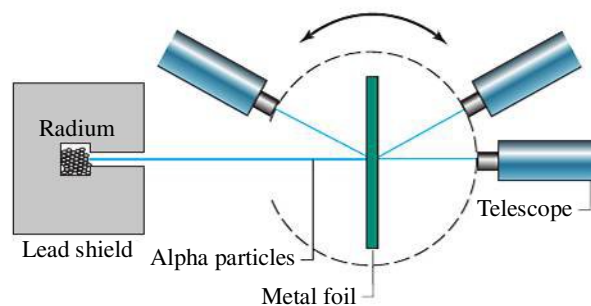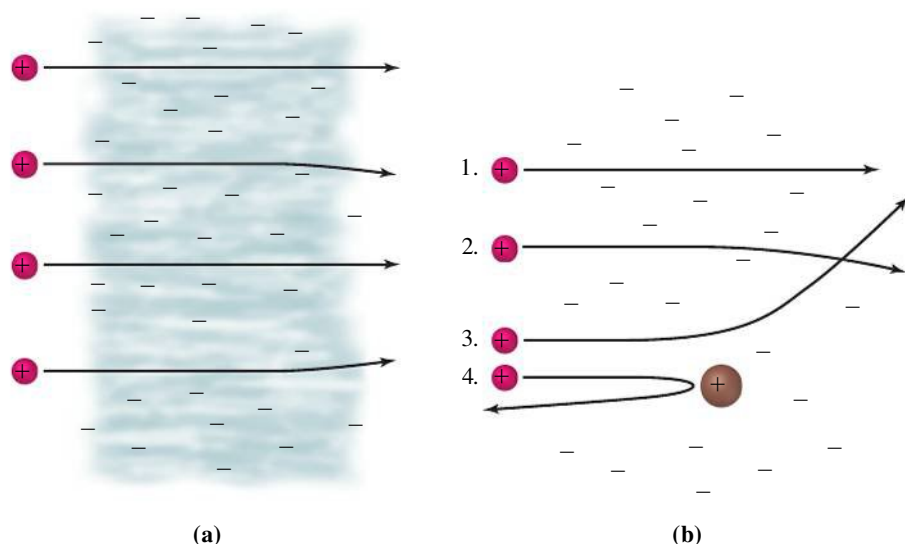
▲ FIGURE 2-12
Explaining the results of α-particle scattering experiments
(a) Rutherford's expectation was that small, positively charged α particles should pass through the nebulous, positively charged cloud of the Thomson plum-pudding model largely undeflected. Some would be slightly deflected by passing near electrons (present to neutralize the positive charge of the cloud). **(b)** Rutherford's explanation was based on a nuclear atom. With an atomic model having a small, dense, positively charged nucleus and extranuclear electrons, we would expect the four different types of paths actually observed:

1. undeflected straight-line paths exhibited by most of the α particles
2. slight deflections of α particles passing close to electrons
3. severe deflections of α particles passing close to a nucleus
4. reflections from the foil of α particles approaching a nucleus head-on

Rutherford's initial expectation and his explanation of the α-particle experiments are described in Figure 2-12.

Discovery of Protons and Neutrons

Rutherford's nuclear atom suggested the existence of positively charged fundamental particles of matter in the nuclei of atoms. Rutherford himself discovered these particles, called **protons**, in 1919 in studies involving the scattering of α particles by nitrogen atoms in air. The protons were freed as a result of collisions between α particles and the nuclei of nitrogen atoms. At about this same time, Rutherford predicted the existence in the nucleus of electrically neutral fundamental particles. In 1932, James Chadwick showed that a newly discovered penetrating radiation consisted of beams of *neutral* particles. These particles, called **neutrons**, originated from the nuclei of atoms. Thus, it has been only for about the past 100 years that we have had the atomic model suggested by Figure 2-13.
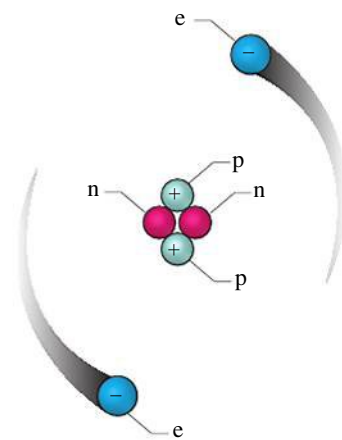
▲ FIGURE 2-13
The nuclear atom— illustrated by the helium atom
In this drawing, electrons are shown much closer to the nucleus than is the case. The actual situation is more like this: If the entire atom were represented by a room, 5 m × 5 m × 5 m, the nucleus would occupy only about as much space as the period at the end of this sentence.

🔍 **2-3 CONCEPT ASSESSMENT**

In light of information presented to this point in the text, explain which of the three assumptions of Dalton's atomic theory (page 37) can still be considered correct and which cannot.

TABLE 2.1   Properties of Three Fundamental Particles

	Electric Charge		Mass	
	SI (C)	Atomic	SI (g)	Atomic (u)[a]
Proton	$+1.6022 \times 10^{-19}$	$+1$	1.6726×10^{-24}	1.0073
Neutron	0	0	1.6749×10^{-24}	1.0087
Electron	-1.6022×10^{-19}	-1	9.1094×10^{-28}	0.00054858

[a]u is the SI symbol for atomic mass unit (abbreviated as amu).

▶ The masses of the proton and neutron are different in the fourth significant figure. The charges of the proton and electron, however, are believed to be exactly equal in magnitude (but opposite in sign). The charges and masses are known much more precisely than suggested here. More precise values are given on the inside back cover.

Properties of Protons, Neutrons, and Electrons

The number of protons in a given atom is called the **atomic number**, or the **proton number, Z**. The number of electrons in the atom is also equal to Z because the atom is electrically neutral. The total number of protons and neutrons in an atom is called the **mass number, A**. The number of neutrons, the **neutron number**, is $A - Z$. An electron carries an atomic unit of negative charge, a proton carries an atomic unit of positive charge, and a neutron is electrically neutral. Table 2.1 presents the charges and masses of protons, neutrons, and electrons in two ways.

The **atomic mass unit** (described more fully on page 46) is defined as exactly 1/12 of the mass of the atom known as carbon-12 (read as carbon twelve). An atomic mass unit is abbreviated as amu and denoted by the symbol u. As we see from Table 2.1, the proton and neutron masses are just slightly greater than 1 u. By comparison, the mass of an electron is only about 1/2000th the mass of the proton or neutron.

The three subatomic particles considered in this section are the only ones involved in the phenomena of interest to us in this text. You should be aware, however, that a study of matter at its most fundamental level must consider many additional subatomic particles. The electron is believed to be a truly fundamental particle. However, modern particle physics now considers the neutron and proton to be composed of other, more fundamental particles.

2-4   Chemical Elements

Now that we have acquired some fundamental ideas about atomic structure, we can more thoroughly discuss the concept of chemical elements.

All atoms of a particular element have the same atomic number, Z, and, conversely, all atoms with the same number of protons are atoms of the same element. The elements shown on the inside front cover have atomic numbers from $Z = 1$ to $Z = 112$. Each element has a name and a distinctive symbol. **Chemical symbols** are one- or two-letter abbreviations of the name (usually the English name). The first (but never the second) letter of the symbol is capitalized; for example: carbon, C; oxygen, O; neon, Ne; and silicon, Si. Some elements known since ancient times have symbols based on their Latin names, such as Fe for iron (*ferrum*) and Pb for lead (*plumbum*). The element sodium has the symbol Na, based on the Latin *natrium* for sodium carbonate. Potassium has the symbol K, based on the Latin *kalium* for potassium carbonate. The symbol for tungsten, W, is based on the German *wolfram*.

Elements beyond uranium ($Z = 92$) do not occur naturally and must be synthesized in particle accelerators (described in Chapter 25). Elements of the very highest atomic numbers have been produced only on a limited number of occasions, a few atoms at a time. Inevitably, controversies have arisen about

▶ The discovery of element 112 has recently been authenticated by IUPAC. However, element 112 has not yet been given a name or symbol.

▶ Other atomic symbols not based on English names include Cu, Ag, Sn, Sb, Au, and Hg.
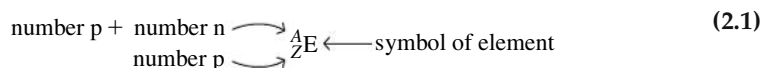
which research team discovered a new element and, in fact, whether a discovery was made at all. However, international agreement has been reached on the first 112 elements; each one, except element 112, has an official name and symbol.
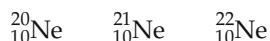
Isotopes

To represent the composition of any particular atom, we need to specify its number of protons (p), neutrons (n), and electrons (e). We can do this with the symbolism

$$\text{number p} + \text{number n} \longrightarrow {}^{A}_{Z}\text{E} \longleftarrow \text{symbol of element}$$

$$\text{number p} \longrightarrow \qquad \qquad \qquad \qquad \qquad \qquad \text{(2.1)}$$

This symbolism indicates that the atom is element E and that it has atomic number Z and mass number A. For example, an atom of aluminum represented as ${}^{27}_{13}\text{Al}$ has 13 protons and 14 neutrons in its nucleus and 13 electrons outside the nucleus. (Recall that an atom has the same number of electrons as protons.)
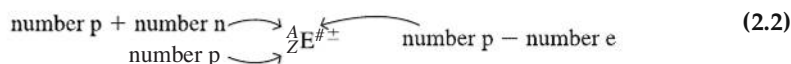
   Contrary to what Dalton thought, we now know that atoms of an element do not necessarily all have the same mass. In 1912, J. J. Thomson measured the mass-to-charge ratios of positive ions formed from neon atoms. From these ratios he deduced that about 91% of the atoms had one mass and that the remaining atoms were about 10% heavier. All neon atoms have 10 protons in their nuclei, and most have 10 neutrons as well. A very few neon atoms, however, have 11 neutrons and some have 12. We can represent these three different types of neon atoms as

$$ {}^{20}_{10}\text{Ne} \qquad {}^{21}_{10}\text{Ne} \qquad {}^{22}_{10}\text{Ne} $$

   Atoms that have the *same* atomic number (Z) but *different* mass numbers (A) are called **isotopes**. Of all Ne atoms on Earth, 90.51% are ${}^{20}_{10}\text{Ne}$. The percentages of ${}^{21}_{10}\text{Ne}$ and ${}^{22}_{10}\text{Ne}$ are 0.27% and 9.22%, respectively. These percentages—90.51%, 0.27%, 9.22%—are the **percent natural abundances** of the three neon isotopes. Sometimes the mass numbers of isotopes are incorporated into the names of elements, such as neon-20 (neon twenty). Percent natural abundances are always based on *numbers*, not masses. Thus, 9051 of every 10,000 neon atoms are neon-20 atoms. Some elements, as they exist in nature, consist of just a single type of atom and therefore do not have naturally occurring isotopes.* Aluminum, for example, consists only of aluminum-27 atoms.

Ions

When atoms lose or gain electrons, for example, in the course of a chemical reaction, the species formed are called **ions** and carry net charges. Because an electron is negatively charged, adding electrons to an electrically neutral atom produces a negatively charged ion. Removing electrons results in a positively charged ion. The number of protons does not change when an atom becomes an ion. For example, ${}^{20}\text{Ne}^{+}$ and ${}^{22}\text{Ne}^{2+}$ are ions. The first one has 10 protons, 10 neutrons, and *9* electrons. The second one also has 10 protons, but 12 neutrons and *8* electrons. The charge on an ion is equal to the number of protons *minus* the number of electrons. That is

$$\text{number p} + \text{number n} \longrightarrow {}^{A}_{Z}\text{E}^{\#\pm} \qquad \text{number p} - \text{number e}$$

$$\text{number p} \longrightarrow \qquad \qquad \qquad \qquad \qquad \qquad \text{(2.2)}$$

   Another example is the ${}^{16}\text{O}^{2-}$ ion. In this ion, there are 8 protons (atomic number 8), 8 neutrons (mass number − atomic number), and *10* electrons ($8 - 10 = -2$).

──────────

*   *Nuclide* is the general term used to describe an atom with a particular atomic number and mass number. Although there are several elements with only one naturally occurring nuclide, it is possible to produce additional nuclides of these elements—isotopes—by artificial means (Section 25-3). The artificial isotopes are radioactive, however. In all, the number of synthetic isotopes exceeds the number of naturally occurring ones by several fold.

◀ Because neon is the only element with $Z = 10$, the symbols ${}^{20}\text{Ne}$, ${}^{21}\text{Ne}$, and ${}^{22}\text{Ne}$ convey the same meaning as ${}^{20}_{10}\text{Ne}$, ${}^{21}_{10}\text{Ne}$, and ${}^{22}_{10}\text{Ne}$.

◀ Odd-numbered elements tend to have fewer isotopes than do even-numbered elements. Section 25-7 will explain why.

◀ Usually all the isotopes of an element share the same name and atomic symbol. The exception is hydrogen. Isotope ${}^{2}_{1}\text{H}$ is called deuterium (symbol D), and ${}^{3}_{1}\text{H}$ is tritium (T).

◀ In this expression, #± indicates that the charge is written with the number (#) *before* the + or − sign. However, when the charge is 1+ or 1−, the number 1 is not included.

EXAMPLE 2-3   Relating the Numbers of Protons, Neutrons, and Electrons in Atoms and Ions

Through an appropriate symbol, indicate the number of protons, neutrons, and electrons in **(a)** an atom of barium-135 and **(b)** the double negatively charged ion of selenium-80.

Analyze

Given the name of an element, we can find the symbol and the atomic number, Z, for that element from a list of elements or a periodic table. To determine the number of protons, neutrons, and electrons, we make use of the following relationships:

$$Z = \text{number p} \qquad A = \text{number p} + \text{number n} \qquad \text{charge} = \text{number p} - \text{number e}$$

The relationships above are summarized in expression (2.2).

Solve

(a) We are given the name (barium) and the mass number of the atom (135). From a list of the elements or a periodic table we obtain the symbol (Ba) and the atomic number ($Z = 56$), leading to the symbolic representation

$$^{135}_{56}\text{Ba}$$

From this symbol one can deduce that the neutral atom has 56 protons; a neutron number of $A - Z = 135 - 56 = 79$ neutrons; and a number of electrons equal to Z, that is, 56 electrons.

(b) We are given the name (selenium) and the mass number of the ion (80). From a list of the elements or a periodic table we obtain the symbol (Se) and the atomic number (34). Together with the fact that the ion carries a charge of $2-$, we have the data required to write the symbol

$$^{80}_{34}\text{Se}^{2-}$$

From this symbol, we can deduce that the ion has 34 protons; a neutron number of $A - Z = 80 - 34 = 46$ neutrons; and 36 electrons, leading to a net charge of $+34 - 36 = -2$.

Assess

When writing the symbol for a particular atom or ion, we often omit the atomic number. For example, for $^{135}_{56}\text{Ba}$ and $^{80}_{34}\text{Se}^{2-}$, we often use the simpler representations ^{135}Ba and $^{80}\text{Se}^{2-}$.

PRACTICE EXAMPLE A: Use the notation $^{A}_{Z}\text{E}$ to represent the isotope of silver having a neutron number of 62.

PRACTICE EXAMPLE B: Use the notation $^{A}_{Z}\text{E}$ to represent a tin ion having the same number of electrons as an atom of the isotope cadmium-112. Explain why there can be more than one answer.


🔍 2-4   CONCEPT ASSESSMENT

What is the single exception to the statement that all atoms comprise protons, neutrons, and electrons?

▶ Ordinarily we expect like-charged objects (such as protons) to repel each other. The forces holding protons and neutrons together in the nucleus are very much stronger than ordinary electrical forces (Section 25-6).

▶ This definition also establishes that one atomic mass unit (1 u) is *exactly* 1/12 the mass of a carbon-12 atom.

Isotopic Masses

We cannot determine the mass of an individual atom just by adding up the masses of its fundamental particles. When protons and neutrons combine to form a nucleus, a very small portion of their original mass is converted to energy and released. However, we cannot predict exactly how much this so-called nuclear binding energy will be. Determining the masses of individual atoms, then, is something that must be done by experiment, in the following way. By international agreement, one type of atom has been chosen and assigned a specific mass. This standard is an atom of the isotope carbon-12, which is assigned a mass of exactly 12 atomic mass units, that is, 12 u. Next, the masses of other atoms relative to carbon-12 are determined with a **mass spectrometer**. In this device, a beam of gaseous ions passing through electric and magnetic fields separates into components of differing masses. The

196 198 200 202 204

Mass spectrum of
mercury vapor

Detector

Stream of
positive ions
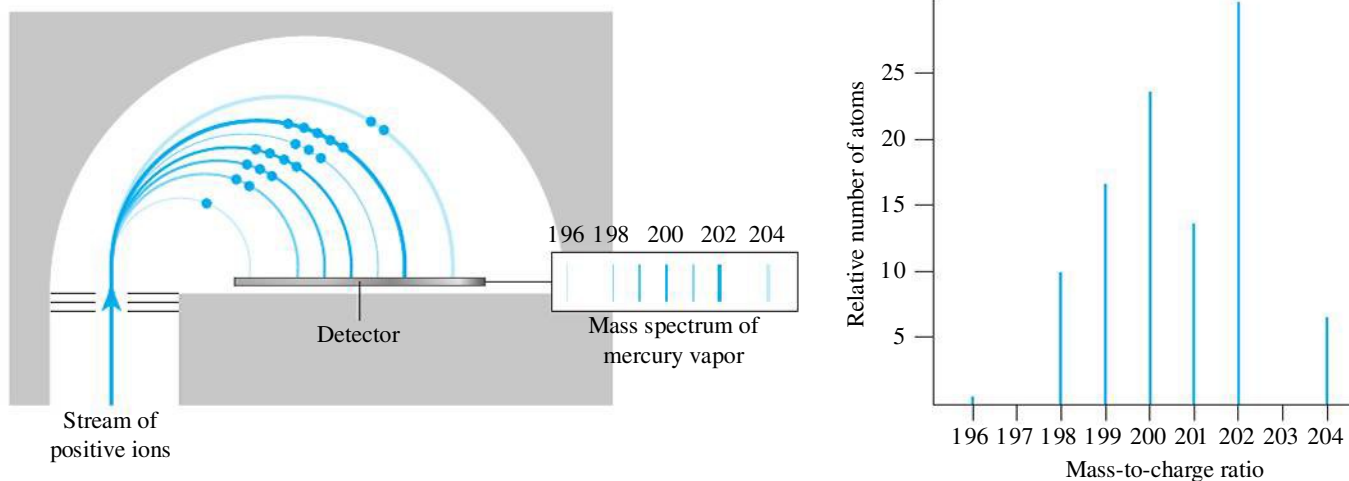
▲ FIGURE 2-14
A mass spectrometer and mass spectrum
In this mass spectrometer, a gaseous sample is ionized by bombardment with electrons in the lower part of the apparatus (not shown). The positive ions thus formed are subjected to an electrical force by the electrically charged velocity selector plates and a magnetic force by a magnetic field perpendicular to the page. Only ions with a particular velocity pass through and are deflected into circular paths by the magnetic field. Ions with different masses strike the detector (here a photographic plate) in different regions. The more ions of a given type, the greater the response of the detector (intensity of line on the photographic plate). In the mass spectrum shown for mercury, the response of the ion detector (intensity of lines on photographic plate) has been converted to a scale of relative numbers of atoms. The percent natural abundances of the mercury isotopes are ^{196}Hg, 0.146%; ^{198}Hg, 10.02%; ^{199}Hg, 16.84%; ^{200}Hg, 23.13%; ^{201}Hg, 13.22%; ^{202}Hg, 29.80%; and ^{204}Hg, 6.85%.

◄ The primary standard for atomic masses has evolved over time. For example, Dalton originally assigned H a mass of 1 u. Later, chemists took naturally occurring oxygen at 16 u to be the definition of the atomic-weight scale. Concurrently, physicists defined the oxygen-16 isotope as 16 u. This resulted in conflicting values. In 1971 the adoption of carbon-12 as the universal standard resolved this disparity.

separated ions are focused on a measuring instrument, which records their presence and amounts. Figure 2-14 illustrates mass spectrometry and a typical mass spectrum.

Although mass numbers are whole numbers, the actual masses of individual atoms (in atomic mass units, u) are never whole numbers, except for carbon-12. However, they are very close in value to the corresponding mass numbers, as we can see for the isotope oxygen-16. From mass spectral data the ratio of the mass of ^{16}O to ^{12}C is found to be 1.33291. Thus, the mass of the oxygen-16 atom is

$$1.33291 \times 12 \text{ u} = 15.9949 \text{ u}$$

which is very nearly equal to the mass number of 16.

EXAMPLE 2-4   **Establishing Isotopic Masses by Mass Spectrometry**

With mass spectral data, the mass of an oxygen-16 atom is found to be 1.06632 times that of a nitrogen-15 atom. Given that ^{16}O has a mass of 15.9949 u (see above), what is the mass of a nitrogen-15 atom, in u?

Analyze

Given the ratio (mass of ^{16}O)/(mass of ^{15}N) = 1.06632 and the mass of ^{16}O, 15.9949 u, we solve for the mass of ^{15}N.

Solve

We know that

$$\frac{\text{mass of } ^{16}\text{O}}{\text{mass of } ^{15}\text{N}} = 1.06632$$

(continued)

We solve the expression above for the mass of ^{15}N and then substitute 15.9949 u for the mass of ^{16}O. We obtain the result

$$\text{mass of }^{15}N = \frac{\text{mass of }^{16}O}{1.06632} = \frac{15.9949 \text{ u}}{1.06632} = 15.0001 \text{ u}$$

Assess

The mass of ^{15}N is very nearly 15, as we should expect. If we had mistakenly multiplied instead of dividing by the ratio 1.06632, the result would have been slightly larger than 16 and clearly incorrect.

PRACTICE EXAMPLE A: What is the ratio of masses for $^{202}Hg/^{12}C$, if the isotopic mass for ^{202}Hg is 201.97062 u?

PRACTICE EXAMPLE B: An isotope with atomic number 64 and mass number 158 is found to have a mass ratio relative to that of carbon-12 of 13.16034. What is the isotope, what is its atomic mass in u, and what is its mass relative to oxygen-16?

2-5 Atomic Mass

▶ Carbon-14, used for radiocarbon dating, is formed in the upper atmosphere. The amount of carbon-14 on Earth is too small to affect the atomic mass of carbon.

KEEP IN MIND

that the fractional abundance is the percent abundance divided by 100%. Thus, a 98.93% abundance is a 0.9893 abundance.

In a table of atomic masses, the value listed for carbon is 12.0107, yet the atomic mass standard is *exactly* 12. Why the difference? The atomic mass standard is based on a sample of carbon containing only atoms of carbon-12, whereas naturally occurring carbon contains some carbon-13 atoms as well. The existence of these two isotopes causes the observed atomic mass to be greater than 12. The **atomic mass (weight)*** of an element is the average of the isotopic masses, *weighted* according to the naturally occurring abundances of the isotopes of the element. In a weighted average, we must assign greater importance—give greater weight—to the quantity that occurs more frequently. Since carbon-12 atoms are much more abundant than carbon-13, the weighted average must lie much closer to 12 than to 13. This is the result that we get by applying the following general equation, where the right-hand side of the equation includes one term for each naturally occurring isotope.

$$\begin{array}{l}\text{at. mass}\\\text{of an}\\\text{element}\end{array} = \left(\begin{array}{l}\text{fractional}\\\text{abundance of}\\\text{isotope 1}\end{array} \times \begin{array}{l}\text{mass of}\\\text{isotope 1}\end{array}\right) + \left(\begin{array}{l}\text{fractional}\\\text{abundance of}\\\text{isotope 2}\end{array} \times \begin{array}{l}\text{mass of}\\\text{isotope 2}\end{array}\right) + \dots \quad \textbf{(2.3)}$$

The first term on the right side of equation (2.3) represents the contribution from isotope 1; the second term represents the contribution from isotope 2; and so on.

We will use equation (2.3), with appropriate data, in Example 2-6, but first let us illustrate the ideas of fractional abundance and a weighted average in a different way in establishing the atomic mass of naturally occurring carbon. The mass spectrum of carbon shows that 98.93% of carbon atoms are carbon-12 with a mass of exactly 12 u; the rest are carbon-13 atoms with a mass of 13.0033548378 u. Therefore:

$$\begin{array}{l}\text{at. mass of naturally}\\\text{occurring carbon}\end{array}$$
$$= 0.9893 \times 12 \text{ u} + (1 - 0.9893) \times 13.0033548378 \text{ u}$$
$$= 13.0033548378 \text{ u} - 0.9893 \times (13.0033548378 \text{ u} - 12 \text{ u})$$
$$= 13.0033548378 \text{ u} - 0.9893 \times (1.0033548378 \text{ u})$$
$$= 13.0033548378 \text{ u} - 0.9893$$
$$= 12.0107 \text{ u}$$

*Since Dalton's time, atomic masses have been called atomic weights. They still are by most chemists, yet what we are describing here is mass, not weight. Old habits die hard.

It is important to note that, in the setup above, 12 u and the "1" appearing in the factor $(1 - 0.9893)$ are exact numbers. Thus, by applying the rules for significant figures (see Chapter 1), the atomic mass of carbon can be reported with four decimal places.

To determine the atomic mass of an element having three naturally occurring isotopes, such as potassium, we would have to include three contributions in the weighted average, and so on.

The percent natural abundances of most of the elements remain very nearly constant from one sample of matter to another. For example, the proportions of ^{12}C and ^{13}C atoms are the same in samples of pure carbon (diamond), carbon dioxide gas, and a mineral form of calcium carbonate (calcite). We can treat all natural carbon-containing materials as if there were a single *hypothetical* type of carbon atom with a mass of 12.0107 u. This means that once weighted-average atomic masses have been determined and tabulated, we can simply use these values in calculations requiring atomic masses.

Sometimes a qualitative understanding of the relationship between isotopic masses, percent natural abundances, and weighted-average atomic mass is all that we need, and no calculation is necessary, as illustrated in Example 2-5. Example 2-6 and the accompanying Practice Examples provide additional applications of equation (2.3).

The table of atomic masses (inside the front cover) shows that some atomic masses are stated more precisely than others. For example, the atomic mass of F is given as 18.9984 u and that of Kr is given as 83.798 u. In fact, the atomic mass of fluorine is known even more precisely (18.9984032 u); the value of 18.9984 u has been rounded off to six significant figures. Why is the atomic mass of F known so much more precisely than that of Kr? Only one type of fluorine atom occurs naturally: fluorine-19. Determining the atomic mass of

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EXAMPLE 2-5   Understanding the Meaning of a Weighted-Average Atomic Mass

The two naturally occurring isotopes of lithium, lithium-6 and lithium-7, have masses of 6.01512 u and 7.01600 u, respectively. Which of these two occurs in greater abundance?

Analyze

Look up the atomic mass of Li and compare it with the masses of ^6Li and ^7Li. If the atomic mass of Li is closer to that of ^6Li, then ^6Li is the more abundant isotope. If the atomic mass of Li is closer to that of ^7Li, then ^7Li is the more abundant isotope.

Solve

From a table of atomic masses (inside the front cover), we see that the atomic mass of lithium is 6.941 u. Because this value—a weighted-average atomic mass—is much closer to 7.01600 u than to 6.01512 u, lithium-7 must be the more abundant isotope.

Assess

Atomic masses of specific isotopes can be determined very precisely. The values given above for ^6Li and ^7Li have been rounded to five decimal places. The precise values are 6.015122795 u and 7.01600455 u.

PRACTICE EXAMPLE A: The two naturally occurring isotopes of boron, boron-10 and boron-11, have masses of 10.0129370 u and 11.0093054 u, respectively. Which of these two occurs in greater abundance?

PRACTICE EXAMPLE B: Indium has two naturally occurring isotopes and a weighted atomic mass of 114.818 u. One of the isotopes has a mass of 112.904058 u. Which of the following must be the second isotope: ^{111}In, ^{112}In, ^{114}In, or ^{115}In? Which of the two naturally occurring isotopes must be the more abundant?

EXAMPLE 2-6 **Relating the Masses and Natural Abundances of Isotopes to the Atomic Mass of an Element**

Bromine has two naturally occurring isotopes. One of them, bromine-79, has a mass of 78.9183 u and an abundance of 50.69%. What must be the mass and percent natural abundance of the other, bromine-81?

Analyze

Although the atomic mass of Br is not given explicitly, it is a known quantity. From the inside front cover, we find that the atomic mass of Br is 79.904 u. We need to apply two key concepts: (1) the atomic mass of Br is a weighted average of the masses of ^{79}Br and ^{81}Br, and (2) the percent natural abundances of ^{79}Br and ^{81}Br must add up to 100%.

Solve

The atomic mass of Br is a weighted average of the masses of ^{79}Br and ^{81}Br:

$$\text{atomic mass} = \begin{pmatrix} \text{fraction of atoms} \\ \text{that are } ^{79}\text{Br} \times \\ \text{mass of } ^{79}\text{Br} \end{pmatrix} + \begin{pmatrix} \text{fraction of atoms} \\ \text{that are } ^{81}\text{Br} \times \\ \text{mass of } ^{81}\text{Br} \end{pmatrix}$$

Because the percent natural abundances must total 100%, the percent natural abundance of ^{81}Br is 100% − 50.69% = 49.31%. Substituting 79.904 u for the atomic mass, 78.9183 u for the mass of ^{79}Br, and the fractional abundances of the two isotopes, we obtain

$$79.904 \text{ u} = (0.5069 \times 78.9183 \text{ u}) + (0.4931 \times \text{mass of } ^{81}\text{Br})$$

$$= 40.00 \text{ u} + (0.4931 \times \text{mass of } ^{81}\text{Br})$$

$$\text{mass of } ^{81}\text{Br} = \frac{79.904 \text{ u} - 40.00 \text{ u}}{0.4931} = 80.92 \text{ u}$$

To four significant figures, the natural abundance of the bromine-81 isotope is 49.31% and its mass is 80.92 u.

Assess

We can check the final result by working the problem in reverse and using numbers that are slightly rounded. The atomic mass of Br is 50.69% × 78.92 u + 49.31% × 80.92 u ≈ $\frac{1}{2}$(79 u + 81 u) = 80 u. The estimated atomic mass (80 u) is close to the actual atomic mass of 79.904 u.

PRACTICE EXAMPLE A: The masses and percent natural abundances of the three naturally occurring isotopes of silicon are ^{28}Si, 27.9769265325 u, 92.223%; ^{29}Si, 28.976494700 u, 4.685%; ^{30}Si, 29.973377017 u, 3.092%. Calculate the weighted-average atomic mass of silicon.

PRACTICE EXAMPLE B: Use data from Example 2-5 to determine the percent natural abundances of lithium-6 and lithium-7.

fluorine means establishing the mass of this type of atom as precisely as possible. The atomic mass of krypton is known less precisely because krypton has six naturally occurring isotopes. Because the percent distribution of the isotopes of krypton differs very slightly from one sample to another, the weighted-average atomic mass of krypton cannot be stated with high precision.
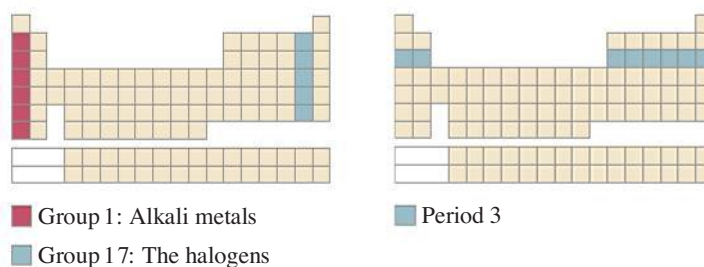
🔍 **2-5   CONCEPT ASSESSMENT**

The value listed for chromium in the table of atomic masses inside the front cover is 51.9961 u. Should we conclude that naturally occurring chromium atoms are all of the type $^{52}_{24}$Cr? The same table lists a value of 65.409 u for zinc. Should we conclude that zinc occurs as a mixture of isotopes? Explain.

2-6   Introduction to the Periodic Table

Scientists spend a lot of time organizing information into useful patterns. Before they can organize information, however, they must possess it, and it must be correct. Botanists had enough information about plants to organize their field in the eighteenth century. Because of uncertainties in atomic masses and because many elements remained undiscovered, chemists were not able to organize the elements until a century later.

We can distinguish one element from all others by its particular set of observable physical properties. For example, sodium has a low density of 0.971 g/cm^3 and a low melting point of 97.81 °C. No other element has this same combination of density and melting point. Potassium, though, also has a low density (0.862 g/cm^3) and low melting point (63.65 °C), much like sodium. Sodium and potassium further resemble each other in that both are good conductors of heat and electricity, and both react vigorously with water to liberate hydrogen gas. Gold, conversely, has a density (19.32 g/cm^3) and melting point (1064 °C) that are very much higher than those of sodium or potassium, and gold does not react with water or even with ordinary acids. It does resemble sodium and potassium in its ability to conduct heat and electricity, however. Chlorine is very different still from sodium, potassium, and gold. It is a gas under ordinary conditions, which means that the melting point of solid chlorine (−101 °C) is far below room temperature. Also, chlorine is a nonconductor of heat and electricity.

Even from these very limited data, we get an inkling of a useful classification scheme of the elements. If the scheme is to group together elements with similar properties, then sodium and potassium should appear in the same group. And if the classification scheme is in some way to distinguish between elements that are good conductors of heat and electricity and those that are not, chlorine should be set apart from sodium, potassium, and gold. The classification system we need is the one shown in Figure 2-15 (and inside the front cover), known as the **periodic table** of the elements. In

▲ FIGURE 2-15
Periodic table of the elements
Atomic masses are relative to carbon-12. For certain radioactive elements, the numbers listed in parentheses are the mass numbers of the most stable isotopes. Metals are shown in tan, nonmetals in blue, and metalloids in green. The noble gases (also nonmetals) are shown in pink.

KEEP IN MIND

that the periodic table shown in Figure 2-15 is the one currently recommended by IUPAC. The discovery of element 112 has recently been authenticated by IUPAC (in May 2009) but the element has not yet been named. Elements with atomic numbers greater than 112 have been reported but not fully authenticated. In Figure 2-15, lutetium (Lu) and lawrencium (Lr) are the last members of the lanthanide and actinide series, respectively. A strong argument* has been made for placing Lu and Lr in group 3, meaning the lanthanide series would end with ytterbium (Yb) and the actinide series would end with nobelium (Nb). To date, IUPAC has not endorsed placing Lu and Lr in group 3.

* See W. B. Jensen, *J. Chem. Educ.*, **59**, 634 (1982).

Chapter 9, we will describe how the periodic table was formulated, and we will also learn its theoretical basis. For the present, we will consider only a few features of the table.

Features of the Periodic Table   In the periodic table, elements are listed according to increasing atomic number starting at the upper left and arranged in a series of horizontal rows. This arrangement places similar elements in *vertical* **groups**, or **families**. For example, sodium and potassium are found together in a group labeled 1 (called the *alkali metals*). We should expect other members of the group, such as cesium and rubidium, to have properties similar to sodium and potassium. Chlorine is found at the other end of the table in a group labeled 17. Some of the groups are given distinctive names, mostly related to an important property of the elements in the group. For example, the group 17 elements are called the *halogens*, a term derived from Greek, meaning "salt former."

▶ That elements in one group have similar properties is perhaps the most useful simplifying feature of atomic properties. Significant differences within a group do occur. The manner and reason for such differences is much of what we try to discover in studying chemistry.

■ Group 1: Alkali metals   ■ Period 3
■ Group 17: The halogens

Each element is listed in the periodic table by placing its symbol in the middle of a box in the table. The atomic number (Z) of the element is shown above the symbol, and the weighted-average atomic mass of the element is shown below its symbol. Some periodic tables provide other information, such as density and melting point, but the atomic number and atomic mass are generally sufficient for our needs. Elements with atomic masses in parentheses, such as plutonium, Pu (244), are produced synthetically, and the number shown is the mass number of the most stable isotope.

It is customary also to divide the elements into two broad categories—**metals** and **nonmetals**. In Figure 2-15, colored backgrounds are used to distinguish the metals (tan) from the nonmetals (blue and pink). Except for mercury, a liquid, metals are solids at room temperature. They are generally malleable (capable of being flattened into thin sheets), ductile (capable of being drawn into fine wires), and good conductors of heat and electricity, and have a lustrous or shiny appearance. The properties of nonmetals are generally opposite those of metals; for example, nonmetals are poor conductors of heat and electricity. Several of the nonmetals, such as nitrogen, oxygen, and chlorine, are gases at room temperature. Some, such as silicon and sulfur, are brittle solids. One—bromine—is a liquid.

▶ There is lack of agreement on just which elements to label as metalloids. However, they are generally considered either to lie adjacent to the stair-step line or to be close by.

Two other highlighted categories in Figure 2-15 are a special group of nonmetals known as the **noble gases** (pink), and a small group of elements, often called **metalloids** (green), that have some metallic and some nonmetallic properties.

The *horizontal* rows of the table are called **periods**. (The periods are numbered at the extreme left in the periodic table inside the front cover.) The first period of the table consists of just two elements, hydrogen and helium. This is followed by two periods of eight elements each, lithium through neon and sodium through argon. The fourth and fifth periods contain 18 elements each, ranging from potassium through krypton and from rubidium through xenon. The sixth period is a long one of 32 members. To fit this period in a table that is held to a maximum width of 18 members, 15 members of the period are placed at the bottom of the periodic table. This series of 15 elements start with lanthanum ($Z = 57$), and these elements are called the **lanthanides**. The seventh and final period is incomplete (some members are yet to be discovered), but it is known to be a long one. A 15-member series is also extracted from the

seventh period and placed at the bottom of the table. Because the elements in this series start with actinium ($Z = 89$), they are called the **actinides**.

The labeling of the groups of the periodic table has been a matter of some debate among chemists. The 1-18 numbering system used in Figure 2-15 is the one most recently adopted. Group labels previously used in the United States consisted of a letter and a number, closely following the method adopted by Mendeleev, the developer of the periodic table. As seen in Figure 2-15, the A groups 1 and 2 are separated from the remaining A groups (3 to 8) by B groups 1 through 8. The International Union of Pure and Applied Chemistry (IUPAC) recommended the simple 1 to 18 numbering scheme in order to avoid confusion between the American number and letter system and that used in Europe, where some of the A and B designations were switched! Currently, the IUPAC system is officially recommended by the American Chemical Society (ACS) and chemical societies in other nations. Because both numbering systems are in use, we show both in Figure 2-15 and in the periodic table inside the front cover. However, except for an occasional reminder of the earlier system, we will use the IUPAC numbering system in this text.

◄ Mendeleev's arrangement of the elements in the original periodic table was based on observed chemical and physical properties of the elements and their compounds. The arrangement of the elements in the modern periodic table is based on atomic properties–atomic number and electron configuration.

Useful Relationships from the Periodic Table

The periodic table helps chemists describe and predict the properties of chemical compounds and the outcomes of chemical reactions. Throughout this text, we will use it as an aid to understanding chemical concepts. One application of the table worth mentioning here is how it can be used to predict likely charges on simple monatomic ions.

Main-group elements are those in groups 1, 2, and 13 to 18. When main-group metal atoms in groups 1 and 2 form ions, they lose the same number of electrons as the IUPAC group number. Thus, Na atoms (group 1) lose one electron to become Na^+, and Ca atoms (group 2) lose two electrons to

---

EXAMPLE 2-7   Describing Relationships Based on the Periodic Table

Refer to the periodic table on the inside front cover, and indicate

    (a) the element that is in group 14 and the fourth period;
    (b) two elements with properties similar to those of molybdenum (Mo);
    (c) the ion most likely formed from a strontium atom.

Analyze

For **(a)**, the key concept is that the rows (periods) are numbered 1 through 7, starting from the top of the periodic table, and the groups are numbered 1 through 18, starting from the left side. For **(b)**, the key concept is that elements in the same group have similar properties. For **(c)**, the key concept is that main-group metal atoms in groups 1 and 2 form positive ions with charges of +1 and +2, respectively.

Solve

    (a) The elements in the fourth period range from K ($Z = 19$) to Kr ($Z = 36$). Those in group 14 are C, Si, Ge, Sn, and Pb. The only element that is common to both of these groupings is Ge ($Z = 32$).
    (b) Molybdenum is in group 6. Two other members of this group that should resemble it are chromium (Cr) and tungsten (W).
    (c) Strontium (Sr) is in group 2. It should form the ion Sr^{2+}.

Assess

In Chapter 8, we will examine in greater detail reasons for the arrangement of the periodic table.

PRACTICE EXAMPLE A: Write a symbol for the ion most likely formed by an atom of each of the following: Li, S, Ra, F, I, and Al.

PRACTICE EXAMPLE B: Classify each of the following elements as a main-group or transition element. Also, specify whether they are metals, metalloids, or nonmetals: Na, Re, S, I, Kr, Mg, U, Si, B, Al, As, H.

become Ca^{2+}. Aluminum, in group 13, loses three electrons to form Al^{3+} (here the charge is "group number minus 10"). The few other metals in groups 13 and higher form more than one possible ion, a matter that we deal with in Chapter 9.

When nonmetal atoms form ions, they gain electrons. The number of electrons gained is normally 18 minus the IUPAC group number. Thus, an O atom gains $18 - 16 = 2$ electrons to become O^{2-}, and a Cl atom gains $18 - 17 = 1$ electron to become Cl^-. The "18 minus group number" rule suggests that an atom of Ne in group 18 gains no electrons: $18 - 18 = 0$. The very limited tendency of the noble gas atoms to form ions is one of several characteristics of this family of elements.

The elements in groups 3 to 12 are the **transition elements**, and because all of them are metals, they are also called the **transition metals**. Like the main-group metals, the transition metals form positive ions, but the number of electrons lost is not related in any simple way to the group number, mostly because transition metals can form two or more ions of differing charge.

2-7   The Concept of the Mole and the Avogadro Constant

Starting with Dalton, chemists have recognized the importance of relative numbers of atoms, as in the statement that *two* hydrogen atoms and *one* oxygen atom combine to form *one* molecule of water. Yet it is physically impossible to count every atom in a macroscopic sample of matter. Instead, some other measurement must be employed, which requires a relationship between the measured quantity, usually mass, and some known, but uncountable, number of atoms. Consider a practical example of mass substituting for a desired number of items. Suppose you want to nail down new floorboards on the deck of a mountain cabin, and you have calculated how many nails you will need. If you have an idea of how many nails there are in a pound, then you can buy the nails by the pound.

The SI quantity that describes an amount of substance by relating it to a number of particles of that substance is called the *mole* (abbreviated *mol*). A **mole** is the amount of a substance that contains the same number of elementary entities as there are atoms in exactly 12 g of pure carbon-12. The "number of elementary entities (atoms, molecules, and so on)" in a mole is the **Avogadro constant, N_A.**

▶ Because the value of Avogadro's number depends, in part, on a measurement, the value has changed slightly over the years. The values recommended since 1986 by the Committee on Data for Science and Technology (CODATA) are listed below.

Year	Avogadro's Number
1986	6.0221367×10^{23}
1998	$6.02214199 \times 10^{23}$
2002	6.0221415×10^{23}
2006	$6.02214179 \times 10^{23}$

$$N_A = 6.02214179 \times 10^{23} \ mol^{-1} \qquad \text{(2.4)}$$

The Avogadro constant consists of a number, $6.02214179 \times 10^{23}$, known as Avogadro's *number*, and a unit, mol^{-1}. The unit mol^{-1} signifies that the entities being counted are those present in 1 mole.

The value of Avogadro's number is based on both a definition and a measurement. A mole of carbon-12 is *defined* to be 12 g. If the mass of one carbon-12 atom is *measured* by using a mass spectrometer (see Figure 2-14), the mass would be about 1.9926×10^{-23} g. The ratio of these two masses provides an estimate of Avogadro's number. In actual fact, accurate determinations of Avogadro's number make use of other measurements, not the measurement of the mass of a single atom of carbon-12.

Often the value of N_A is rounded off to $6.022 \times 10^{23} \ mol^{-1}$, or even to $6.02 \times 10^{23} \ mol^{-1}$.

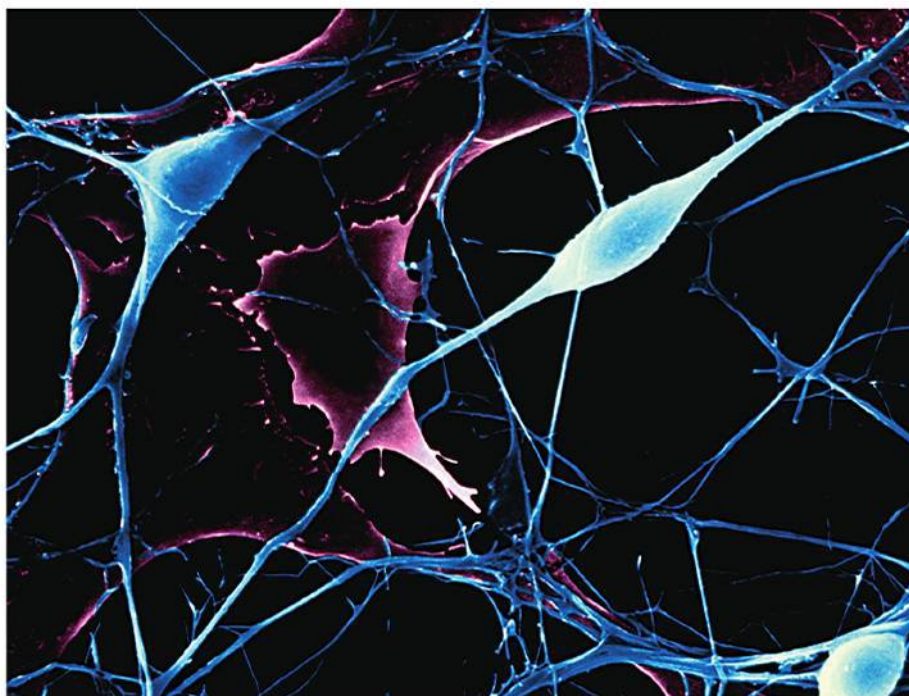If a substance contains atoms of only a single isotope, then

▶ When rounding Avogadro's number or any other accurately known value, keep one more significant figure than that of the least accurate number in the calculation to avoid rounding errors.

$$1 \ mol \ ^{12}C = 6.02214 \times 10^{23} \ ^{12}C \ atoms = 12.0000 \ g$$
$$1 \ mol \ ^{16}O = 6.02214 \times 10^{23} \ ^{16}O \ atoms = 15.9949 \ g \ (and \ so \ on)$$

8

CONTENTS

Electrons in Atoms

This image of two neurons (gray objects) is produced by an electron microscope that relies on the wave properties of electrons discussed in this chapter.

At the end of the nineteenth century, some observers of the scientific scene believed that it was nearly time to close the books on the field of physics. They thought that with the accumulated knowledge of the previous two or three centuries, the main work left to be done was to apply this body of physics—classical physics—to such fields as chemistry and biology.

Only a few fundamental problems remained, including an explanation of certain details of light emission and a phenomenon known as the photoelectric effect. But the solution to these problems, rather than marking an end in the study of physics, spelled the beginning of a new golden age of physics. These problems were solved through a bold new proposal—the quantum theory—a scientific breakthrough of epic proportions. In this chapter, we will see that to explain phenomena at the atomic and molecular level, classical physics is inadequate—only the quantum theory will do.

The aspect of quantum mechanics emphasized in this chapter is how electrons are described through features known as quantum numbers and electron orbitals. The model of atomic structure developed here will explain many of the topics discussed in the next several chapters: periodic

trends in the physical and chemical properties of the elements, chemical bonding, and intermolecular forces.

8-1   Electromagnetic Radiation

Our understanding of the electronic structures of atoms will be gained by studying the interactions of electromagnetic radiation and matter. The chapter begins with background information about electromagnetic radiation, and then turns to connections between electromagnetic radiation and atomic structure. The best approach to learning material in this chapter is to concentrate on the basic ideas relating to atomic structure, many of which are illustrated through the in-text examples. At the same time, pursue further details of interest in some of the Are You Wondering features and portions of Sections 8-6, 8-8, and 8-10.

Electromagnetic radiation is a form of energy transmission in which electric and magnetic fields are propagated as waves through empty space (a vacuum) or through a medium, such as glass. A **wave** is a disturbance that transmits energy through space or a material medium. Anyone who has sat in a small boat on a large body of water has experienced wave motion. The wave moves across the surface of the water, and the disturbance alternately lifts the boat and allows it to drop. Although water waves may be more familiar, let us use a simpler example to illustrate some important ideas and terminology about waves—a traveling wave in a rope.

◄ Water waves, sound waves, and seismic waves (which produce earthquakes) are unlike electromagnetic radiation. They require a material medium for their transmission.

Imagine tying one end of a long rope to a post and holding the other end in your hand (Fig. 8-1). Imagine also that you have marked one small segment of the rope with red ink. As you move your hand up and down, you set up a wave motion in the rope. The wave travels along the rope toward the distant post, but the colored segment simply moves up and down. In relation to the center line (the broken line in Figure 8-1), the wave consists of *crests*, or high points, where the rope is at its greatest height above the center line, and *troughs*, or low points, where the rope is at its greatest depth below the center line. The maximum height of the wave above the center line or the maximum depth below is called the **amplitude**. The distance between the tops of two successive crests (or the bottoms of two troughs) is called the **wavelength**, designated by the Greek letter lambda, λ.

Wavelength is one important characteristic of a wave. Another feature, **frequency**, designated by the Greek letter nu, ν, is the number of crests or troughs that pass through a given point per unit of time. Frequency has the unit, time^{-1}, usually s^{-1} (per second), meaning the number of events or cycles per second. The product of the length of a wave (λ) and the frequency (ν) shows how far the wave front travels in a unit of time. This is the speed of the wave. Thus, if the wavelength in Figure 8-1 were 0.5 m and the frequency, 3 s^{-1} (meaning three complete up-and-down hand motions per second), the speed of the wave would be 0.5 m $\times$ 3 s^{-1} = 1.5 m/s.

We cannot actually see an electromagnetic wave as we do the traveling wave in a rope, but we can try to represent it as in Figure 8-2. As the figure shows, the magnetic field component lies in a plane perpendicular to the electric field component. An electric field is the region around an electrically charged particle. The presence of an electric field can be detected by measuring the force on an electrically charged object when it is brought into the field. A magnetic field is found in the region surrounding a magnet. According to a theory proposed by James Clerk Maxwell (1831–1879) in 1865, electromagnetic radiation—a propagation of electric and magnetic fields—is produced by an accelerating electrically charged particle (a charged particle whose velocity changes). Radio waves, for example, are a form of electromagnetic radiation produced by causing oscillations (fluctuations) of the electric current in a specially designed electrical circuit. With visible light, another
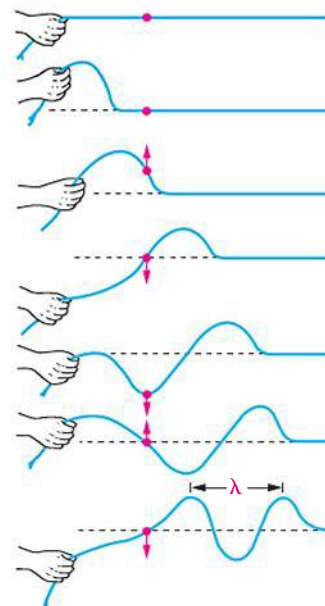
▲ FIGURE 8-1
The simplest wave motion—traveling wave in a rope
As a result of the up-and-down hand motion (top to bottom), waves pass along the long rope from left to right. This one-dimensional moving wave is called a traveling wave. The wavelength of the wave, λ—the distance between two successive crests—is identified.
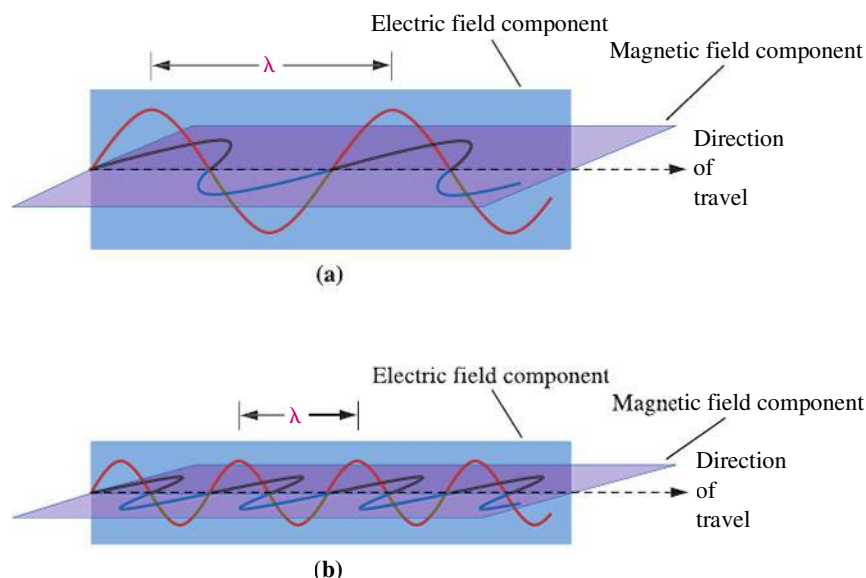
▲ FIGURE 8-2
Electromagnetic waves
This sketch of two different electromagnetic waves shows the propagation of mutually perpendicular oscillating electric and magnetic fields. For a given wave, the wavelengths, frequencies, and amplitudes of the electric and magnetic field components are identical. If these views are of the same instant of time, we would say that **(a)** has the longer wavelength and lower frequency, and **(b)** has the shorter wavelength and higher frequency.

form of electromagnetic radiation, the accelerating charged particles are the electrons in atoms or molecules.

Frequency, Wavelength, and Speed of Electromagnetic Radiation

▶ Electromagnetic waves are *transverse* waves—the electric and magnetic fields are *perpendicular* to the perceived direction of motion. So, to a first approximation, are water waves. Sound waves, by contrast, are *longitudinal*. This effect is the result of small pulses of pressure that move in the *same* direction as the sound travels.

The SI unit for frequency, s^{-1}, is the **hertz (Hz)**, and the basic SI wavelength unit is the meter (m). Because many types of electromagnetic radiation have very short wavelengths, however, smaller units, including those listed below, are also used. The angstrom, named for the Swedish physicist Anders Ångström (1814–1874), is not an SI unit.

$$1 \text{ centimeter (cm)} = 1 \times 10^{-2} \text{ m}$$
$$1 \text{ millimeter (mm)} = 1 \times 10^{-3} \text{ m}$$
$$1 \text{ micrometer } (\mu m) = 1 \times 10^{-6} \text{ m}$$
$$1 \text{ nanometer (nm)} = 1 \times 10^{-9} \text{ m} = 1 \times 10^{-7} \text{ cm} = 10 \text{ Å}$$
$$1 \text{ angstrom (Å)} = 1 \times 10^{-10} \text{ m} = 1 \times 10^{-8} \text{ cm} = 100 \text{ pm}$$
$$1 \text{ picometer (pm)} = 1 \times 10^{-12} \text{ m} = 1 \times 10^{-10} \text{ cm} = 10^{-2} \text{ Å}$$

▶ The speed of light is commonly rounded off to $3.00 \times 10^8 \text{ m s}^{-1}$.

A distinctive feature of electromagnetic radiation is its *constant* speed of $2.99792458 \times 10^8 \text{ m s}^{-1}$ in a vacuum, often referred to as the **speed of light**. The speed of light is represented by the symbol c, and the relationship between this speed and the frequency and wavelength of electromagnetic radiation is

$$c = \nu \times \lambda \tag{8.1}$$

Figure 8-3 indicates the wide range of possible wavelengths and frequencies for some common types of electromagnetic radiation and illustrates this important fact: The wavelength of electromagnetic radiation is shorter for high frequencies and longer for low frequencies. Example 8-1 illustrates the use of equation (8.1).

Frequency, s^{-1}

10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4}

γ rays   Radio

X rays   Micro-
wave

Ultra-   Infra-
violet   red

10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4}

Wavelength, m

Visible

λ = 390   450   500   550   600   650   700   760 nm

▲ FIGURE 8-3
The electromagnetic spectrum
The visible region, which extends from violet at the shortest wavelength to red at the longest wavelength, is only a small portion of the entire spectrum. The approximate wavelength and frequency ranges of some other forms of electromagnetic radiation are also indicated.

EXAMPLE 8-1   Relating Frequency and Wavelength of Electromagnetic Radiation

Most of the light from a sodium vapor lamp has a wavelength of 589 nm. What is the frequency of this radiation?

Analyze

To use equation (8.1), we first convert the wavelength of the light from nanometers to meters, since the speed of light is in $m\,s^{-1}$. Then, we rearrange it to the form $\nu = c/\lambda$ and solve for ν.

Solve

Change the units of λ from nanometers to meters.

$$\lambda = 589\ \text{nm} \times \frac{1 \times 10^{-9}\ \text{m}}{1\ \text{nm}} = 5.89 \times 10^{-7}\ \text{m}$$

$$c = 2.998 \times 10^{8}\ \text{m}\,\text{s}^{-1}$$

$$\nu = ?$$

Rearrange equation (8.1) to the form $\nu = c/\lambda$, and solve for ν.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m}\,\text{s}^{-1}}{5.89 \times 10^{-7}\ \text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1} = 5.09 \times 10^{14}\ \text{Hz}$$

Assess

The essential element here is to recognize the need to change the units of λ. This change is often needed when converting wavelength to frequency and vice versa.

PRACTICE EXAMPLE A: The light from red LEDs (light-emitting diodes) is commonly seen in many electronic devices. A typical LED produces 690 nm light. What is the frequency of this light?

PRACTICE EXAMPLE B: An FM radio station broadcasts on a frequency of 91.5 megahertz (MHz). What is the wavelength of these radio waves in meters?

▶ FIGURE 8-4
Examples of interference
(a) Stones and ripples.
(b) CD reflection.

(a)

(b)

An Important Characteristic of Electromagnetic Waves

The properties of electromagnetic radiation that we will use most extensively are those just introduced—amplitude, wavelength, frequency, and speed. Another essential characteristic of electromagnetic radiation, which will underpin our discussion of atomic structure later in the chapter, is described next.

▶ The *wave nature o flight* is demonstrated by its ability to be dispersed by diffraction and refraction.

If two pebbles are dropped close together into a pond, ripples (waves) emerge from the points of impact of the two stones. The two sets of waves intersect, and there are places where the waves disappear and places where the waves persist, creating a crisscross pattern (Fig. 8-4a). Where the waves are "in step" upon meeting, their crests coincide, as do their troughs. The waves combine to produce the highest crests and deepest troughs in the water. The waves are said to be *in phase*, and the addition of the waves is called *constructive interference* (Fig. 8-5a). Where the waves meet in such a way that the peak of one wave occurs at the trough of another, the waves cancel and the water is flat (Fig. 8-5b). These out-of-step waves are said to be *out o fphase*, and the cancellation of the waves is called *destructive inter ference*.

KEEP IN MIND

that destructive interference occurs when waves are out of phase by one-half wavelength. If waves are out of phase by more or less than this, but also not completely in phase, then only partial destructive interference occurs.

An everyday illustration of interference involving electromagnetic waves is seen in the rainbow of colors that shine from the surface of a compact disc (Fig. 8-4b). White light, such as sunlight, contains all the colors of the rainbow. The colors differ in wavelength (and frequency), and when these different wavelength components are reflected off the tightly spaced grooves of the CD,

(a)

(b)
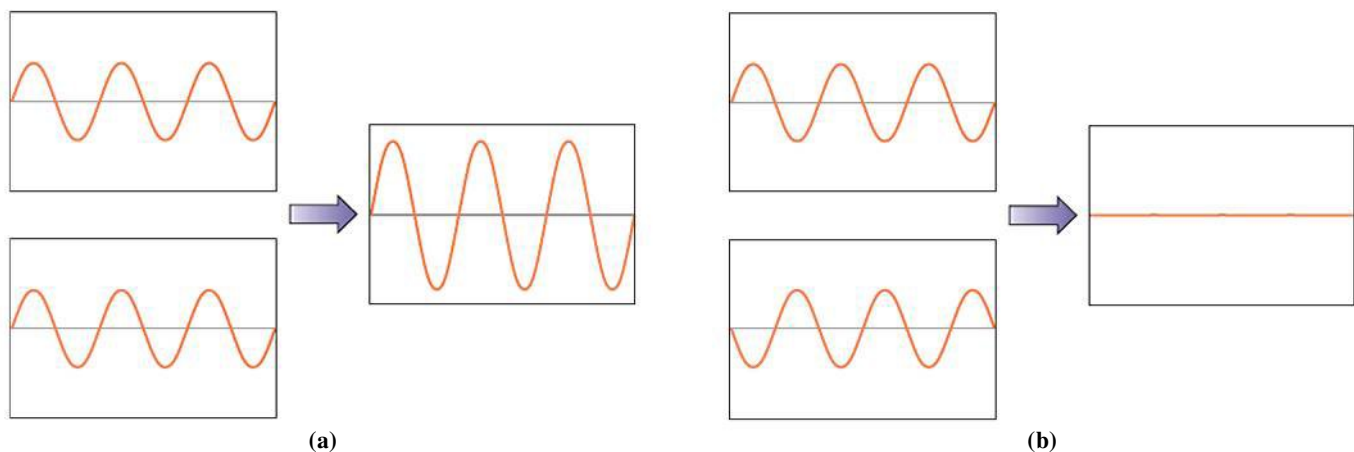
▲ FIGURE 8-5
Interference in two overlapping light waves
(a) In constructive interference, the troughs and crests are in step (in phase), leading to addition of the two waves. **(b)** In destructive interference, the troughs and crests are out of step (out of phase), leading to cancellation of the two waves.

they travel slightly different distances. This creates phase differences that depend on the angle at which we hold the CD to the light source. The light waves in the beam interfere with each other, and, for a given angle between the incoming and reflected light, all colors cancel except one. Light waves of that color interfere constructively and reinforce one another. Thus, as we change the angle of the CD to the light source, we see different colors. The dispersion of different wavelength components of a light beam through the interference produced by reflection from a grooved surface is called **diffraction**.

Diffraction is a phenomenon that can be explained only as a property of waves. Both the physical picture and mathematics of interference and diffraction are the same for water waves and electromagnetic waves.

The Visible Spectrum

The speed of light is lower in any medium than it is in a vacuum. Also, the speed is different in different media. As a consequence, light is refracted, or bent, when it passes from one medium to another (Fig. 8-6). Moreover, although electromagnetic waves all have the same speed in a vacuum, waves of different wavelengths have slightly different speeds in air and other media. Thus, when a beam of white light is passed through a transparent medium, the wavelength components are refracted differently. The light is dispersed into a band of colors, a *spectrum*. In Figure 8-7(a), a beam of white light (for example, sunlight) is dispersed by a glass prism into a continuous band of colors corresponding to all the wavelength components from red to violet. This is the visible spectrum shown in Figure 8-3 and also seen in a rainbow, where the medium that disperses the sunlight is droplets of water (Fig. 8-7b).
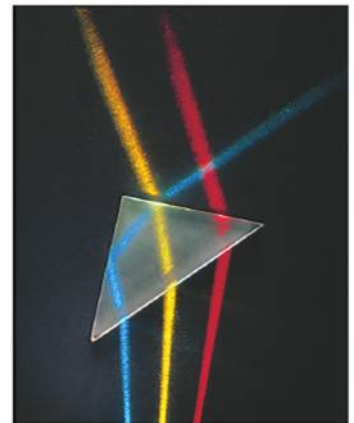
▲ FIGURE 8-6
Refraction of light
Light is refracted (bent) as it passes from air into the glass prism, and again as it emerges from the prism into air. This photograph shows that red light is refracted the least and blue light the most. The blue light strikes the prism at such an angle that the beam undergoes an internal reflection before it emerges from the prism.

🔍 **8-1   CONCEPT ASSESSMENT**

Red laser light is passed through a device called a frequency doubler. What is the approximate color of the light that exits the frequency doubler? How are the wavelengths of the original light and the frequency-doubled light related?

▶ The *importance of light* to chemistry is that light is a form of energy and that by studying light–matter interactions we can detect energy changes in atoms and molecules. Another means of monitoring the energy of a system is through observations of heat transfer. Light can be more closely controlled and thus gives us more detailed information than can be obtained with heat measurements.


(a)

(b)

▲ FIGURE 8-7
The spectrum of "white" light
(a) Dispersion of light through a prism. Red light is refracted the least and violet light the most when "white" light is passed through a glass prism. The other colors of the visible spectrum are found between red and violet. (b) Rainbow near a waterfall. Here, water droplets are the dispersion medium.

8-2   Atomic Spectra

The visible spectrum in Figure 8-7 is said to be a *continuous spectrum* because the light being diffracted consists of many wavelength components. If the source of a spectrum produces light having only a relatively small number of wavelength components, then a *discontinuous spectrum* is observed. For example, if the light source is an electric discharge passing through a gas, only certain colors are seen in the spectrum (Fig. 8-8a and b). Or, if the light source is a gas flame into which an ionic compound has been introduced, the flame may acquire a distinctive color indicative of the metal ion present (Fig. 8-8c–e). In each of these cases, the emitted light produces a spectrum consisting of only a limited number of discrete wavelength components, observed as colored lines with dark spaces between them. These discontinuous spectra are called **atomic**, or **line**, **spectra**.

The production of the line spectrum of helium is illustrated in Figure 8-9. The light source is a lamp containing helium gas at a low pressure. When an electric discharge is passed through the lamp, helium atoms absorb energy, which they then emit as light. The light is passed through a narrow slit and then dispersed by a prism. The colored components of the light are detected and recorded on photographic film. Each wavelength component appears as
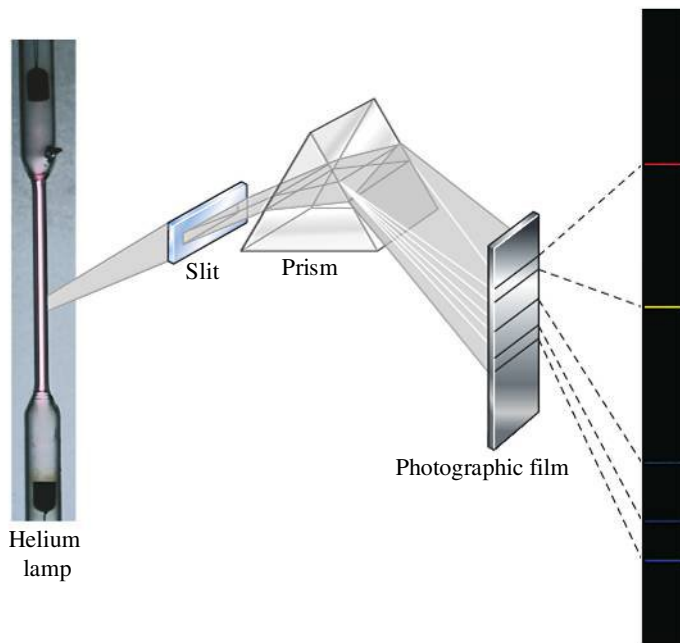

(a)

(b)

(c)

(d)

(e)
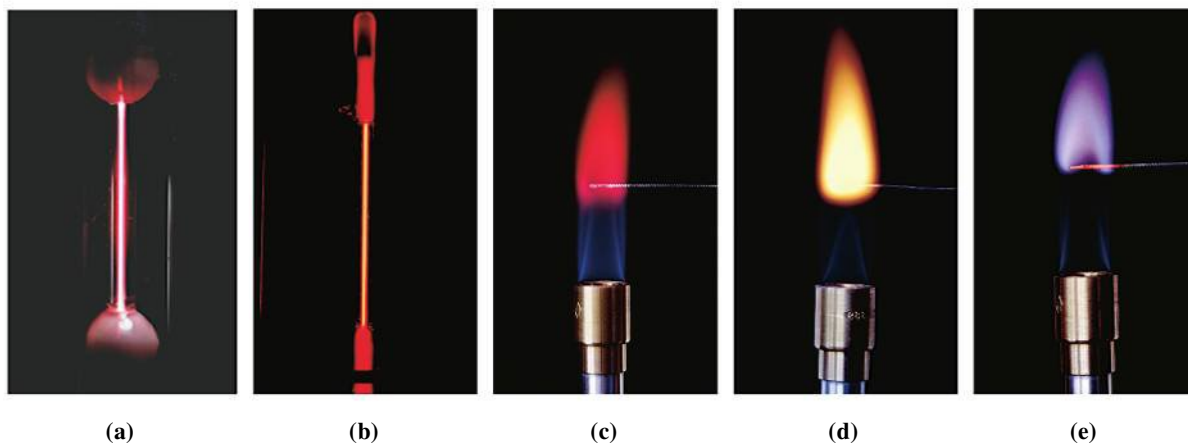
▲ FIGURE 8-8
Sources for light emission
Light emitted by an electric discharge through (a) hydrogen gas and (b) neon gas. Light emitted when compounds of the alkali metals are excited in the gas flames: (c) lithium, (d) sodium, and (e) potassium.

The atomic, or line, spectrum of helium
The apparatus pictured here, in which the spectral lines are photographed, is called a *spectrograph*. If the observations are made by visual sighting alone, the device is called a *spectroscope*. If the positions and brightness of the lines are measured and recorded by other than visual or photographic means, the term generally used is *spectrometer*.

an image of the slit—a thin line. In all, there are five lines in the spectrum of helium that can be seen with the unaided eye.

Each element has its own distinctive line spectrum—a kind of atomic fingerprint. Robert Bunsen (1811–1899) and Gustav Kirchhoff (1824–1887) developed the first spectroscope and used it to identify elements. In 1860, they discovered a new element and named it cesium (Latin, *caesius*, sky blue) because of the distinctive blue lines in its spectrum. They discovered rubidium in 1861 in a similar way (Latin, *rubidius*, deepest red). Still another element characterized by its unique spectrum is helium (Greek, *helios*, the sun). Its spectrum was observed during the solar eclipse of 1868, but helium was not isolated on Earth for another 27 years.

Among the most extensively studied atomic spectra has been the hydrogen spectrum. Light from a hydrogen lamp appears to the eye as a reddish purple color (Fig. 8-8a). The principal wavelength component of this light is red light of wavelength 656.3 nm. Three other lines appear in the visible spectrum of atomic hydrogen, however: a greenish blue line at 486.1 nm, a violet line at 434.0 nm, and another violet line at 410.1 nm. The visible atomic spectrum of hydrogen is shown in Figure 8-10. In 1885, Johann Balmer, apparently through trial and error, deduced a formula for the wavelengths of these spectral lines. Balmer's equation, rearranged to a form based on frequency, is

$$\nu = 3.2881 \times 10^{15}\,\text{s}^{-1}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{8.2}$$

In this equation, ν is the frequency of the spectral line, and n must be an *integer* (whole number) *greater than two*. If $n = 3$ is substituted into the equation, the

◀ Bunsen designed a special gas burner for his spectroscopic studies. This burner, the common laboratory Bunsen burner, produces very little background radiation to interfere with spectral observations.
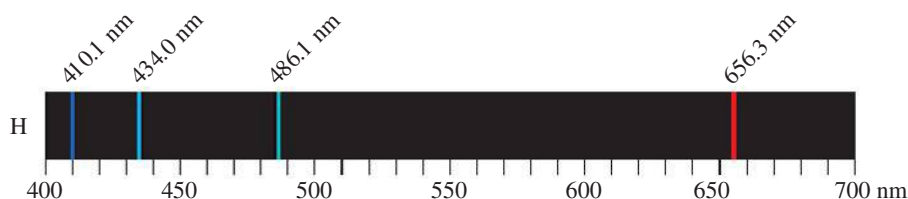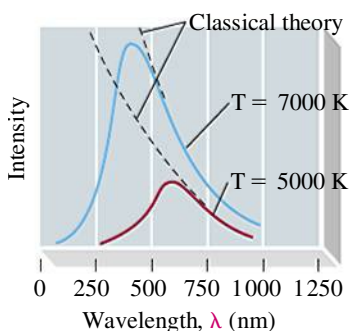

▲ FIGURE 8-10
The Balmer series for hydrogen atoms—a line spectrum
The four lines shown are the only ones visible to the unaided eye. Additional, closely spaced lines lie in the ultraviolet (UV) region.

▲ Light emission by molten iron.

▲ FIGURE 8-11
Spectrum of radiation given off by a heated body

A red-hot object has a spectrum that peaks around 675 nm, whereas a white-hot object has a spectrum that has comparable intensities for all wavelengths in the visible region. The sun has a blackbody temperature of about 5750 K. Objects emit radiation at *all* temperatures, not just at high temperatures. For example, night-vision goggles makes infrared radiation emitted by objects visible in the dark.

▶ Planck's equation can be used to develop relationships among frequency, wavelength, and energy. By using this information, the relative energies of radiation on the electromagnetic spectrum can be compared.

frequency of the red line is obtained. If $n = 4$ is used in equation 8.2, the frequency of the greenish blue line is obtained, and so on.

The fact that atomic spectra consist of only limited numbers of well-defined wavelength lines provides a great opportunity to learn about the structures of atoms. For example, it suggests that only a limited number of energy values are available to excited gaseous atoms. Classical (nineteenth-century) physics, however, was not able to provide an explanation of atomic spectra. The key to this puzzle lay in a great breakthrough of modern science—the quantum theory.

🔍 **8-2   CONCEPT ASSESSMENT**

When comet Schumacher-Levy crashed into Jupiter's surface, scientists viewed the event with spectrographs. What did they hope to discover?

8-3   Quantum Theory

We are aware that hot objects emit light of different colors, from the dull red of an electric-stove heating element to the bright white of a light bulb filament. Light emitted by a hot radiating object can be dispersed by a prism to produce a continuous color spectrum. As seen in Figure 8-11, the light intensity varies smoothly with wavelength, peaking at a wavelength fixed by the source temperature. As with atomic spectra, classical physics could not provide a complete explanation of light emission by heated solids, a process known as *blackbody radiation*. Classical theory predicts that the intensity of the radiation emitted would increase indefinitely, as indicated by the dashed lines in Figure 8-11. In 1900, to explain the fact that the intensity does not increase indefinitely, Max Planck (1858–1947) made a revolutionary proposal: *Energy, like matter, is discontinuous.* Here, then, is the essential difference between the classical physics of Planck's time and the new quantum theory that he proposed: Classical physics places no limitations on the amount of energy a system may possess, whereas quantum theory limits this energy to a discrete set of specific values. The *difference* between any two allowed energies of a system also has a specific value, called a **quantum** of energy. This means that when the energy increases from one allowed value to another, it increases by a tiny jump, or quantum. Here is a way of thinking about a quantum of energy: It bears a similar relationship to the total energy of a system as a single atom does to an entire sample of matter.

The model Planck used for the emission of electromagnetic radiation was that of a group of atoms on the surface of the heated object oscillating together with the same frequency. Planck's assumption was that the group of atoms, the oscillator, must have an energy corresponding to the equation

$$\epsilon = nh\nu$$

where ϵ is the energy, n is a positive integer, ν is the oscillator frequency, and h is a constant that had to be determined by experiment. By using his theory and experimental data for the distribution of frequencies with temperature, Planck established the following value for the constant **h**. We now call it **Planck's constant**, and it has the value

$$h = 6.62607 \times 10^{-34} \, \text{J s}$$

Planck's postulate can be rephrased in this more general way: The energy of a quantum of electromagnetic radiation is proportional to the frequency of the radiation—the higher the frequency, the greater the energy. This is summarized by what we now call Planck's equation.

$$E = h\nu \tag{8.3}$$

8-2 ARE YOU WONDERING...

How Planck's ideas account for the fact that the intensity of blackbody radiation drops off at higher frequencies?

Planck was aware of the work of Ludwig Boltzmann, who, with James Maxwell, had derived an equation to account for the distribution of molecular speeds. Boltzmann had shown that the relative chance of finding a molecule with a particular speed was related to its energy by the following expression.

$$\text{relative chance} \propto e^{\left(-\frac{\text{kinetic energy}}{k_\text{B}T}\right)}$$

where k_B is the Boltzmann constant, and T is the Kelvin temperature. You will also notice that the curve of intensity versus wavelength in Figure 8-11 bears a strong resemblance to the distribution of molecular speeds in Figure 6-15. Planck assumed that the energies of the substance oscillating to emit blackbody radiation were distributed according to the Boltzmann distribution law. That is, the relative chance of an oscillator having the energy $nh\nu$ is proportional to $e^{-nh\nu/k_\text{B}T}$, where n is an integer, 1, 2, 3, and so on. So this expression shows that the chance of an oscillator having a high frequency is lower than for oscillators having lower frequencies because as n increases, $e^{-nh\nu/k_\text{B}T}$, decreases. The assumption that the energy of the oscillators in the light-emitting source cannot have continuous values leads to excellent agreement between theory and experiment.

▲ Max Planck (1858–1947)

At the time Planck made his quantum hypothesis, scientists had had no previous experience with macroscopic physical systems that required the existence of separate energy levels and that energy may only be emitted or absorbed in specific quanta. Their experience was that there were no theoretical limits on the energy of a system and that the transfer of energy was continuous. Thus it is not surprising that scientists, including Planck himself, were initially skeptical of the quantum hypothesis. It had been designed to explain radiation from heated bodies and certainly could not be accepted as a general principle until it had been tested on other applications.

Only after the quantum hypothesis was successfully applied to phenomena other than blackbody radiation did it acquire status as a great new scientific theory. The first of these successes came in 1905 with Albert Einstein's quantum explanation of the photoelectric effect.
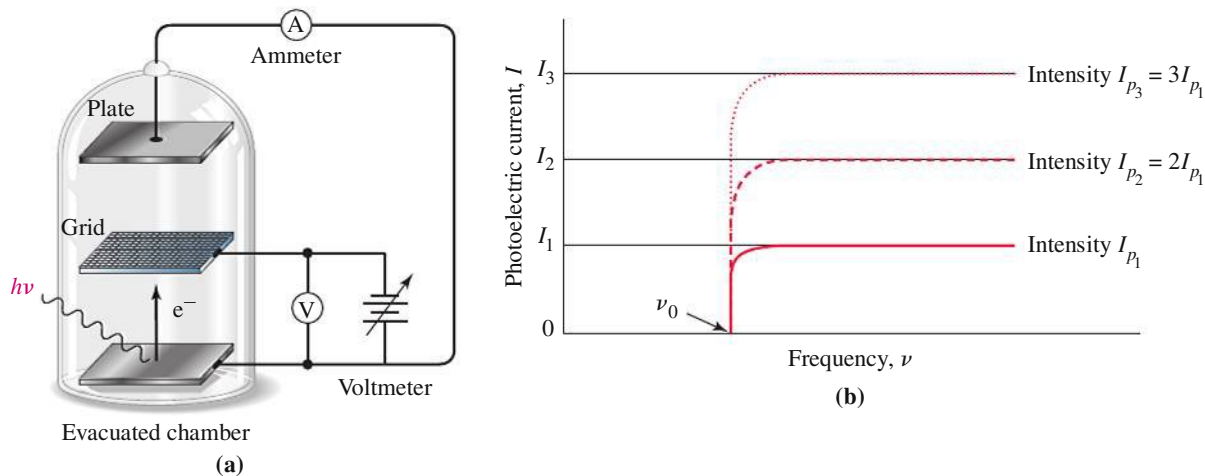
The Photoelectric Effect

In 1888, Heinrich Hertz discovered that when light strikes the surface of certain metals, electrons are ejected. This phenomenon is called the **photoelectric effect** and its salient feature is that electron emission only occurs when the frequency of the incident light exceeds a particular threshold value (ν_0). When this condition is met,

- the number of electrons emitted depends on the intensity of the incident light, but
- the kinetic energies of the emitted electrons depend on the frequency of the light.

These observations, especially the dependency on frequency, could not be explained by classical wave theory. However, Albert Einstein showed that they are exactly what would be expected with a particle interpretation of radiation. In 1905, Einstein proposed that electromagnetic radiation has particle-like qualities and that "particles" of light, subsequently called **photons** by G. N. Lewis, have a characteristic energy given by Planck's equation, $E = h\nu$.

In the particle model, a photon of energy $h\nu$ strikes a bound electron, which absorbs the photon energy. If the photon energy, $h\nu$, is greater than the energy

◀ Light–matter interactions usually involve *one photon per atom or electron*. Thus, to escape from a photoelectric surface, an electron must do so with the energy from a single photon collision. The electron cannot accumulate the energy from several hits by photons.

(a)

(b)

▲ FIGURE 8-12
The photoelectric effect
(a) Schematic diagram of the apparatus for photoelectric effect measurements.
(b) The photoelectric current, I_p, appears only if the frequency (ν) is greater than the threshold value (ν_0). For $\nu > \nu_0$, the current (I_p) increases as the intensity of the light is increased. (c) Stopping voltage of photoelectrons as a function of frequency of incident radiation. The stopping voltage (V_s) is plotted against the frequency of the incident radiation. The threshold frequency (ν_0) of the metal is found by extrapolation.

(c)

▶ With the advent of lasers we have observed the simultaneous absorption of two photons by one electron. Instances of two adjacent molecules cooperatively absorbing one photon are also known. Such occurrences are exceptions to the more normal one photon/one electron phenomena.

binding the electron to the surface (a quantity known as the *work function*), a photoelectron is liberated. Thus, the lowest frequency light producing the photoelectric effect is the threshold frequency, and any energy in excess of the work function appears as kinetic energy in the emitted photoelectrons.

In the discussion that follows, based on the experimental setup shown in Figure 8-12, we will see how the threshold frequency and work function are evaluated. Also, we will see that the photoelectric effect provides an independent evaluation of Planck's constant, h.

In Figure 8-12, light (designated $h\nu$) is allowed to shine on a piece of metal in an evacuated chamber. The electrons emitted by the metal (photoelectrons) travel to the upper plate and complete an electric circuit set up to measure the photoelectric current through an ammeter. Figure 8-12(b) illustrates the variation of the photoelectric current, I_p, detected by the ammeter as the frequency (ν) and intensity of the incident light is increased. We see that no matter how intense the light, no current flows if the frequency is below the threshold frequency, ν_0, and no photoelectric current is produced. In addition no matter how weak the light, there is a photoelectric current if $\nu > \nu_0$. The magnitude of the photoelectric current is, as shown in Figure 8-12(b), directly proportional to the intensity of the light, so that the number of photoelectrons increases with the intensity of the incident light. Therefore, we can associate light intensity with the number of photons arriving at a point per unit time.

A second circuit is set up to measure the velocity of the photoelectrons, and hence their kinetic energy. In this circuit, a potential difference (voltage) is maintained between the photoelectric metal and an open-grid electrode placed below the upper plate. For electric current to flow, electrons must pass through the openings in the grid and onto the upper plate. The negative potential on the grid acts to slow down the approaching electrons. As the potential difference between the grid and the emitting metal is increased, a point is reached at which the photoelectrons are stopped at the grid and the current ceases to flow through the ammeter. The potential difference at this point is called the *stopping voltage*, V_s. At the stopping voltage, the kinetic energy of the photoelectrons has been converted

to potential energy, expressed through the following equation (in which $m, u,$ and e are the mass, speed, and charge of an electron, respectively).

$$\frac{1}{2}mu^2 = eV_s$$

As a result of experiments of the type just described, we find that V_s is proportional to the frequency of the incident light but independent of the light intensity. Also, as shown in Figure 8-12, if the frequency, ν, is below the *threshold frequency*, ν_0, no photoelectric current is produced. At frequencies greater than ν_0, the empirical equation for the stopping voltage is

$$V_s = k(\nu - \nu_0)$$

The constant k is independent of the metal used, but ν_0 varies from one metal to another. Although there is no relation between V_s and the light intensity, the

◄ Albert Einstein received a Nobel Prize for his work on the photoelectric effect. He is better known for his development of the theory of relativity, and $E = mc^2$.
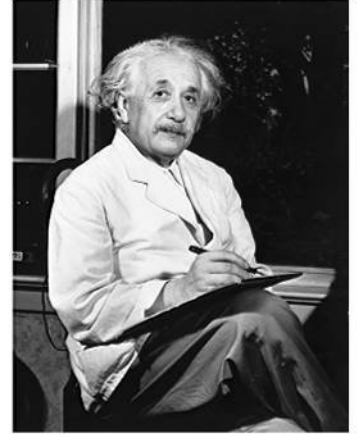
▲ **Albert Einstein (1879–1955)**

? 8-3   ARE YOU WONDERING...

How the energy of a photon is manifested?

We begin with an important relationship between the mass and velocity of a particle given by Einstein. Let the mass of a particle when the particle and the measuring device are at rest be denoted as m_0. If we remeasure the mass when the particle moves with a velocity u, we find that its mass increases according to the equation

$$m = \frac{m_0}{\sqrt{1 - u^2/c^2}}$$

where m is the particle mass, referred to as the *relativistic mass*, and c is the speed of light. For particles moving at speeds less than 90% of the speed of light, the relativistic mass (m) is essentially the same as the rest mass (m_0).

We have seen that the kinetic energy of a particle is given by

$$E_K = \frac{1}{2}mu^2$$

However, because photons travel at the speed of light they must have zero rest mass (otherwise their relativistic mass m would become infinite). So where is their energy?

Although photons have zero rest mass, they do possess momentum, which is defined as the relativistic mass times the velocity of the particle, because they are in motion. Einstein's theory of special relativity states that a particle's energy and momentum ($p = mu$, recall page 217) are related by the expression

$$E^2 = (pc)^2 + (m_0c^2)^2$$

where m_0 is the rest mass of the particle. For photons traveling at the speed of light c, the rest mass is zero. Hence

$$E = pc = h\nu$$
$$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

Photons possess momentum, and it is this momentum that is transferred to an electron in a collision. In all collisions between photons and electrons, momentum is conserved. Thus, we see that the wave and the photon models are intimately connected. The energy of a photon is related to the frequency of the wave by Planck's equation, and the momentum of the photon is related to the wavelength of the wave by the equation just derived! When a photon collides with an electron, it transfers momentum to the electron, which accelerates to a new velocity. The energy of the photon decreases, and, as a consequence, its wavelength increases. This phenomenon, called the Compton effect, was discovered in 1923 and confirmed the particulate nature of light.

photoelectric current, I_p, is proportional to the intensity of the light as illustrated in Figure 8-12b.

The work function is a quantity of work and, hence, of energy. One way to express this quantity is as the product of Planck's constant and the threshold frequency: $E = h\nu_0$. Another way is as the product of the charge on the electron, e, and the potential, V_0, that has to be overcome in the metal: $E = eV_0$. Thus, the threshold frequency for the photoelectric effect is given by the expression

$$\nu_0 = \frac{eV_0}{h}$$

Since the work function (eV_0) is a characteristic of the metal used in the experiment, then ν_0 is also a characteristic of the metal, as confirmed by experiment.

When a photon of energy $h\nu$ strikes an electron, the electron overcomes the work function eV_0 and is liberated with kinetic energy $\left(\frac{1}{2}\right)mu^2$. Thus, by the law of conservation of energy, we have

$$\frac{1}{2}mu^2 + eV_0 = h\nu$$

which gives

$$eV_s = \frac{1}{2}mu^2 = h\nu - eV_0$$

which is identical to the empirically determined equation for V_s with $k = h/e$ when $h\nu_0 = eV_0$. Careful experiments showed that the constant h had the same value as determined by Planck for blackbody radiation. The additional fact that the number of photoelectrons increases with the intensity of light indicates that we should associate light intensity with the number of photons arriving at a point per unit time.


🔍 8-3   CONCEPT ASSESSMENT

The wavelength of light needed to eject electrons from hydrogen atoms is 91.2 nm. When light of 80.0 nm is shone on a sample of hydrogen atoms, electrons are emitted from the hydrogen gas. If, in a different experiment, the wavelength of the light is changed to 70.0 nm, what is the effect compared to the use of 80.0 nm light? Are more electrons emitted? If not, what happens?

Photons of Light and Chemical Reactions

Chemical reactions that are induced by light are called *photochemical reactions*. Because they are essential to these reactions, we can think of photons as "reactants" and we can designate them in chemical equations by the symbol $h\nu$. The reactions by which ozone molecules, O_3, are produced from oxygen molecules, O_2, are represented below.

$$O_2 + h\nu \longrightarrow O + O$$
$$O_2 + O + M \longrightarrow O_3 + M^*$$
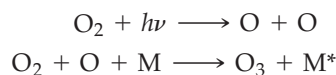
The radiation required in the first reaction is UV radiation with wavelength less than 242.4 nm. O atoms from the first reaction then combine with O_2 to form O_3. In the second reaction, a "third body," M, such as $N_2(g)$, is needed to carry away excess energy to prevent immediate dissociation of O_3 molecules.

▶ The reactions shown here describing the formation ozone from oxygen gas are the reactions that occur in the atmosphere to produce ozone.

Photochemical reactions involving ozone are the subject of Example 8-2. There we see that the product of Planck's constant h and frequency (ν) yields the energy of a single photon of electromagnetic radiation in the unit joule. Invariably, this energy is only a tiny fraction of a joule. Often it is useful to deal with the much larger energy of a mole of photons (6.02214×10^{23} photons).

EXAMPLE 8-2   Using Planck's Equation to Calculate the Energy of Photons of Light

For radiation of wavelength 242.4 nm, the longest wavelength that will bring about the photodissociation of O_2, what is the energy of **(a)** one photon, and **(b)** a mole of photons of this light?

Analyze

To use Planck's equation, we need the frequency of the radiation. We can get this from equation (8.1) after first expressing the wavelength in meters. Planck's equation is written for one photon of light. We emphasize this by including the unit in the value of h. Once we have the energy per photon, we can multiply it by the Avogadro constant to convert to a per-mole basis.

Solve

   (a) First, calculate the frequency of the radiation.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \,\text{m s}^{-1}}{242.4 \times 10^{-9} \,\text{m}} = 1.237 \times 10^{15} \,\text{s}^{-1}$$

   Then, calculate the energy of a single photon.

$$E = h\nu = 6.626 \times 10^{-34} \times \frac{\text{J s}}{\text{photon}} \times 1.237 \times 10^{15} \,\text{s}^{-1}$$

$$= 8.196 \times 10^{-19} \,\text{J/photon}$$

   (b) Calculate the energy of a mole of photons.

$$E = 8.196 \times 10^{-19} \,\text{J/photon} \times 6.022 \times 10^{23} \,\text{photons/mol}$$

$$= 4.936 \times 10^{5} \,\text{J/mol}$$

Assess

We can see from this example that when the energy of a single photon is expressed in SI units, the energy is rather small and perhaps difficult to interpret. However, the amount of energy carried by a *mole* of photons is something we can easily relate to. As shown above, light with a wavelength of 242.4 nm has an energy content of 493.6 kJ/mol, which is similar in magnitude to the internal energy and enthalpy changes of chemical reactions (see Chapter 7).


PRACTICE EXAMPLE A: The protective action of ozone in the atmosphere comes through ozone's absorption of UV radiation in the 230 to 290 nm wavelength range. What is the energy, in kilojoules per mole, associated with radiation in this wavelength range?

PRACTICE EXAMPLE B: Chlorophyll absorbs light at energies of 3.056×10^{-19} J/photon and 4.414×10^{-19} J/photon To what color and frequency do these absorptions correspond?

8-4   The Bohr Atom

The Rutherford model of a nuclear atom (Section 2-3) does not indicate how electrons are arranged outside the nucleus of an atom. According to classical physics, stationary, negatively charged electrons would be pulled into the positively charged nucleus. This suggests that the electrons in an atom must be in motion, like the planets orbiting the sun. However, again according to classical physics, orbiting electrons should be constantly accelerating and should radiate energy. By losing energy, the electrons would be drawn ever closer to the nucleus and soon spiral into it. In 1913, Niels Bohr (1885–1962) resolved this problem by using Planck's quantum hypothesis. In an interesting blend of classical and quantum theory, Bohr postulated that for a hydrogen atom:

1. The electron moves in circular orbits about the nucleus with the motion described by classical physics.

2. The electron has only a fixed set of allowed orbits, called *stationary states*. The allowed orbits are those in which certain properties of the electron have unique values. Even though classical theory would predict otherwise, *as long as an electron remains in a given orbit, its energy is constant and no energy is emitted*. The particular property of the electron having only certain allowed values, leading to only a discrete set of allowed orbits, is called the *angular momentum*. Its possible
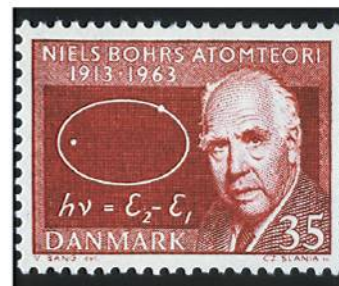

▲ **Niels Bohr (1885–1962)**
In addition to his work on the hydrogen atom, Bohr headed the Institute of Theoretical Physics in Copenhagen, which became a mecca for theoretical physicists in the 1920s and 1930s.

Bohr model of the hydrogen atom
A portion of the hydrogen atom is pictured. The nucleus is at the center, and the electron is found in one of the discrete orbits, $n = 1, 2,$ and so on. Excitation of the atom raises the electron to higher-numbered orbits, as shown with black arrows. Light is emitted when the electron falls to a lower-numbered orbit. Two transitions that produce lines in the Balmer series of the hydrogen spectrum are shown in the approximate colors of the spectral lines.
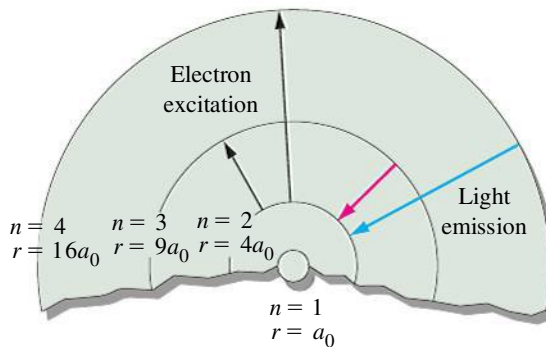
KEEP IN MIND

that momentum (p) is the product of the mass and the velocity of a particle. If the particle undergoes a circular motion, then the particle possesses angular momentum.

values are $nh/2\pi$, where n must be an integer. Thus the quantum numbers progress: $n = 1$ for the first orbit; $n = 2$ for the second orbit; and so on.

3. An electron can pass only from one allowed orbit to another. In such transitions, fixed discrete quantities of energy (quanta) are involved—either absorbed or emitted.

The atomic model of hydrogen based on these ideas is pictured in Figure 8-13. The allowed states for the electron are numbered, $n = 1, n = 2, n = 3$, and so on. These *integral* numbers, which arise from Bohr's assumption that only certain values are allowed for the angular momentum of the electron, are called **quantum numbers**.

The Bohr theory predicts the radii of the allowed orbits in a hydrogen atom.

$$r_n = n^2 a_0, \text{ where } n = 1, 2, 3, \ldots \quad \text{and} \quad a_0 = 53 \text{ pm } (0.53 \text{ Å}) \qquad \textbf{(8.4)}$$

▶ According to the Bohr model, lower energy orbits are closer to the nucleus and electrons associated with low energy orbits must absorb more energy to be removed from the atom.

The theory also allows us to calculate the electron velocities in these orbits and, most important, the energy. When the electron is free of the nucleus, by convention, it is said to be at a *zero* of energy. When a free electron is attracted to the nucleus and confined to the orbit n, the electron energy becomes negative, with its value lowered to

▶ Think of a person on a stairway going up steps (excitation) or down steps (emission). The person must stop on a step—in-between levels are not available.

$$E_n = \frac{-R_H}{n^2} \qquad \textbf{(8.5)}$$

R_H is a numerical constant with a value of 2.179×10^{-18} J.

With expression (8.5), we can calculate the energies of the allowed energy states, or *energy levels*, of the hydrogen atom. These levels can be represented schematically as in Figure 8-14. This representation is called an **energy-level diagram**. Example 8-3 shows how Bohr's model can be used to predict whether certain energy levels are possible (allowed) or impossible (not allowed).

Normally, the electron in a hydrogen atom is found in the orbit closest to the nucleus ($n = 1$). This is the lowest allowed energy, or the **ground state**. When the electron gains a quantum of energy, it moves to a higher level ($n = 2, 3,$ and so on) and the atom is in an **excited state**. When the electron drops from a higher to a lower numbered orbit, a unique quantity of energy is emitted—the difference in energy between the two levels. Equation (8.5) can be used to derive an expression for the difference in energy between two levels, where n_f is the final level and n_i is the initial one.
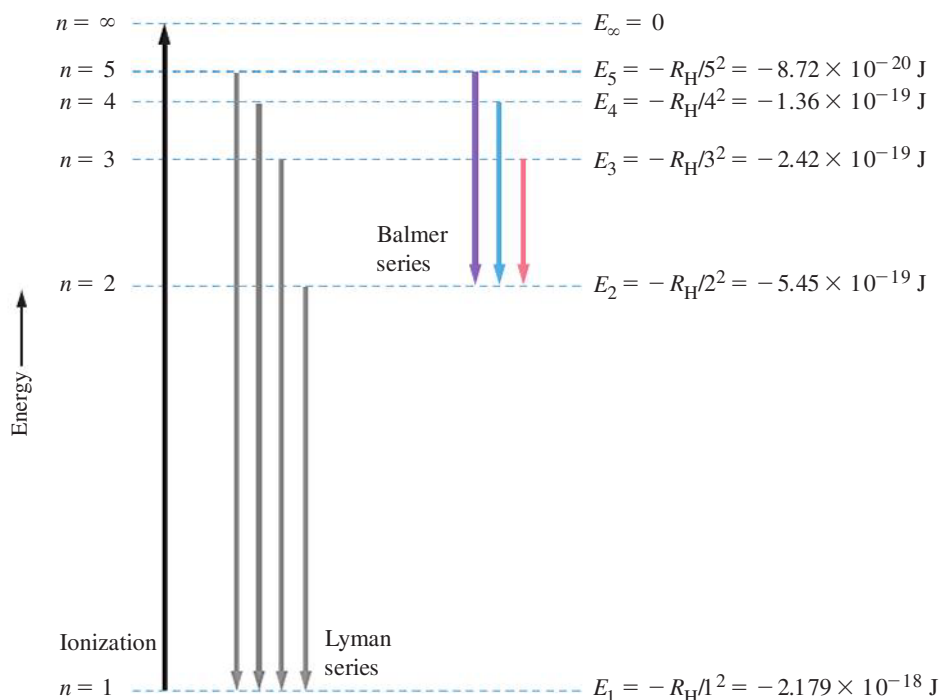
▶ Notice the resemblance of this equation to the Balmer equation (8.2). In addition to developing a theory of atomic structure to account for Rutherford's atomic model, Bohr sought a theoretical explanation of the Balmer equation.

$$\Delta E = E_f - E_i = \frac{-R_H}{n_f^2} - \frac{-R_H}{n_i^2} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.179 \times 10^{-18} \text{ J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad \textbf{(8.6)}$$

The energy of the photon, E_{photon}, either absorbed or emitted, is equal to the magnitude of this energy difference. Because $E_{photon} = h\nu$ and $E_{photon} = |\Delta E|$, we can write

$$|\Delta E| = E_{photon} = h\nu$$

$n = \infty$ — — — — — — — — — $E_\infty = 0$

$n = 5$ — — — — — — — — — $E_5 = -R_H/5^2 = -8.72 \times 10^{-20}$ J
$n = 4$ — — — — — — — — — $E_4 = -R_H/4^2 = -1.36 \times 10^{-19}$ J

$n = 3$ — — — — — — — — — $E_3 = -R_H/3^2 = -2.42 \times 10^{-19}$ J

Balmer series

$n = 2$ — — — — — — — — — $E_2 = -R_H/2^2 = -5.45 \times 10^{-19}$ J

Energy

Ionization   Lyman series

$n = 1$ — — — — — — — — — $E_1 = -R_H/1^2 = -2.179 \times 10^{-18}$ J

◀ FIGURE 8-14
Energy-level diagram for the hydrogen atom
If the electron acquires 2.179×10^{-18} J of energy, it moves to the orbit $n = \infty$; ionization of the H atom occurs (black arrow). Energy emitted when the electron falls from higher-numbered orbits to the orbit $n = 1$ is in the form of ultraviolet light, which produces a spectral series called the Lyman series (gray lines). Electron transitions to the orbit $n = 2$ yield lines in the Balmer series (recall Figure 8-10); three of the lines are shown here (in color). Transitions to $n = 3$ yield spectral lines in the infrared.

EXAMPLE 8-3   Understanding the Meaning of Quantization of Energy

Is it likely that there is an energy level for the hydrogen atom, $E_n = -1.00 \times 10^{-20}$ J?

Analyze

Rearrange equation (8.5) for n^2 and solve for n. If the value of n is an integer, then the given energy corresponds to an energy level for the hydrogen atom.

Solve

Let us rearrange equation (8.5), solve for n^2, and then for n.

$$n^2 = \frac{-R_H}{E_n}$$

$$= \frac{-2.179 \times 10^{-18} \text{ J}}{-1.00 \times 10^{-20} \text{ J}} = 2.179 \times 10^2 = 217.9$$

$$n = \sqrt{217.9} = 14.76$$

Because the value of n is not an integer, this is not an allowed energy level for the hydrogen atom.

Assess

Equation (8.5) places a severe restriction on the energies allowed for a hydrogen atom.

PRACTICE EXAMPLE A: Is there an energy level for the hydrogen atom, $E_n = -2.69 \times 10^{-20}$ J?

PRACTICE EXAMPLE B: The energy of an electron in a hydrogen atom is -4.45×10^{-20} J. What level does it occupy?

---

where $|\Delta E|$ represents the *magnitude* of the energy difference between the energy levels involved in the electronic transition.

Example 8-4 uses equation (8.6) as a basis for calculating the lines in the hydrogen emission spectrum. Because the differences between energy levels are limited in number, so too are the energies of the emitted photons. Therefore, only certain wavelengths (or frequencies) are observed for the spectral lines.

EXAMPLE 8-4   Calculating the Wavelength of a Line in the Hydrogen Spectrum

Determine the wavelength of the line in the Balmer series of hydrogen corresponding to the transition from $n = 5$ to $n = 2$.

Analyze

This problem is an application of equation (8.6). After the energy difference is calculated, we can obtain the photon frequency by rearranging $|\Delta E| = E_{photon} = h\nu$. Equation (8.1) is then used to get the wavelength.

Solve

The specific data for equation (8.6) are $n_i = 5$ and $n_f = 2$.

$$\Delta E = 2.179 \times 10^{-18}\,\text{J}\left(\frac{1}{5^2} - \frac{1}{2^2}\right)$$

$$= 2.179 \times 10^{-18} \times (0.04000 - 0.25000)$$

$$= -4.576 \times 10^{-19}\,\text{J}$$

Rearranging $E_{photon} = \Delta E = h\nu$ gives the frequency

$$\nu = \frac{E_{photon}}{h} = \frac{4.576 \times 10^{-19}\,\text{J photon}^{-1}}{6.626 \times 10^{-34}\,\text{J s photon}^{-1}} = 6.906 \times 10^{14}\,\text{s}^{-1}$$

Rearranging $c = \lambda\nu$ for the wavelength gives the following result:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8\,\text{m s}^{-1}}{6.906 \times 10^{14}\,\text{s}^{-1}} = 4.341 \times 10^{-7}\,\text{m} = 434.1\,\text{nm}$$

Assess

Note the good agreement between this result and the data in Figure 8-10. The color of the spectral line is determined by the energy difference, ΔE, while the intensity is determined by the number of hydrogen atoms undergoing this transition. The greater the number of atoms undergoing the same transition, the greater the number of emitted photons, resulting in greater intensity.

PRACTICE EXAMPLE A: Determine the wavelength of light absorbed in an electron transition from $n = 2$ to $n = 4$ in a hydrogen atom.

PRACTICE EXAMPLE B: Refer to Figure 8-14 and determine which transition produces the longest wavelength line in the Lyman series of the hydrogen spectrum. What is the wavelength of this line in nanometers and in angstroms?

The Bohr Theory and Spectroscopy

As shown in Example 8-4, the Bohr theory provides a model for understanding the emission spectra of atoms. Emission spectra are obtained when the individual atoms in a collection of atoms (roughly 10^{20} of them) are excited to the various possible excited states of the atom. The atoms then relax to states of lower energy by emitting photons of frequency given by

$$\nu_{photon} = \frac{E_i - E_f}{h} \tag{8.7}$$

Thus, the quantization of the energy states of atoms leads to line spectra.

Earlier in this chapter, we learned how the emission spectrum of a sample can be measured by dispersing emitted light through a prism and determining the wavelengths of the individual components of that light. We can conceive of an alternate technique in which we pass electromagnetic radiation, such as white light, through a sample of atoms in their ground states and then pass the emerging light through a prism. Now we observe which frequencies of light the atoms *absorb*. This form of spectroscopy is called *absorption spectroscopy*. The two types of spectroscopy—emission and absorption—are illustrated in Figure 8-15.
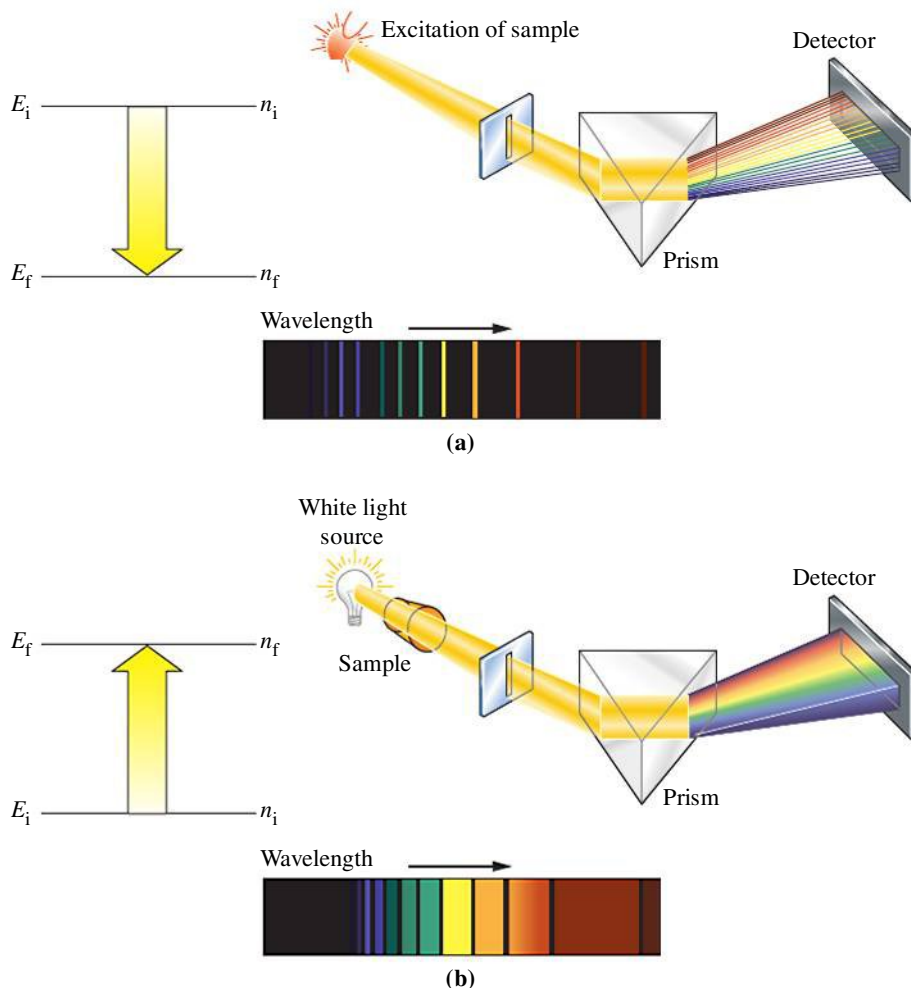
◀ FIGURE 8-15
**Emission and absorption
spectroscopy**
(a) Emission spectroscopy. Bright
lines are observed on a dark
background of the photographic
plate. (b) Absorption spectroscopy.
Dark lines are observed on a bright
background on the photographic
plate.

For absorption of a photon to take place, the energy of the photon must exactly match the energy difference between the final and initial states, that is,

$$\nu = \frac{E_f - E_i}{h} \tag{8.8}$$

Note that the farther apart the energy levels, the shorter the wavelength of the photon needed to induce a transition.

You may have also noticed that in equation (8.7) the energy difference is expressed as $E_i - E_f$, whereas in equation (8.8) it is $E_f - E_i$. This is done to signify that energy is conserved during photon absorption and emission. That is, during emission $E_f = E_i - h\nu$, so that $\nu = (E_i - E_f)/h$. During photon absorption, $E_f = E_i + h\nu$, so that $\nu = (E_f - E_i)/h$.

Spectroscopic techniques have been used extensively in the study of molecular structures. Other forms of spectroscopy available to chemists are described elsewhere in the text.

Emission spectra are generally more complicated than absorption spectra. An excited sample will contain atoms in a variety of states, each being able to drop down to any of several lower states. An absorbing sample generally is cool and transitions are possible only from the ground state. The hydrogen Balmer lines are not seen, for example, in absorption from cold hydrogen atoms.

The Bohr Theory and the Ionization Energy of Hydrogen

The Bohr model of the atom helps to clarify the mechanism of formation of cations. In the special case where the energy of a photon interacting with a hydrogen atom is just enough to remove an electron from the ground state

$(n = 1)$, the electron is freed, the atom is ionized, and the energy of the free electron is zero.

$$h\nu_{\text{photon}} = E_i = -E_1$$

The quantity E_i is called the *ionization energy* of the hydrogen atom. If $n_i = 1$ and $n_f = \infty$ are substituted in the Bohr expression for an electron initially in the ground state of an H atom, then

$$h\nu_{\text{photon}} = E_i = -E_1 = \frac{R_{\text{H}}}{1^2} = R_{\text{H}}$$

The ideas just developed about the ionization of atoms are applied in Example 8-5, where they are coupled with another aspect of the Bohr model: The model also works for hydrogen-like species, such as the ions He^+ and Li^{2+}, which have only one electron. For these species, the nuclear charge (atomic number) appears in the energy-level expression. That is,

$$E_n = \frac{-Z^2 R_{\text{H}}}{n^2} \qquad (8.9)$$

Inadequacies of the Bohr Model

Despite the accomplishments of the Bohr model for the hydrogen atom and hydrogen-like ions, the Bohr theory has a number of weaknesses. From an experimental point of view, the theory cannot explain the emission spectra of atoms and ions with more than one electron, despite numerous attempts to do

---

EXAMPLE 8-5   Using the Bohr Model

Determine the kinetic energy of the electron ionized from a Li^{2+} ion in its ground state, using a photon of frequency $5.000 \times 10^{16} \, s^{-1}$.

Analyze

When a photon of a given energy ionizes a species, any excess energy is transferred as kinetic energy to the electron; that is, $E_{\text{photon}} = IE + KE_{\text{electron}}$. The energy of the electron in the Li^{2+} ion is calculated by using equation (8.9), and the energy of the photon is calculated by using Planck's relationship. The difference is the kinetic energy of the electron.

Solve

$$E_1 = \frac{-3^2 \times 2.179 \times 10^{-18} \, J}{1^2} = -1.961 \times 10^{-17} \, J$$

The energy of a photon of frequency $5.000 \times 10^{16} \, s^{-1}$ is

$$E = h\nu = 6.626 \times 10^{-34} \times \frac{J \, s}{\text{photon}} \times 5.000 \times 10^{16} \, s^{-1} = 3.313 \times 10^{-17} \, J \, \text{photon}^{-1}$$

The kinetic energy of the electron is given by $KE_{\text{electron}} = E_{\text{photon}} - IE$; that is,

kinetic energy $= 3.313 \times 10^{-17} \, J - 1.961 \times 10^{-17} \, J = 1.352 \times 10^{-17} \, J$

Assess

Notice the similarity between the energy conservation expression used in solving this problem ($E_{\text{photon}} = IE + KE_{\text{electron}}$) and the one used in explaining the photoelectric effect ($E_{\text{photon}} = eV_0 + KE_{\text{electron}}$).

PRACTICE EXAMPLE A: Determine the wavelength of light emitted in an electron transition from $n = 5$ to $n = 3$ in a Be^{3+} ion.

PRACTICE EXAMPLE B: The frequency of the $n = 3$ to $n = 2$ transition for an unknown hydrogen-like ion occurs at a frequency 16 times that of the hydrogen atom. What is the identity of the ion?

so. In addition, the theory cannot explain the effect of magnetic fields on emission spectra. From a fundamental standpoint, the Bohr theory is an uneasy mixture of classical and nonclassical physics. Bohr understood at the time that there is no fundamental basis for the postulate of quantized angular momentum forcing an electron into a circular orbit. He made the postulate only so that his theory would agree with experiment.

Modern quantum mechanics replaced the Bohr theory in 1926. The quantization of energy and angular momentum arose out of the postulates of this new quantum theory and required no extra assumptions. Moreover, the circular orbits of the Bohr theory do not occur in quantum mechanics. In summary, the Bohr theory gave the paradigm shift—the quantum leap—from classical physics to the new quantum physics, and we must not underestimate its importance as a scientific development.

🔍 8-4   CONCEPT ASSESSMENT

Which of the following electronic transitions in a hydrogen atom will lead to the emission of a photon with the shortest wavelength, $n = 1$ to $n = 4$, $n = 4$ to $n = 2$, $n = 3$ to $n = 2$?

8-5   Two Ideas Leading to a New Quantum Mechanics

In the previous section, we examined some successes of the Bohr theory and pointed out its inability to deal with multielectron atoms. A decade or so after Bohr's work on hydrogen, two landmark ideas stimulated a new approach to quantum mechanics. Those ideas are considered in this section and the new quantum mechanics—wave mechanics—in the next.

Wave–Particle Duality

To explain the photoelectric effect, Einstein suggested that light has particle-like properties, which are displayed through photons. Other phenomena, however, such as the dispersion of light into a spectrum by a prism, are best understood in terms of the wave theory of light. Light, then, appears to have a *dual* nature.

In 1924, Louis de Broglie, considering the nature of light and matter, offered a startling proposition: *Small particles of matter may at times display wave-like properties.* How did de Broglie come up with such a suggestion? He was aware of Einstein's famous equation

$$E = mc^2$$

where m is the relativistic mass of the photon and c is the speed of light. He combined this equation with the Planck relationship for the energy of a photon $E = h\nu$ as follows

$$h\nu = mc^2$$

$$\frac{h\nu}{c} = mc = p$$

where p is the momentum of the photon. Using $\nu\lambda = c$, we have

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

In order to use this equation for a material particle, such as an electron, de Broglie substituted for the momentum, p, its equivalent—the product of the

▲ **Louis de Broglie (1892–1987)**
De Broglie conceived of the wave–particle duality of small particles while working on his doctorate degree. He was awarded the Nobel Prize in physics 1929 for this work.
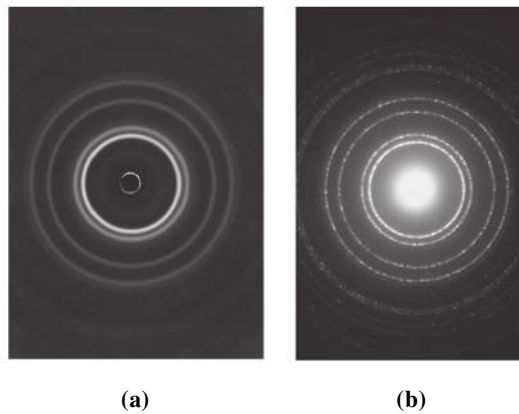
▶ FIGURE 8-16
Wave properties of electrons demonstrated.
(a) Diffraction of X-rays by metal foil.
(b) Diffraction of electrons by metal foil, confirming the wave-like properties of electrons.

(a)   (b)

KEEP IN MIND

that in equation (8.10), wavelength is in meters, mass is in kilograms, and velocity is in meters per second. Planck's constant must also be expressed in units of mass, length, and time. This requires replacing the joule by the equivalent units $kg\, m^2\, s^{-2}$.

mass of the particle, m, and its velocity, u. When this is done, we arrive at de Broglie's famous relationship.

$$\lambda = \frac{h}{p} = \frac{h}{mu} \qquad (8.10)$$

De Broglie called the waves associated with material particles "matter waves." If matter waves exist for small particles, then beams of particles, such as electrons, should exhibit the characteristic properties of waves, namely diffraction (recall page 298). If the distance between the objects that the waves scatter from is about the same as the wavelength of the radiation, diffraction occurs and an interference pattern is observed. For example, X-rays are highly energetic photons with an associated wavelength of about 1 Å (100 pm). X-rays are scattered by the regular array of atoms in the metal aluminum, where the atoms are about 2 Å (200 pm) apart, producing the diffraction pattern shown in Figure 8-16.

In 1927, C. J. Davisson and L. H. Germer of the United States showed that a beam of slow electrons is diffracted by a crystal of nickel. In a similar experiment in that same year, G. P. Thomson of Scotland directed a beam of electrons at a thin metal foil. He obtained the same pattern for the diffraction of electrons by aluminum foil as with X-rays of the same wavelength (Fig. 8-16).

Thomson and Davisson shared the 1937 Nobel Prize in physics for their electron diffraction experiments. George P. Thomson was the son of J. J. Thomson, who had won the Nobel Prize in physics in 1906 for his discovery of the electron. It is interesting to note that Thomson the father showed that the electron is a particle, and Thomson the son showed that the electron is a wave. Father and son together demonstrated the **wave–particle duality** of electrons.

The wavelength calculated in Example 8-6, 24.2 pm, is about one-half the radius of the first Bohr orbit of a hydrogen atom. It is only when wavelengths are comparable to atomic or nuclear dimensions that wave–particle duality is important. The concept has little meaning when applied to large (macroscopic) objects, such as baseballs and automobiles, because their wavelengths are too small to measure. For these macroscopic objects, the laws of classical physics are quite adequate.

The Uncertainty Principle

The laws of classical physics permit us to make precise predictions. For example, we can calculate the exact point at which a rocket will land after it is fired. The more precisely we measure the variables that affect the rocket's trajectory (path), the more accurate our calculation (prediction) will be. In effect, there is no limit to the accuracy we can achieve. In classical physics, nothing is left to chance—physical behavior can be predicted with certainty.

EXAMPLE 8-6   Calculating the Wavelength Associated with a Beam of Particles

What is the wavelength associated with electrons traveling at one-tenth the speed of light?

Analyze

To calculate the wavelength, we use equation (8.10). To use it, we have to collect the electron mass, the electron velocity, and Planck's constant, and then adjust the units so that they are expressed in terms of kg, m, and s.

Solve

The electron mass, expressed in kilograms, is 9.109×10^{-31} kg (recall Table 2.1).
The electron velocity is $u = 0.100 \times c = 0.100 \times 3.00 \times 10^8 \, \mathrm{m \, s^{-1}} = 3.00 \times 10^7 \, \mathrm{m \, s^{-1}}$.
Planck's constant $h = 6.626 \times 10^{-34} \, \mathrm{J \, s} = 6.626 \times 10^{-34} \, \mathrm{kg \, m^2 \, s^{-2} \, s} = 6.626 \times 10^{-34} \, \mathrm{kg \, m^2 \, s^{-1}}$.
Substituting these data into equation (8.10), we obtain

$$\lambda = \frac{6.626 \times 10^{-34} \, \mathrm{kg \, m^2 \, s^{-1}}}{(9.109 \times 10^{-31} \, \mathrm{kg})(3.00 \times 10^7 \, \mathrm{m \, s^{-1}})}$$
$$= 2.42 \times 10^{-11} \, \mathrm{m} = 24.2 \, \mathrm{pm}$$

Assess

By converting the unit J to $\mathrm{kg \, m^2 \, s^{-2}}$, we are able to obtain the wavelength in meters.

PRACTICE EXAMPLE A: Assuming Superman has a mass of 91 kg, what is the wavelength associated with him if he is traveling at one-fifth the speed of light?

PRACTICE EXAMPLE B: To what velocity (speed) must a beam of protons be accelerated to display a de Broglie wavelength of 10.0 pm? Obtain the proton mass from Table 2.1.

During the 1920s, Niels Bohr and Werner Heisenberg considered hypothetical experiments to establish just how precisely the behavior of subatomic particles can be determined. The two variables that must be measured are the position of the particle (x) and its momentum ($p = mu$). The conclusion they reached is that there must *always* be uncertainties in measurement such that the product of the uncertainty in position, Δx, and the uncertainty in momentum, Δp, is

$$\Delta x \Delta p \geq \frac{h}{4\pi} \qquad \textbf{(8.11)}$$

The significance of this expression, called the **Heisenberg uncertainty principle**, is that we cannot measure position and momentum with great precision simultaneously. An experiment designed to locate the position of a particle with great precision cannot also measure the momentum of the particle precisely, and vice versa. In simpler terms, if we know precisely where a particle is, we cannot also know precisely where it has come from or where it is going. If we know precisely how a particle is moving, we cannot also know precisely where it is. In the subatomic world, things must always be "fuzzy." Why should this be so?

The de Broglie relationship (equation 8.10) implies that for a wavelength λ, the momentum of the associated particle is precisely known. However, since the wave itself is spread out over all space, we do not know exactly where the particle is! To get around this inability to locate the particle, we can combine several waves of different wavelengths into a "wave packet" to produce an interference pattern that tends to localize the wave, as suggested in Figure 8-17. However, because each wavelength in the wave packet corresponds to a specific, but different, momentum, the momentum of the particle corresponding to the collection of waves has become uncertain. So as we combine more and more waves to localize the particle, the momentum becomes more and more uncertain. And, conversely, the more precisely we want to know the momentum of a particle the fewer and fewer wavelengths we should combine, meaning that the position

▲ **Werner Heisenberg (1901–1976)**
In addition to his enunciation of the uncertainty principle, for which he won the Nobel Prize in physics in 1932, Heisenberg also developed a mathematical description of the hydrogen atom that gave the same results as Schrödinger's equation (page 323). Heisenberg (left) is shown here dining with Niels Bohr.

▶ The uncertainty principle is not easy for most people to accept. Einstein spent a good deal of time from the middle 1920s until his death in 1955 attempting, unsuccessfully, to disprove it.
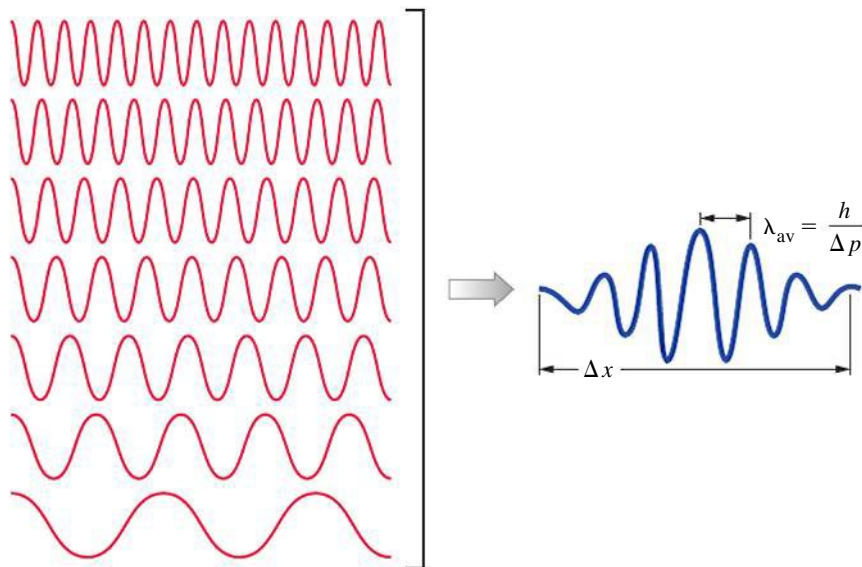
▲ FIGURE 8-17
The uncertainty principle interpreted graphically
A collection of waves with varying wavelengths (left) can combine into a "wave packet" (right). The superposition of the different wavelengths yields an average wavelength (λ_{av}) and causes the wave packet to be more localized (Δx) than the individual waves. The greater the number of wavelengths that combine, the more precisely an associated particle can be located, that is, the smaller Δx. However, because each of the wavelengths corresponds to a different value of momentum according to the de Broglie relationship, the greater is the uncertainty in the resultant momentum.

becomes more spread out. Thus as we proceed downward in size to atomic dimensions, it is no longer valid to consider a particle to be like a hard sphere. Instead, it becomes more and more wavelike, and it is no longer possible to determine with precision both its position and its momentum.

The unit electron-volt (eV). One electron-volt is the energy acquired by an electron as it falls through an electric potential difference of 1 volt. ▼

Once we understand that the consequence of wave–particle duality is the uncertainty principle, we realize that a fundamental error of the Bohr model was to constrain an electron to a one-dimensional orbit (1-D in the sense that the electron cannot move off a circular path of a fixed radius). We are now ready to turn our attention to a modern description of electrons in atoms.

EXAMPLE 8-7   Calculating the Uncertainty of the Position of an Electron

A 12 eV electron can be shown to have a speed of 2.05×10^6 m/s. Assuming that the precision (uncertainty) of this value is 1.5%, with what precision can we simultaneously measure the position of the electron?

Analyze

When given an uncertainty as a percentage, we have to convert it to a fraction by dividing by 100%. The uncertainty of the velocity is then obtained by multiplying this number by the actual velocity.

Solve

The uncertainty in the electron speed is

$$\Delta u = 0.015 \times 2.05 \times 10^6 \, \mathrm{m\,s^{-1}} = 3.1 \times 10^4 \, \mathrm{m\,s^{-1}}$$

The electron mass, 9.109×10^{-31} kg (recall Table 2.1), is known much more precisely than the electron speed, which means that

$$\Delta p = m\Delta u = 9.109 \times 10^{-31} \, \mathrm{kg} \times 3.1 \times 10^4 \, \mathrm{m\,s^{-1}}$$
$$= 2.8 \times 10^{-26} \, \mathrm{kg\,m\,s^{-1}}$$

From equation (8.11), the uncertainty in the electron's position is

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.63 \times 10^{-34} \, \text{kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 2.8 \times 10^{-26} \, \text{kg m s}^{-1}} = 1.9 \times 10^{-9} \, \text{m} = 1.9 \times 10^3 \, \text{pm}$$

Assess

The uncertainty of the electron's position is about 10 atomic diameters. Given the uncertainty in its speed, there is no way to pin down the electron's position with any greater precision.

PRACTICE EXAMPLE A: Superman has a mass of 91 kg and is traveling at one-fifth the speed of light. If the speed at which Superman travels is known with a precision of 1.5%, what is the uncertainty in his position?

PRACTICE EXAMPLE B: What is the uncertainty in the speed of a beam of protons whose position is known with the uncertainty of 24 nm?

🔍 8-5   CONCEPT ASSESSMENT

An electron has a mass approximately 1/2000th of the mass of a proton. Assuming that a proton and an electron have similar wavelengths, how would their speeds compare?

8-6   Wave Mechanics

De Broglie's relationship suggests that electrons are matter waves and thus should display wavelike properties. A consequence of this wave–particle duality is the limited precision in determining an electron's position and momentum imposed by the Heisenberg uncertainty principle. How then are we to view electrons in atoms? To answer this question, we must begin by identifying two types of waves.
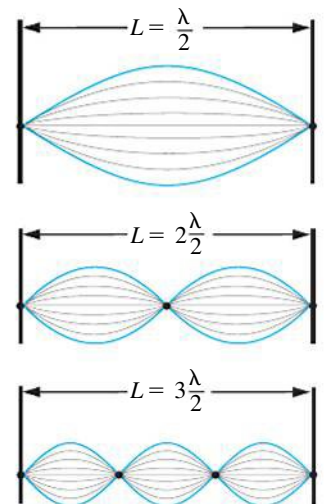
Standing Waves

On an ocean, the wind produces waves on the surface whose crests and troughs travel great distances. These are called *traveling waves*. In the traveling wave shown in Figure 8-1, every portion of a very long rope goes through an identical up-and-down motion. The wave transmits energy along the entire length of the rope. An alternative form of a wave is seen in the vibrations in a plucked guitar string, suggested by Figure 8-18.

Segments of the string experience up-and-down displacements with time, and they oscillate or vibrate between the limits set by the blue curves. The important aspect of these waves is that the crests and troughs of the wave occur at fixed positions and the amplitude of the wave at the fixed ends is zero. Of special interest is the fact that the magnitudes of the oscillations differ from point to point along the wave, including certain points, called *nodes*, that undergo no displacement at all. A wave with these characteristics is called a **standing wave**.

We might say that the permitted wavelengths of standing waves are quantized. They are equal to twice the path length (L) divided by a whole number (n), that is,

$$\lambda = \frac{2L}{n} \quad \text{where } n = 1, 2, 3, \ldots \text{ and the total number of nodes} = n + 1 \quad \textbf{(8.12)}$$

The plucked guitar string represents a one-dimensional standing wave, and so does an electron in a Bohr orbit. Bohr surmised that for an electron to be stable in a circular orbit, it has to be represented by a standing wave and that an integral number of wavelengths have to fit the circumference of the orbit (Fig. 8-19). Also, the fact that Bohr orbits are one dimensional (they are defined by a single

▲ FIGURE 8-18
Standing waves in a string
The string can be set into motion by plucking it. The blue boundaries outline the range of displacements at each point for each standing wave. The relationships between the wavelength, string length, and the number of nodes—points that are not displaced—are given by equation (8.12). The nodes are marked by bold dots.

▶ Beating a drum produces a two-dimensional standing wave, and ringing a spherical bell produces a three-dimensional standing wave.
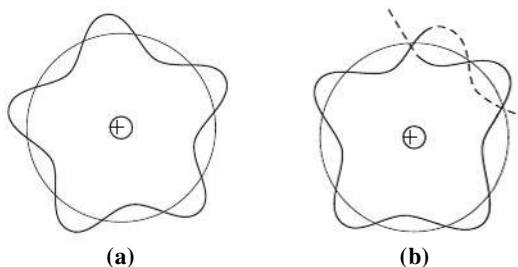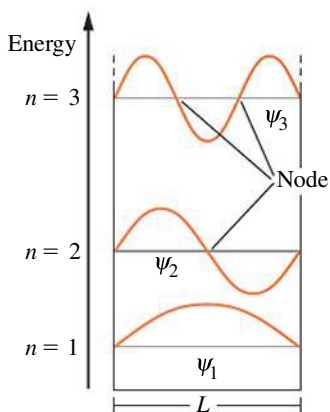

▲ FIGURE 8-19
The electron as a matter wave
These patterns are two-dimensional cross-sections of a much more complicated three-dimensional wave. The wave pattern in **(a)**, a *standing wave*, is an acceptable representation. It has an integral number of wavelengths (five) about the nucleus; successive waves reinforce one another. The pattern in **(b)** is unacceptable. The number of wavelengths is nonintegral, and successive waves tend to cancel each other; that is, the crest in one part of the wave overlaps a trough in another part of the wave, and there is no resultant wave at all.

dimension, the radius) also points up a serious deficiency in the Bohr model: The matter waves of electrons in the hydrogen atom must be three dimensional.

Particle in a Box: Standing Waves, Quantum Particles, and Wave Functions

In 1927, Erwin Schrödinger, an expert on the theory of vibrations and standing waves, suggested that an electron (or any other particle) exhibiting wavelike properties should be describable by a mathematical equation called a **wave function**. The wave function, denoted by the Greek letter psi, ψ, should correspond to a standing wave within the boundary of the system being described. The simplest system for which we can write a wave function is another one-dimensional system, that of a quantum particle confined to move in a one-dimensional box, a line. The wave function for this so-called "particle in a box" looks like those of a guitar string (Fig. 8-18), but now it represents the matter waves of a particle. Since the particle is constrained to be in the box, the waves also must be in the box, as illustrated in Figure 8-20.

If the length of the box is L and the particle moves along the x direction, then the equation for the standing wave is

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, 3, \ldots \quad \textbf{(8.13)}$$

where the quantum number, n, labels the wave function.

This wave function is a sine function. To illustrate, consider the case where $n = 2$.

When

$x = 0,$	$\sin 2\pi x/L = \sin 0 = 0,$	and $\psi_n(x) = 0$
$x = L/4,$	$\sin 2\pi(L/4)/L = \sin \pi/2 = 1,$	and $\psi_n(x) = (2/L)^{1/2}$
$x = L/2,$	$\sin 2\pi(L/2)/L = \sin \pi = 0,$	and $\psi_n(x) = 0$
$x = 3L/4$	$\sin 2\pi(3L/4)/L = \sin 3\pi/2 = -1$	and $\psi_n(x) = -(2/L)^{1/2}$
$x = L$	$\sin 2\pi(L)/L = \sin 2\pi = 0,$	and $\psi_n(x) = 0$

At one end of the box ($x = 0$), both the sine function and the wave function are zero. At one-fourth the length of the box ($x = L/4$), the sine function and the wave function both reach their maximum values. At the midpoint of the box, both are again zero; the wave function has a node. At three-fourths the box length, both functions reach their minimum values (negative quantities), and at the farther end of the box, both functions are again zero.

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$
The wave functions

▲ FIGURE 8-20
The standing waves of a particle in a one-dimensional box
The first three wave functions and their energies are shown in relation to the position of the particle within the box. The wave function changes sign at the nodes.

8-4   ARE YOU WONDERING...

How did we arrive at Equation (8.13)?

The answer to how we arrived at equation (8.13) lies in the equation that gives the form of the wave function and the boundaries to which the quantum mechanical particle is confined. The particle-in-a-box model assumes that the electron is free in the box but is unable to get out of the box. This means that the wave function will be a standing wave inside the box. If you are familiar with differential calculus, you will recognize the equation below as a differential equation. Specifically, it describes a one-dimensional standing wave for the simple system of a particle in a box. The solution to this equation is the wave function for the system.

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi$$

Notice the form of the wave equation: By differentiating the wave function twice, we obtain the wave function times a constant. Many functions satisfy this requirement. For example, two trigonometric functions that have this property are the sine and cosine functions. First, let us consider the function $\psi = A\cos(ax)$ and differentiate twice with respect to x:

$$\frac{d\psi}{dx} = -aA\sin(ax)$$

$$\frac{d^2\psi}{dx^2} = -a^2A\cos(ax) = -a^2\psi$$

where we can identify $a = (2\pi/\lambda)$ and A is an arbitrary factor to be determined. Second, for the sine function,

$$\frac{d\psi}{dx} = aA\cos(ax)$$

$$\frac{d^2\psi}{dx^2} = -a^2A\sin(ax) = -a^2\psi$$

Therefore, both functions are acceptable from this point of view. However, the function must form a standing wave in the box, with a value of zero at the edges of the box. When $x = 0$, $\cos 0 = 1$ and $\sin 0 = 0$, and so the sine function is the appropriate function. The determination of A is not quite as straightforward, and we need to know how to interpret the wave function to determine the value of A. In carrying out this procedure, we have used the boundary conditions of the system to help decide on the correct form of the wave function, which is a common procedure when solving quantum mechanical problems.

Finally, if we identify $a = (2\pi/\lambda)$ and use the standing wave requirement in equation (8.12), then
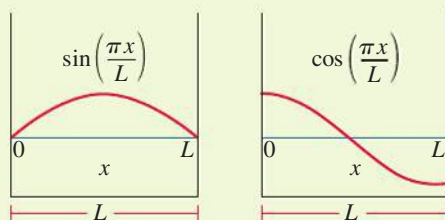
$$a = \frac{2\pi}{\lambda} = \frac{2\pi}{2L/n} = \frac{n\pi}{L}$$

and the function is

$$\psi_n = A\sin\left(\frac{n\pi x}{L}\right)$$

where n is identified as a quantum number, $n = 1, 2, 3, 4, \ldots$

(continued)

▲ Illustration of why a cosine function is an unacceptable solution for the particle in a box. The sine function correctly goes to zero at the edge of the box, but the cosine function does not.

What sense can we make of the wave function and the quantum number? First, consider the quantum number, n. What can we relate it to? The particle that we are considering is freely moving (not acted upon by any outside forces) with a kinetic energy given by the expression

$$E_k = \frac{1}{2}mu^2 = \frac{m^2u^2}{2m} = \frac{p^2}{2m}$$ (8.14)

Now, to associate this kinetic energy with a wave, we can use de Broglie's relationship ($\lambda = h/p$) to get

$$E_k = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

The wavelengths of the matter wave have to fit the standing wave conditions described earlier for the standing waves of a guitar string (equation 8.12). Substituting the wavelength of the matter wave from equation (8.12) into the equation for the energy of the wave yields

$$E_k = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m(2L/n)^2} = \frac{n^2h^2}{8mL^2}$$

So we see that the standing wave condition naturally gives rise to quantization of the wave's energy, with the allowable values determined by the value of n. Note also that as we decrease the size of the box, the kinetic energy of the particle increases, and according to the uncertainty principle, our knowledge of the momentum must decrease. A final noteworthy point is that the energy of the particle *cannot be zero*. The lowest possible energy, corresponding to $n = 1$, is called the **zero-point energy**. Because the zero-point energy is not zero, the particle cannot be at rest. This observation is consistent with the uncertainty principle because the position and momentum both must be uncertain, and there is nothing uncertain about a particle at rest.

The particle-in-a-box model helps us see the origin of the quantization of energy, but how are we to interpret the wave function, ψ? What does it mean that the value of the wave function can be positive or negative? Actually, unlike the trajectory of a classical particle, the wave function of a particle has no physical significance. We need to take a different approach, one suggested by the German physicist Max Born in 1926. From the electron-as-particle standpoint, we have a special interest in the *probability* that the electron is at some particular point; from the electron-as-wave standpoint, our interest is in *electron charge density*. In a classical wave (such as visible light), the amplitude of the wave corresponds to ψ, and the intensity of the wave to ψ^2. The intensity relates to the photon density—the number of photons present in a region. For an electron

wave, then, ψ^2 relates to electron charge density. Electron probability is proportional to electron charge density, and both these quantities are associated with ψ^2. Thus, in Born's interpretation of the wave function, the total probability of finding an electron in a small volume of space is the product of the square of the wave function, ψ^2, and the volume of interest. The factor ψ^2 is called the electron probability density.

Now let us return to a particle constrained to a one-dimensional path in a box and look at the probabilities for the wave functions. These are shown in Figure 8-21. First, notice that even where the wave function is negative, the probability density is positive, as it should be in all cases. Next, look at the probability density for the wave function corresponding to $n = 1$. The highest value of ψ^2 is at the center of the box; that is, the particle is most likely to be found there. The probability density for the state with $n = 2$ indicates that the particle is most likely to be found between the center of the box and the walls.

A final consideration of the particle-in-a-box model concerns its extension to a three-dimensional box. In this case, the particle can move in all three directions—x, y, and z—and the quantization of energy is described by the following expression.

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

where there is one quantum number for each dimension. Thus, a three-dimensional system needs three quantum numbers. With these particle-in-a-box ideas, we can now discuss solving the quantum mechanical problem of the hydrogen atom.

$$\psi_n^2(x) = \frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)$$
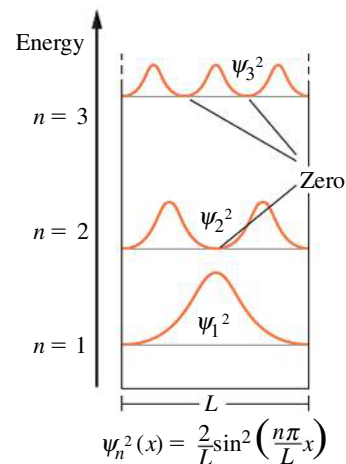
The probabilities

▲ FIGURE 8-21
The probabilities of a particle in a one-dimensional box
The squares of the first three wave functions and their energies are shown in relation to the position of the particle within the box. There is no chance of finding the particle at the points where $\psi^2 = 0$.

EXAMPLE 8-8   Using the Wave Functions of a Particle in a One-Dimensional Box

What is the fraction, as a percentage, of the total probability of finding, between points at 0 pm and 30 pm, an electron in the $n = 5$ level of a one-dimensional box 150 pm long?

Analyze

If an electron is in the $n = 5$ level, then we have a 100% chance of finding it in that level. The $n = 5$ wave function has 4 nodes 30 pm apart, and there are five maxima in ψ^2 at 15 pm, 45 pm, 75 pm, 105 pm, and 135 pm for a one-dimensional box 150 pm long.

Solve

The position at 30 pm corresponds to a node in the wave function, and there are four of these (not counting the nodes at each end of the box). The total area between 0 and 30 pm of ψ^2 represents 25% of the total probability, and so between 0 pm and 30 pm, we expect to find 25% of the probability.

Assess

We must remember that the particle we are considering exhibits wave–particle duality, making it inappropriate to ask a question about how it gets from one side of the node to the other (but that is an appropriate question for a *classical* particle). All we know is that in the $n = 5$ state, for example, the particle is in the box somewhere. When we make a measurement, we'll find the particle on one side of a node or the other. Between 0 and 30 pm, we have a 25% chance of finding the particle, and the maximum chance occurs at 15 pm.

PRACTICE EXAMPLE A: What is the fraction, as a percentage of the total probability of finding, between points at 50 pm and 75 pm, an electron in the $n = 6$ level of a one-dimensional box 150 pm long?

PRACTICE EXAMPLE B: A particle is confined to a one-dimensional box 300 pm long. For the state having $n = 3$, at what points (not counting the ends of the box) does the particle have zero probability of being found?

EXAMPLE 8-9   **Calculating Transition Energy and Photon Wavelengths for the Particle in a Box**

What is the energy difference between the ground state and the first excited state of an electron contained in a one-dimensional box 1.00×10^2 pm long? Calculate the wavelength of the photon that could excite the electron from the ground state to the first excited state.

Analyze

The energy of an electron (E_n) in level n is

$$E_n = \frac{n^2 h^2}{8mL^2}$$

We can write expressions for E_n and E_{n+1}, subtract them, and then substitute the values for $h, m,$ and L. The ground state corresponds to $n = 1$, and the first excited state corresponds to $n = 2$. Finally, we can calculate the wavelength of the photon from the Planck relationship and $c = \lambda\nu$.

Solve

The energies for the states $n = 1$ and $n = 2$ are

$$E_{\text{ground state}} = E_1 = \frac{h^2}{8mL^2}(1^2)$$

$$E_{\text{first excited state}} = E_2 = \frac{h^2}{8mL^2}(2^2)$$

The energy difference is

$$\Delta E = E_2 - E_1 = \frac{3h^2}{8mL^2}$$

The electron mass is 9.109×10^{-31} kg, Planck's constant $h = 6.626 \times 10^{-34}$ J s, and the length of the box is 1.00×10^{-10} m. (Recall: 1 pm = 10^{-12} m.) Substituting these data into the equation, we obtain

$$\Delta E = \frac{3(6.626 \times 10^{-34}\,\text{J s})^2}{8(9.109 \times 10^{-31}\,\text{kg})(1.00 \times 10^{-10}\,\text{m})^2}$$
$$= 1.81 \times 10^{-17}\,\text{J}$$

By using Planck's constant and this value as the energy of a photon, we can calculate the frequency of the photon and then the wavelength. Combining these steps,

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}\,\text{J s} \times 3.00 \times 10^8\,\text{m s}^{-1}}{1.81 \times 10^{-17}\,\text{J}} = 11.0 \times 10^{-9}\,\text{m} = 11.0\,\text{nm}$$

Assess

If we needed the energy of the photon in kJ mol^{-1}, we would have had to multiply 1.8×10^{-17} J by 10^{-3} kJ/J and $N_A = 6.022 \times 10^{23}$ mol^{-1}.

PRACTICE EXAMPLE A: Calculate the wavelength of the photon emitted when an electron in a box 5.0×10^1 pm long falls from the $n = 5$ level to the $n = 3$ level.

PRACTICE EXAMPLE B: A photon of wavelength 24.9 nm excites an electron in a one-dimensional box from the ground state to the first excited state. Estimate the length of the box.

🔍 **8-6**   **CONCEPT ASSESSMENT**

For a particle in a one-dimensional box, in which state (value of *n*) is the greatest probability of finding the particle at one-quarter the length of the box from either end?

Wave Functions of the Hydrogen Atom

In 1927, Schrödinger showed that the wave functions of a quantum mechanical system can be obtained by solving a wave equation that has since become known as the **Schrödinger equation**. We will not go into the details of its

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? 8-5   ARE YOU WONDERING...

What is the Schrödinger equation for the hydrogen atom?

To obtain the Schrödinger equation, we start with the equation for a standing wave in one dimension:

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi$$

The next step is to substitute de Broglie's relationship for the wavelength of a matter wave.

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{h}p\right)^2 \psi$$

Finally, we use the relationship between momentum and kinetic energy, equation 8.14, to obtain

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E_k\psi$$

This is the Schrödinger equation of a free particle moving in one dimension. If the particle is subjected to a force, $V(x)$, then we have

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + V(x)\psi = E_{\text{total}}\psi$$

Extending this treatment to three dimensions, we obtain the Schrödinger equation for the hydrogen atom or hydrogen-like ion, where we understand $V(r)$ to be $(-e)(Ze)/4\pi\epsilon_0 r)$, the potential energy associated with the interaction of the electron (charge $= -e$), and the nucleus of the one electron atom or ion (charge $= Ze$). (See Appendix B, page B-4.)

$$-\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) - \frac{Ze^2}{r}\psi = E\psi$$

This is the equation that Schrödinger obtained. In the equation above, $\partial^2\psi/\partial x^2$ means that we differentiate ψ twice with respect to x, treating the other variables (y and z) as constants. The notation $\partial^2\psi/\partial x^2$ is used instead of $d^2\psi/dx^2$ because ψ depends on more than one variable.

   Following a suggestion by Eugene Wigner, Schrödinger used spherical polar coordinates to solve it rather than the Cartesian coordinates shown here. That is, he substituted the values of $x, y,$ and z in terms of spherical polar coordinates given in the caption for Figure 8-22 and performed the necessary lengthy algebra to collect the variables $r, \theta,$ and ϕ. The equation he obtained is

$$-\frac{h^2}{8\pi^2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{Ze^2}{r}\psi = E\psi$$

where the mass of the electron has been replaced by the more correct reduced mass of the atom, μ, given by

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}}$$

This is the Schrödinger equation in spherical polar coordinates for a hydrogen-like ion of atomic number Z or the hydrogen atom if $Z = 1$. The solutions are shown in Table 8.1 on page 327.
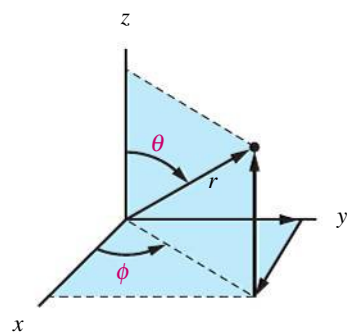
Spherical polar coordinates
$x^2 + y^2 + z^2 = r^2$
$x = r \sin \theta \cos \phi$
$y = r \sin \theta \sin \phi$
$z = r \cos \theta$

▲ FIGURE 8-22
The relationship between spherical polar coordinates and Cartesian coordinates
The coordinates x, y, and z are expressed in terms of the distance r and the angles θ and φ.

solution but just describe and interpret the solution using ideas introduced in the previous discussion.

Solutions of the Schrödinger equation for the hydrogen atom give the wave functions for the electron in the hydrogen atom. These wave functions are called **orbitals** to distinguish them from the orbits of the Bohr theory. The mathematical form of these orbitals is more complex than for the particle in a box, but nonetheless they can be interpreted in a straightforward way.

Wave functions are most easily analyzed in terms of the three variables required to define a point with respect to the nucleus. In the usual Cartesian coordinate system, these three variables are the $x, y,$ and z dimensions. In the spherical polar coordinate system, they are r, the distance of the point from the nucleus, and the angles θ (theta) and ϕ (phi), which describe the orientation of the distance line, r, with respect to the $x, y,$ and z axes (Fig. 8-22). Either coordinate system could be used in solving the Schrödinger equation. However, whereas in the Cartesian coordinate system the orbitals would involve all three variables, $x, y,$ and z, in the spherical polar system the orbitals can be expressed in terms of one function R that depends only on r, and a second function Y that depends on θ and ϕ. That is,

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

The function $R(r)$ is called the **radial wave function**, and the function $Y(\theta, \phi)$ is called the **angular wave function**. Each orbital has three quantum numbers to define it since the hydrogen atom is a three-dimensional system. The particular set of quantum numbers confers a particular functional form to $R(r)$ and $Y(\theta, \phi)$.

Probability densities and the spatial distribution of these densities can be derived from these functional forms. We will first discuss quantum numbers and the orbitals they define, and then the distribution of probability densities associated with the orbitals.

8-7   Quantum Numbers and Electron Orbitals

In the preceding section we stated that by specifying three quantum numbers in a wave function ψ, we obtain an orbital. Here, we explore the combinations of quantum numbers that produce different orbitals. First, though, we need to learn more about the nature of these three quantum numbers.

Assigning Quantum Numbers

The following relationships involving the three quantum numbers arise from the solution of the Schrödinger wave equation for the hydrogen atom. In this solution the values of the quantum numbers are fixed *in the order listed*.

The first number to be fixed is the *principal quantum number*, n, which may have only a positive, nonzero integral value.

$$n = 1, 2, 3, 4, \ldots \tag{8.15}$$

Second is the *orbital angular momentum quantum number*, ℓ, which may be zero or a positive integer, but not larger than $n - 1$ (where n is the principal quantum number).

$$\ell = 0, 1, 2, 3, \ldots, n - 1 \tag{8.16}$$

Third is the *magnetic quantum number*, m_ℓ, which may be a negative or positive integer, including zero, and ranging from $-\ell$ to $+\ell$ (where ℓ is the orbital angular momentum quantum number).

$$m_\ell = -\ell, (-\ell + 1), \ldots, -2, -1, 0, 1, 2 \ldots, (\ell - 1), +\ell \tag{8.17}$$

EXAMPLE 8-10   Applying Relationships Among Quantum Numbers

Can an orbital have the quantum numbers $n = 2$, $\ell = 2$, and $m_\ell = 2$?

Analyze

We must determine whether the given set of quantum numbers is allowed by the rules expressed in equations (8.15), (8.16), and (8.17).

Solve

No. The ℓ quantum number cannot be greater than $n - 1$. Thus, if $n = 2$, ℓ can be only 0 or 1. And if ℓ can be only 0 or 1, m_ℓ cannot be 2; m_ℓ must be 0 if $\ell = 0$ and may be $-1, 0$, or $+1$ if $\ell = 1$.

Assess

It is important that we remember the physical significance of the various quantum numbers, as well as the rules interrelating their values. Quantum number n determines the radial distribution and the average *distance* of the electron and, thus, is most important in determining the *energy* of an electron. Quantum number ℓ determines the angular distribution or *shape* of an orbital. As we will soon see, the relationships among the quantum numbers impart a logical organization of orbitals into shells and subshells.

PRACTICE EXAMPLE A: Can an orbital have the quantum numbers $n = 3$, $\ell = 0$, and $m_\ell = 0$?

PRACTICE EXAMPLE B: For an orbital with $n = 3$ and $m_\ell = 1$, what is (are) the possible value(s) of ℓ?

Principal Shells and Subshells

All orbitals with the same value of n are in the same **principal electronic shell** or **principal level**, and all orbitals with the same n and ℓ values are in the same **subshell**, or **sublevel**.

Principal electronic shells are numbered according to the value of n. The first principal shell consists of orbitals with $n = 1$; the second principal shell of orbitals with $n = 2$; and so on. The value of n relates to the energy and most probable distance of an electron from the nucleus. The higher the value of n, the greater the electron energy and the farther, on average, the electron is from the nucleus. The principal quantum number, therefore, has a physical significance, as do the other quantum numbers. The quantum number ℓ determines the angular distribution, or *shape*, of an orbital and m_ℓ determines the *orientation* of the orbital.

The number of subshells in a principal electronic shell is the same as the number of allowed values of the orbital angular momentum quantum number, ℓ. In the first principal shell, with $n = 1$, the only allowed value of ℓ is 0, and there is a single subshell. The second principal shell ($n = 2$), with the allowed ℓ values of 0 and 1, consists of two subshells; the third principal shell ($n = 3$) has three subshells ($\ell = 0, 1$, and 2); and so on. Or, to put the matter in another way, because there are n possible values of the ℓ quantum number, that is, $0, 1, 2, \ldots (n - 1)$, the number of subshells in a principal shell is equal to the principal quantum number. As a result, there is one subshell in the principal shell with $n = 1$, two subshells in the principal shell with $n = 2$, and so on. The name given to a subshell, regardless of the principal shell in which it is found, depends on the value of the ℓ quantum number. The first four subshells are

s subshell	p subshell	d subshell	f subshell
$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$

The number of orbitals in a subshell is the same as the number of allowed values of m_ℓ for the particular value of ℓ. Recall that the allowed values of m_ℓ are $0, \pm 1, \pm 2, \ldots \pm \ell$, and thus the total number of orbitals in a subshell is $2\ell + 1$. The names of the orbitals are the same as the names of the subshells in which they appear.

s orbitals	*p* orbitals	*d* orbitals	*f* orbitals
$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$
$m_\ell = 0$	$m_\ell = 0, \pm 1$	$m_\ell = 0, \pm 1, \pm 2$	$m_\ell = 0, \pm 1, \pm 2, \pm 3$
one *s* orbital in an *s* subshell	three *p* orbitals in a *p* subshell	five *d* orbitals in a *d* subshell	seven *f* orbitals in an *f* subshell

To designate the particular principal shell in which a given subshell or orbital is found, we use a combination of a number and a letter. For example, the symbol 2*p* is used to designate both the *p* subshell of the second principal shell and any of the three *p* orbitals in that subshell.

The energies of the orbitals for a hydrogen atom, in joules, are given by an equation with a familiar appearance.

$$E_n = -2.178 \times 10^{-18}\left(\frac{1}{n^2}\right) J$$

▶ In Section 8-10 and in Chapter 24, we will see that orbital energies of multielectron atoms also depend on the quantum numbers ℓ and m_ℓ.

It is the same as equation (8.5), the formula derived by Bohr. Orbital energies for a hydrogen atom depend only on the principal quantum number *n*. This means that all the subshells within a principal electronic shell have the same energy, as do all the orbitals within a subshell. Orbitals at the same energy level are said to be **degenerate**. Figure 8-23 shows an energy-level diagram and the arrangement of shells and subshells for a hydrogen atom.

Some of the points discussed in the preceding paragraphs are illustrated in Example 8-11.

▶ FIGURE 8-23
Shells and subshells of a hydrogen atom
The hydrogen atom orbitals are organized into shells and subshells.

Shell   Subshell

$n = 3$ $3s -$ $3p ---$ $3d -----$

$n = 2$ E $2s -$ $2p ---$

$n = 1$ $1s -$

$\ell = 0$ $\ell = 1$ $\ell = 2$

Each subshell is made up of $(2\ell + 1)$ orbitals.
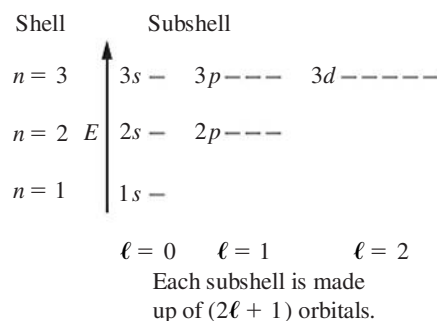
EXAMPLE 8-11   Relating Orbital Designations and Quantum Numbers

Write an orbital designation corresponding to the quantum numbers $n = 4, \ell = 2, m_\ell = 0$.

Analyze

To write orbital designations you need to recall the conventions associated with the quantum numbers *n* and ℓ. For the quantum number *n* we use only the number while for the quantum number ℓ we use the following letters $\ell = 0, s; \ell = 1, p; \ell = 2, d;$ and so on.

Solve

The magnetic quantum number, m_ℓ, is not reflected in the orbital designation. The type of orbital is determined by the ℓ quantum number. Because $\ell = 2$, the orbital is of the *d* type. Because $n = 4$, the orbital designation is 4*d*.

Assess

This is another type of problem in which we need to have memorized the quantum number rules and their designations. This information will be important in the later chapters.

PRACTICE EXAMPLE A: Write an orbital designation corresponding to the quantum numbers $n = 3, \ell = 1$, and $m_\ell = 1$.

PRACTICE EXAMPLE B: Write all the combinations of quantum numbers that define hydrogen-atom orbitals with the same energy as the 3*s* orbital.

8-8 Interpreting and Representing the Orbitals of the Hydrogen Atom

Our major undertaking in this section will be to describe the three-dimensional probability density distributions obtained for the various orbitals in the hydrogen atom. Through the Born interpretation of wave functions (page 320), we will represent the probability densities of the orbitals of the hydrogen atom as surfaces that encompass most of the electron probability. We will see that the probability density for each type of orbital has its own distinctive shape, and like all waves, probability densities exhibit nodes and differing phase behavior. In studying this section, it is important for you to remember that, even though we will offer some additional quantitative information about orbitals, your primary concern should be to acquire a broad qualitative understanding. It is this qualitative understanding that you can apply in our later discussion of how orbitals enter into a description of chemical bonding.

Throughout this discussion, recall that orbitals are wave functions, mathematical solutions of the Schrödinger wave equation. The wave function itself has no physical significance. However, the square of the wave function, ψ^2, is a quantity that is related to probabilities. Probability density distributions based on ψ^2 are three-dimensional, and it is these three-dimensional regions that we mean when we refer to the shape of an orbital.

The forms of the radial wave function $R(r)$ and the angular wave function $Y(\theta, \phi)$ for a one-electron, hydrogen-like atom are shown in Table 8.1. The first thing to note is that the angular part of the wave function for an s orbital,

◀ In Chapter 11, we will discover important uses of the wave function, ψ, itself as a basis for discussing bonding between atoms.

TABLE 8.1 The Angular and Radial Wave Functions of a Hydrogen-Like Atom

Angular Part $Y(\theta, \phi)$	Radial Part $R_{n,\ell}(r)$
$Y(s) = \left(\dfrac{1}{4\pi}\right)^{1/2}$	$R(1s) = 2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma/2}$
	$R(2s) = \dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}(2-\sigma)e^{-\sigma/2}$
	$R(3s) = \dfrac{1}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{3/2}(6-6\sigma+\sigma^2)e^{-\sigma/2}$
$Y(p_x) = \left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$	$R(2p) = \dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma e^{-\sigma/2}$
$Y(p_y) = \left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$	$R(3p) = \dfrac{1}{9\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}(4-\sigma)\sigma e^{-\sigma/2}$
$Y(p_z) = \left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$	
$Y(d_{z^2}) = \left(\dfrac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$	$R(3d) = \dfrac{1}{9\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\sigma/2}$
$Y(d_{x^2-y^2}) = \left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$	
$Y(d_{xy}) = \left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$	$\sigma = \dfrac{2Zr}{na_0}$
$Y(d_{xz}) = \left(\dfrac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\cos\phi$	
$Y(d_{yz}) = \left(\dfrac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\sin\phi$	

$\left(\dfrac{1}{4\pi}\right)^{1/2}$, is always the same, regardless of the principal quantum number. Next, note that the angular parts of the p and d orbitals are also independent of the quantum number n. Therefore all orbitals of a given type (s, p, d, f) have the same angular behavior. Also note that the equations in Table 8.1 are in a general form where the atomic number Z is included. This means that the equations apply to any one-electron atom, that is, to a hydrogen atom or a hydrogen-like ion. Finally, note that the term σ appearing throughout the table is equal to $2Zr/na_0$.

To obtain the wave function for a particular state, we simply multiply the radial part by the angular part. We will now illustrate this by looking at the three major types of orbitals.

s Orbitals

To obtain a complete wave function for the hydrogen $1s$ orbital, we use $Z = 1$ and $n = 1$, and combine the angular and radial wave functions where the red (radial) and blue (angular) colors indicate the origin of the two parts of the wave function.

$$\psi(1s) = R(r) \times Y(\theta, \phi) = \frac{2e^{-r/a_0}}{a_0^{3/2}} \times \frac{1}{\sqrt{4\pi}} = \frac{e^{-r/a_0}}{\sqrt{(\pi a_0^3)}}$$

The term a_0 has the same significance as in the Bohr theory; it is the first Bohr radius—53 pm. By squaring $\psi(1s)$ we obtain an expression for the probability density of finding a $1s$ electron at a distance r from the nucleus in a hydrogen atom.

$$\psi^2(1s) = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 e^{-2r/a_0} \tag{8.18}$$

▶ $\psi^2(1s)$ is the probability density for a $1s$ electron at *one* point a distance r from the nucleus. Equally important is the probability density distribution, which gives the total probability for *all* points at a distance r from the nucleus. In Section 8-10 we will see that this distribution is given by $4\pi r^2 \psi^2$.

How can we represent ψ^2 in expression (8.18)? One way is to pass a plane through the nucleus (for example, the xy plane) and plot a graph of electron probability densities (ψ^2) as perpendicular heights above the many points in the plane at which the electron might be found. The resultant graph, seen in Figure 8-24(a), looks like a symmetrical, cone-shaped "hill" (think of a volcano)

(a)   (b)   (c)
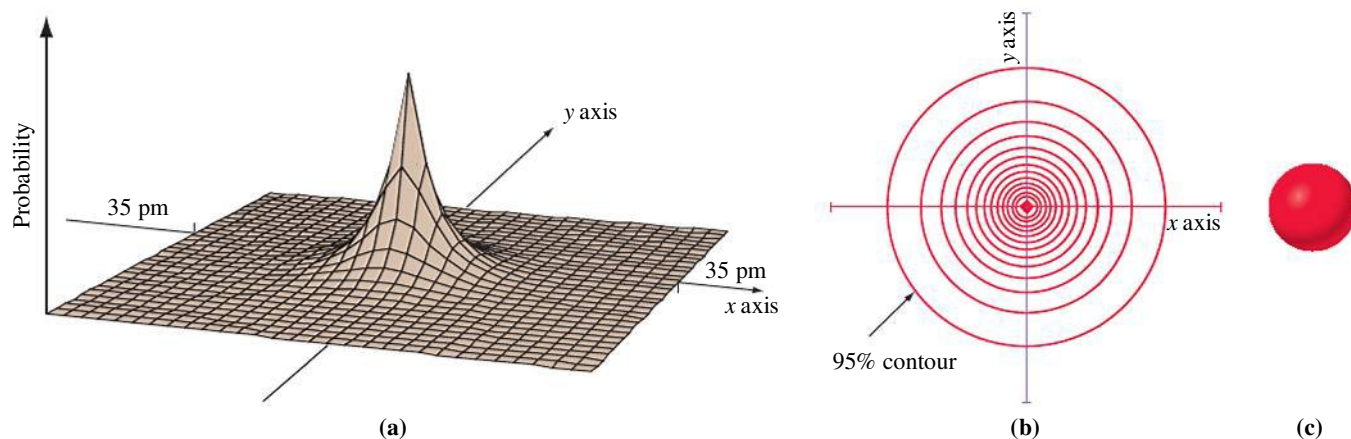
▲ FIGURE 8-24
Three representations of the electron probability density for the 1s orbital
(a) In this diagram the probability density is represented by the height above the xy plane (the xy plane is an arbitrary choice, any plane could have been chosen). **(b)** A contour map of the $1s$ orbital probability density in the xy plane, pointing out the 95% contour. **(c)** A reduced scale 3D representation of the 95% contour of a $1s$ orbital.

of electron probability densities with its peak directly above the nucleus. As in topographical maps of Earth's surface, we can project the three-dimensional surface onto a two-dimensional contour map. The contour map of the "hill" of electron probability densities is shown in Figure 8-24(b). The circular contour lines join points of equal electron probability density. The contours close to the nucleus join points of high probability of finding the electron, those farther away correspond to a lower probability. A simpler way to display the electron probability is to select just one large contour that together with all the contours within it, encompasses an area of high probability of finding the electron. The contour usually chosen is the one outlining an area in which the chance of finding the electron is 95%. The 95% contour just described is for a plane passing through the nucleus, but an electron in a 1s orbital moves in three-dimensional space. The complete 95% probability surface is a sphere, as seen in Figure 8-24(c).

Now let's look at the wave function of the 2s orbital.

$$\psi(2s) = R(r) \times Y(\theta, \phi) = \frac{1}{2\sqrt{2}} \frac{1}{a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \times \frac{1}{\sqrt{4\pi}} = \frac{1}{4} \left(\frac{1}{2\pi a_0^3}\right)^{1/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

The electron probability density for the 2s orbital is given by

$$\psi^2(2s) = \frac{1}{8\pi} \left(\frac{1}{a_0}\right)^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \qquad \textbf{(8.19)}$$

which, when compared to expression (8.18) for the 1s orbital, shows that the 2s electron tends to stay farther from the nucleus than the 1s electron, because the exponential has changed from $-2r/a_0$ for the 1s (equation 8.18) to $-r/a_0$ for the 2s orbital (equation 8.19). The exponential of the 2s orbital decays more slowly than that of the 1s.

The factor $\left(2 - \frac{r}{a_0}\right)$ in the 2s wave function controls the sign of the function. For small values of r, r/a_0 is smaller than two and the wave function is positive, but for large values of r, r/a_0 is larger than two and the wave function is negative. At $r = 2a_0$, the pre-exponential factor is zero and the wave function is said to have a *radial node*. The wave function changes phase (sign) at this radial node.

The fact that the electron probability density of the 2s orbital extends farther from the nucleus than that of the 1s orbital, together with the presence of the node, means that the 95% electron probability density sphere of a 2s orbital is bigger than that of a 1s orbital and contains a sphere of zero probability due to the radial node. These features are illustrated in Figure 8-25, which compares the 1s, 2s, and 3s orbitals. Note that the 3s orbital exhibits two radial nodes and is larger than both the 1s and 2s orbitals. The number of nodes increases as the energy is increased—a characteristic of high-energy standing waves. To highlight the change in phase of an orbital in progressing outward from the nucleus, we have adopted the modern usage of different colors to represent a change in phase. Thus in Figure 8-25 the 1s orbital is a single red color throughout, whereas the 2s orbital starts out red and then switches to blue; and finally, the 3s starts out red, changes to blue and then back to red, reflecting the presence of two radial nodes. We now turn our attention to the p orbitals.

p Orbitals

The radial part of $\psi(2p)$ for a hydrogen atom is

$$R(2p) = \frac{1}{2\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0}$$

3s

2s

1s
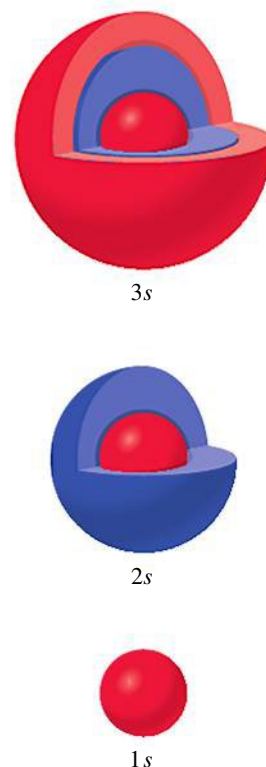
▲ FIGURE 8-25
Three-dimensional representations of the 95% electron probability density for the 1s, 2s, and 3s orbitals
The first three s orbitals of the hydrogen atom. Note the increasing size of the 95% probability density contour in proceeding from 1s to 2s and on to 3s.

Thus, the 2p orbital has no radial nodes at finite values of r. In contrast to the s orbitals, which are nonzero at $r = 0$, the p orbitals vanish at $r = 0$. This difference will have an important consequence when we consider multi-electron atoms.

In contrast to the angular function of the 2s orbital, the angular part of the 2p orbital is not a constant, but a function of θ and ϕ. This means that the electron probability density distribution of a p orbital is not spherically symmetric; that is, it does not have a spherical shape. We see this most easily in Table 8.1 in the functional form of the angular part of the $2p_z$ wave function; it is proportional to $\cos \theta$. Thus the $2p_z$ wave function has an angular maximum along the positive z axis, for there $\theta = 0$ and $\cos 0 = +1$. Along the negative z axis, the p_z wave function has its most negative value, for there $\theta = \pi$ and $\cos \pi = -1$. That the angular part has its maximum magnitude along the z axis is the reason for the designation p_z. Everywhere in the xy plane $\theta = \pi/2$ and $\cos \theta = 0$, so the xy plane is a node. Because this node arises in the angular function, it is called an *angular node*. A similar analysis of the p_x and p_y orbitals shows that they are similar to the p_z orbital, but with angular nodes in the yz and xz planes, respectively.

Figure 8-26 shows the two ways of representing the angular part of the p_z wave function. In Figure 8-26(a), the function $\cos \theta$ is plotted as a function of θ and results in two tangential circles. In Figure 8-26(b), the function $\cos^2 \theta$, which is related to the angular electron probability density, is plotted as a function of θ, resulting in a double teardrop shape. Both these representations are used. What is important to note in part (a) of the figure is the phase of the plot of $\cos \theta$ and in (b), the lack of phase of $\cos^2 \theta$, which is always positive. We shall see later in the text that the phase of the orbital is important in understanding chemical bonding.

The simultaneous display of both the radial and angular parts of $\psi^2(2p)$ is more difficult to achieve, but Figure 8-27 attempts to do this for the 95% probability surface of the p_z orbital. All three of the p orbitals are shown in Figure 8-28 and are seen to be directed along the three perpendicular axes of the Cartesian system. Again we have used different colors to represent the phase alternation in these orbitals. However, we must remember that these refer only to the phases of the original wave function, *not* to ψ^2.

▶ The points at which a wave function changes sign are nodes. However, even though the 2p wave function becomes zero at $r = 0$ and $r = \infty$, these points are not true nodes because the function does not change sign at these points. These points are sometimes called *trivial nodes*.
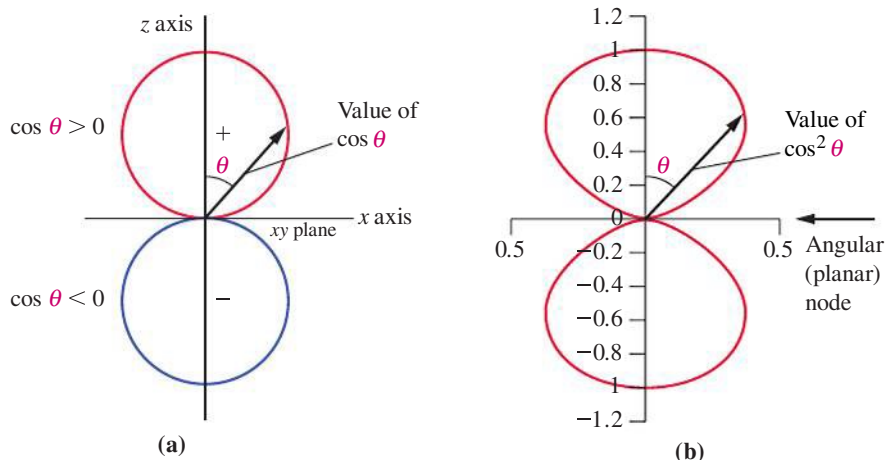
d Orbitals

The d orbitals occur for the first time when $n = 3$. The angular function in these cases possesses two angular (or planar) nodes. Let's illustrate this with the orbital that has an angular function proportional to

$$\sin^2 \theta \cos 2\phi$$

▶ FIGURE 8-26
Two representations of the p orbital angular function
(a) A plot of $\cos \theta$ in the zx plane, representing the angular part of the $2p_z$ wave function. Note the difference in the color of the function in the two lobes representing the phase of the angular wave function.
(b) A plot of $\cos^2 \theta$ in the zx plane, representing the square of the wave function and proportional to the angular probability density of finding the electron.

(a)

(b)

(c)
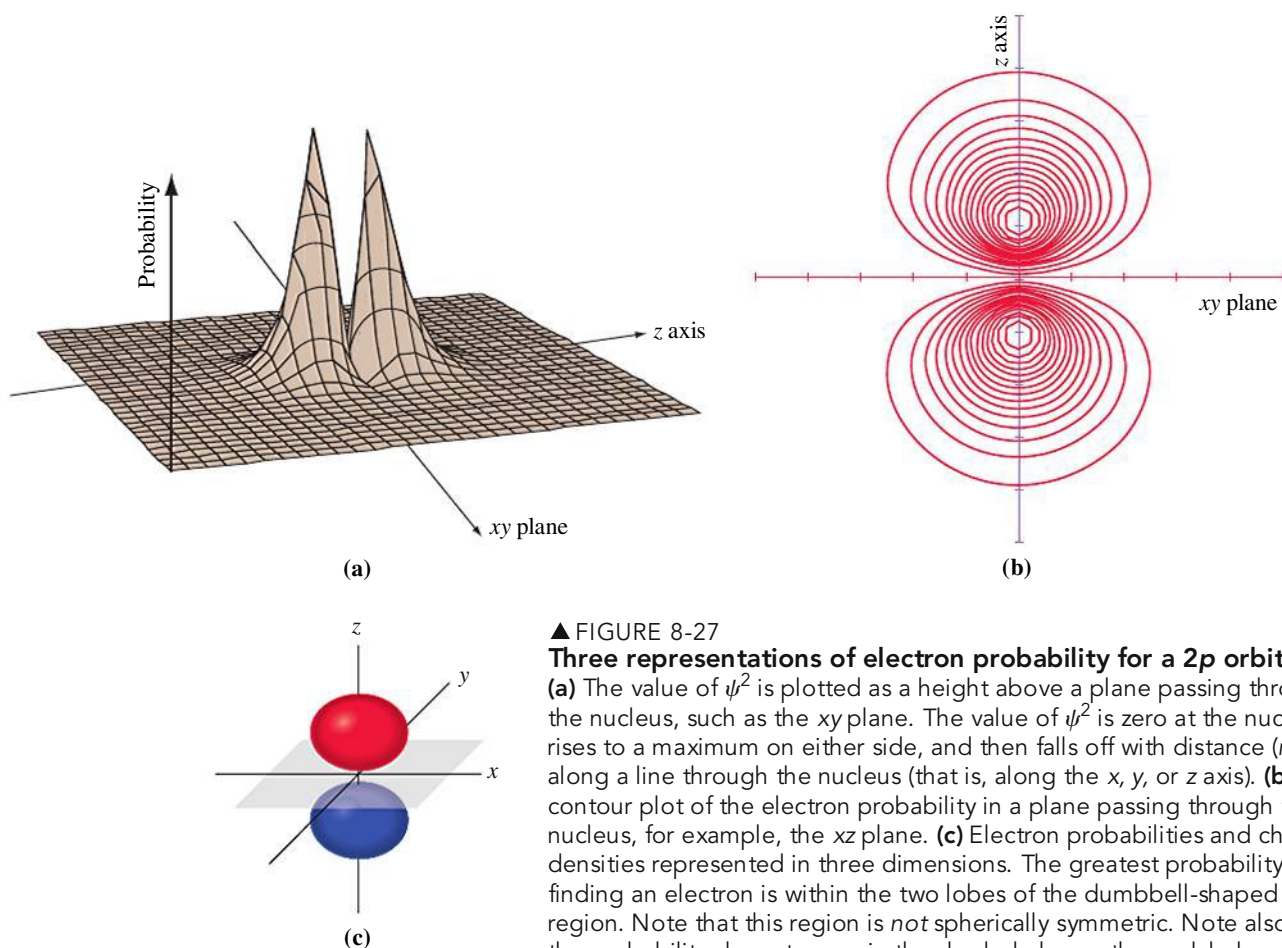
▲ FIGURE 8-27
Three representations of electron probability for a 2p orbital
(a) The value of ψ^2 is plotted as a height above a plane passing through the nucleus, such as the xy plane. The value of ψ^2 is zero at the nucleus, rises to a maximum on either side, and then falls off with distance (r) along a line through the nucleus (that is, along the x, y, or z axis). **(b)** A contour plot of the electron probability in a plane passing through the nucleus, for example, the xz plane. **(c)** Electron probabilities and charge densities represented in three dimensions. The greatest probability of finding an electron is within the two lobes of the dumbbell-shaped region. Note that this region is *not* spherically symmetric. Note also that the probability drops to zero in the shaded plane—the nodal plane (the xy plane). As with the 2s and 3s orbitals, we have indicated changes of phase through different colors.

p_x

p_y

p_z
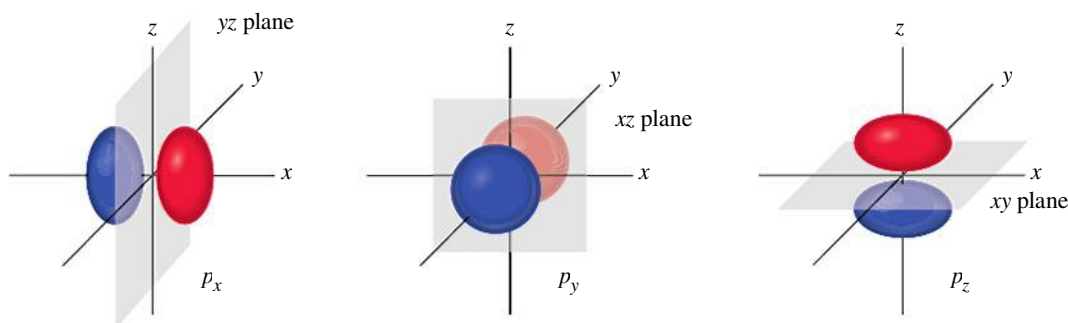
▲ FIGURE 8-28
The three 2p orbitals
The p orbitals are usually represented as directed along the perpendicular x, y, and z axes, and the symbols p_x, p_y and p_z are often used. The p_z orbital has $m_\ell = 0$. The situation with p_x and p_y is more complex, however. Each of these orbitals has contributions from both $m_\ell = 1$ and $m_\ell = -1$. Our main concern is just to recognize that p orbitals occur in sets of three and can be represented in the orientation shown here. In higher-numbered shells, p orbitals have a somewhat different appearance, but we will use these general shapes for all p orbitals. The colors of the lobes signify the different phases of the original wave function.
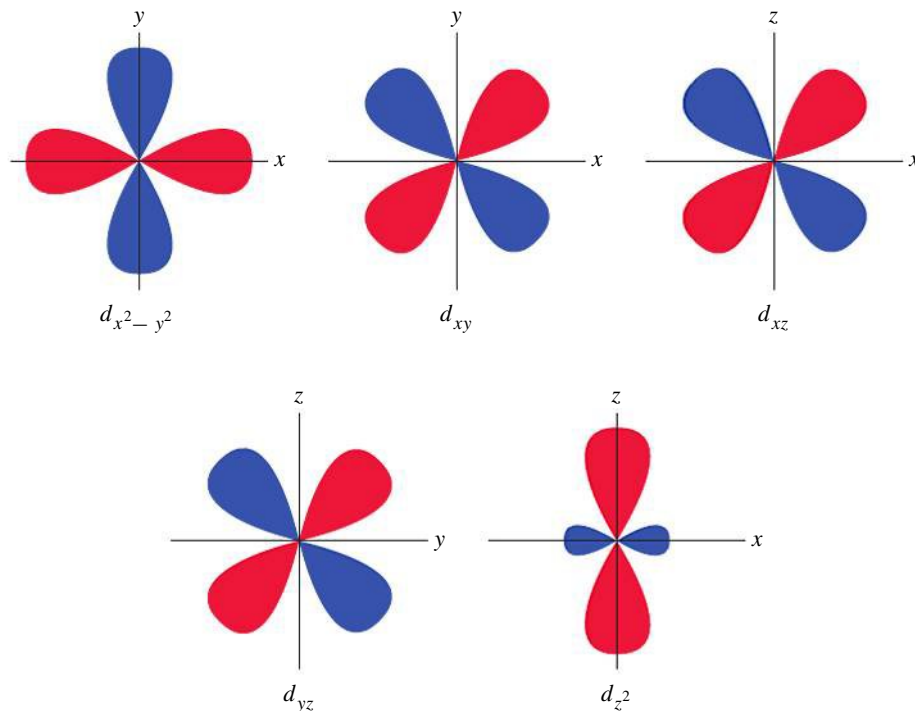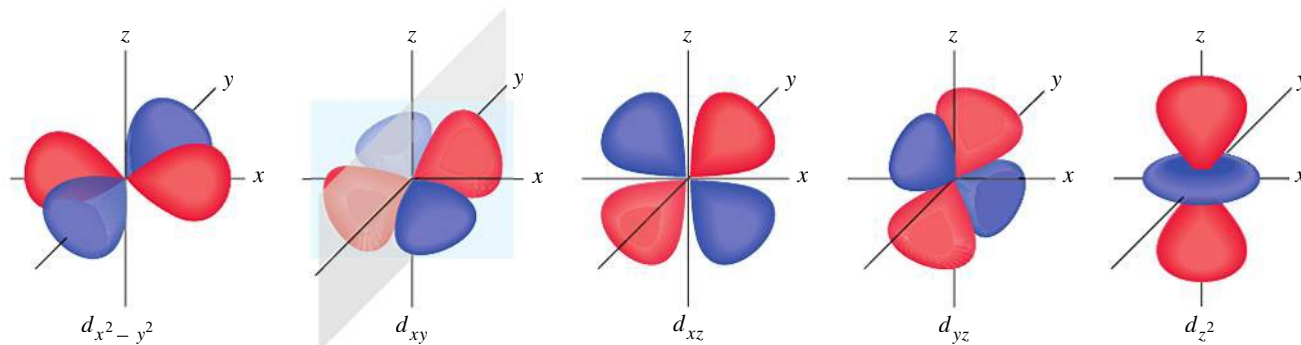
▲ FIGURE 8-29
Cross sections of the five *d* orbitals
The two-dimensional cross sections of the angular functions of the five *d* orbitals in the planes indicated.

How should we visualize this function? We can proceed by setting $\theta = \pi/2$ and plotting the function $\cos 2\phi$. Study Figure 8-22 (page 324) and you will see that the angle $\theta = \pi/2$ corresponds to the *xy* plane, yielding the cross section in the upper left of Figure 8-29. The wave function exhibits positive and negative lobes, indicated by the red and blue lobes, respectively, along the *x* and *y* axes. This orbital, in common with all the other *d* orbitals, is a function of two of the three variables ($x, y,$ and z). It is designated $d_{x^2-y^2}$. The other *d* orbitals, $d_{xy}, d_{xz}, d_{yz},$ and d_{z^2}, are also displayed in Figure 8-29. We observe that four of them have the same basic shape except for orientation with respect to the axes and that d_{z^2} has quite a different shape.

The 95% probability surfaces of the five *d* orbitals are shown in Figure 8-30. Two of the *d* orbitals ($d_{x^2-y^2}$ and d_{z^2}) are seen to be directed along the three

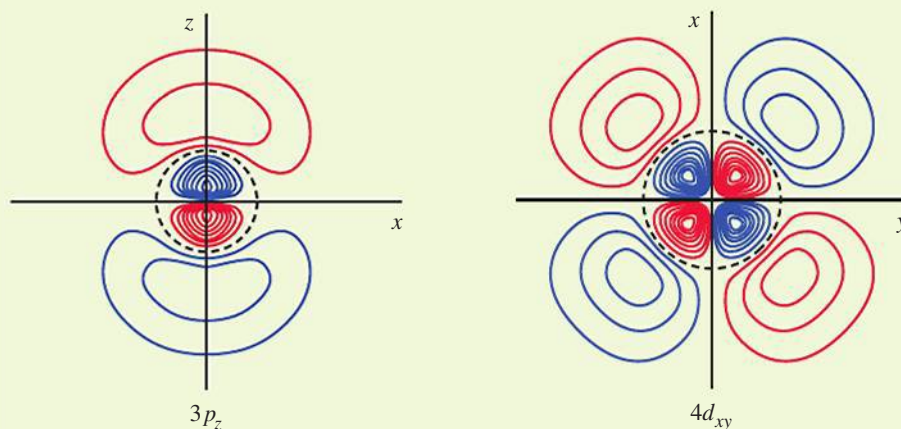
▲ FIGURE 8-30
Representations of the five *d* orbitals
The designations *xy, xz, yz*, and so on, are related to the values of the quantum number m_ℓ, but this is a detail that we will not pursue in the text. The number of nodal surfaces for an orbital is equal to the ℓ quantum number. For *d* orbitals, there are two such surfaces. The nodal planes for the d_{xy} orbital are shown here. (The nodal surfaces for the d_{z^2} orbital are actually cone-shaped.)

perpendicular axes of the Cartesian system, and the remaining three (d_{xy}, d_{xz}, d_{yz}) are seen to point between these Cartesian axes. Again, the relative phases of the lobes of the original wave function are indicated by the different colors. The d orbitals are important in understanding the chemistry of the transition elements, as we will see in Chapter 23.

8-6   ARE YOU WONDERING...

What does a $3p_z$ and a $4d_{xy}$ orbital look like?

When considering the shapes of the atomic orbitals with higher principal quantum number, we can draw on what we have discussed already and include the extra radial nodes that occur. For example, the $3p_z$ orbital has a total of two nodes (number of nodes $= n - 1$); one of these nodes is taken up with the angular node of the angular part of the $3p_z$ wave function, so that the radial part of the wave function will also have a node. Figure 8-31 shows a contour plot of the value of the $3p_z$ wave function in the xz plane in the manner of Figure 8-27(b). We notice that the $3p_z$ orbital has the same general shape as a $2p_z$ orbital due to the angular node, but the radial node has appeared as a circle (dashed in Figure 8-31). The appearance of the $3p_z$ orbital is that of a smaller p orbital inside a larger one. Similarly the $4d_{xy}$ orbital appears as a smaller d_{xy} inside a larger one. In Figure 8-31 the radial node is indicated by the dashed circle and the presence of the node is indicated by the alternation in color. This idea can be extended to enable us to sketch orbitals of increasing principal quantum number.

▲ FIGURE 8-31
**Contour plots for $3p_z$ and the $4d_{xy}$ orbital**
The relative phases in these orbitals are shown by the colors red and blue.
The radial nodes are represented by the dashed circles.

8-7   CONCEPT ASSESSMENT

What type of orbital has three angular nodes and one radial node?

8-9   Electron Spin: A Fourth Quantum Number

Wave mechanics provides three quantum numbers with which we can develop a description of electron orbitals. However, in 1925, George Uhlenbeck and Samuel Goudsmit proposed that some unexplained features of

$$m_s = +\tfrac{1}{2} \qquad m_s = -\tfrac{1}{2}$$
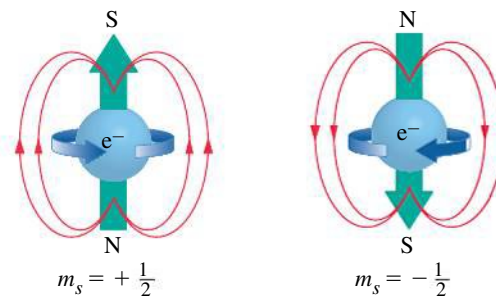
▲ FIGURE 8-32
Electron spin visualized
Two possibilities for electron spin are shown with their associated magnetic fields. Two electrons with opposing spins have opposing magnetic fields that cancel, leaving no net magnetic field for the pair.

the hydrogen spectrum could be understood by assuming that an electron acts as if it spins, much as Earth spins on its axis. As suggested by Figure 8-32, there are two possibilities for **electron spin**. Thus, these two possibilities require a fourth quantum number, the electron spin quantum number m_s. The electron spin quantum number may have a value of $+\tfrac{1}{2}$ (also denoted by the arrow ↑) or $-\tfrac{1}{2}$ (denoted by the arrow ↓); the value of m_s does not depend on any of the other three quantum numbers.

What is the evidence that the phenomenon of electron spin exists? An experiment by Otto Stern and Walter Gerlach in 1920, though designed for another purpose, seems to yield this proof (Fig. 8-33). Silver was vaporized in an oven, and a beam of silver atoms was passed through a nonuniform magnetic field, where the beam split in two. Here is a simplified explanation.

1. An electron, because of its spin, generates a magnetic field.
2. A pair of electrons with opposing spins has no net magnetic field.
3. In a silver atom, 23 electrons have a spin of one type and 24 of the opposite type. The direction of the net magnetic field produced depends only on the spin of the unpaired electron.
4. In a beam of a large number of silver atoms there is an equal chance that the unpaired electron will have a spin of $+\tfrac{1}{2}$ or $-\tfrac{1}{2}$. The magnetic field induced by the silver atoms interacts with the nonuniform field, and the beam of silver atoms splits into two beams.
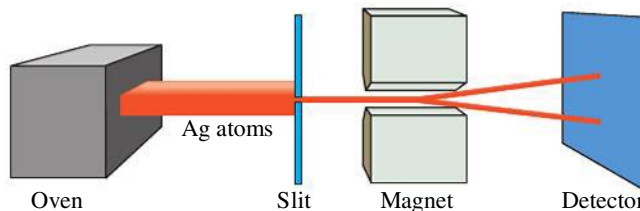
▲ FIGURE 8-33
The Stern–Gerlach experiment
Ag atoms vaporized in the oven are collimated into a beam by the slit, and the beam is passed through a nonuniform magnetic field. The beam splits in two. The beam of atoms would not experience a force if the magnetic field were uniform. The field strength must be stronger in certain directions than in others.

Electronic Structure of the H Atom: Representing the Four Quantum Numbers

Now that we have described the four quantum numbers, we are in a position to bring them together into a description of the electronic structure of the hydrogen atom. The electron in a ground-state hydrogen atom is found at the lowest energy level. This corresponds to the principal quantum number $n = 1$, and because the first principal shell consists only of an s orbital, the orbital quantum number $\ell = 0$. The only possible value of the magnetic quantum number is $m_\ell = 0$. Either spin state is possible for the electron, and we do not know which it is unless we do an experiment like that of Uhlenbeck and Goudsmit's. Thus,

$$n = 1 \qquad \ell = 0 \qquad m_\ell = 0 \qquad m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

Chemists often say that the electron in the ground-state hydrogen atom is in the $1s$ orbital, or that it is a $1s$ electron, and they represent this by the notation

$$1s^1$$

where the superscript 1 indicates one electron in the $1s$ orbital. Either spin state is allowed, but we do not designate the spin state in this notation.

In the excited states of the hydrogen atom, the electron occupies orbitals with higher values of n. Thus, when excited to the level with $n = 2$, the electron can occupy either the $2s$ or one of the $2p$ orbitals; all have the same energy. Because the probability density extends farther from the nucleus in the $2s$ and $2p$ orbitals than in the $1s$ orbital, the excited-state atom is larger than is the ground-state atom. The excited states just described can be represented as

$$2s^1 \text{ or } 2p^1$$
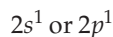
In the remaining sections of the chapter this discussion will be extended to the electronic structures of atoms having more than one electron—*multielectron* atoms.

> **KEEP IN MIND**
>
> that orbitals are mathematical functions and not themselves physical regions in space. However, it is customary to refer to an electron that is described by a particular orbital as being "in the orbital."

EXAMPLE 8-12   **Choosing an Appropriate Combination of the Four Quantum Numbers: n, ℓ, m_ℓ, and m_s**

From the following sets of quantum numbers (n, ℓ, m_ℓ, m_s), identify the set that is correct, and state the orbital designation for those quantum numbers:

$$(2,1,0,0) \quad \left(2,0,1,\frac{1}{2}\right) \quad \left(2,2,0,\frac{1}{2}\right) \quad \left(2,-1,0,\frac{1}{2}\right) \quad \left(2,1,0,-\frac{1}{2}\right)$$

Analyze

We know that if $n = 2$, ℓ has two possible values: 0 or 1. The range of values for m_ℓ is given by equation (8.16), and $m_s = \pm\frac{1}{2}$. By using this information, we can judge which combination is correct.

Solve

(n, ℓ, m_ℓ, m_s)	Comment
$(2,1,0,0)$	The value of m_s is incorrect.
$\left(2,0,1,\frac{1}{2}\right)$	The value of m_ℓ is incorrect.
$\left(2,2,0,\frac{1}{2}\right)$	The value of ℓ is incorrect.
$\left(2,-1,0,\frac{1}{2}\right)$	The value of ℓ is incorrect.
$\left(2,1,0,-\frac{1}{2}\right)$	All the quantum numbers are correct.

(continued)

The correct combination of quantum numbers has $n = 2, \ell = 1, m_\ell = 0$, and $m_s = -\frac{1}{2}$, which corresponds to a $2p$ orbital.

Assess

The combination of quantum numbers identified above for an electron in a $2p$ orbital is one of six possible combinations. The other five combinations for an electron in a $2p$ orbital are $\left(2, 1, 0, \frac{1}{2}\right)$, $\left(2, 1, -1, -\frac{1}{2}\right)$, $\left(2, 1, -1, \frac{1}{2}\right)$, $\left(2, 1, 1, -\frac{1}{2}\right)$, and $\left(2, 1, 1, \frac{1}{2}\right)$.

PRACTICE EXAMPLE A: Determine which set of the following quantum numbers (n, ℓ, m_ℓ, m_s) is wrong and indicate why:

$$(3, 2, -2, 1) \quad \left(3, 1, -2, \frac{1}{2}\right) \quad \left(3, 0, 0, \frac{1}{2}\right) \quad \left(2, 3, 0, \frac{1}{2}\right) \quad \left(1, 0, 0, -\frac{1}{2}\right) \quad \left(2, -1, -1, \frac{1}{2}\right)$$

PRACTICE EXAMPLE B: Identify the error in each set of quantum numbers below:

$$(2, 1, 1, 0) \quad \left(1, 1, 0, \frac{1}{2}\right) \quad \left(3, -1, 1, -\frac{1}{2}\right) \quad \left(0, 0, 0, -\frac{1}{2}\right) \quad \left(2, 1, 2, \frac{1}{2}\right)$$

8-10 Multielectron Atoms

Schrödinger developed his wave equation for the hydrogen atom—an atom containing just one electron. For multielectron atoms, a new factor arises: mutual repulsion between electrons. The repulsion between the electrons means that the electrons in a multielectron atom tend to stay away from one another, and their motions become inextricably entangled. The approximate approach taken to solve this many-particle problem is to consider the electrons, one by one, in the environment established by the nucleus and the other electrons. When this is done, the electron orbitals obtained are of the same types as those obtained for the hydrogen atom; they are called *hydrogen-like* orbitals. Compared with the hydrogen atom, the angular parts of the orbitals of a multielectron atom are unchanged, but the radial parts are different.

We have seen that the solution of the Schrödinger equation for a hydrogen atom gives the energies of the orbitals and that all orbitals with the same principal quantum number n are degenerate—they have the same energy. In a hydrogen atom, the orbitals $2s$ and $2p$ are degenerate, as are $3s, 3p$, and $3d$.

In multielectron atoms, the attractive force of the nucleus for a given electron increases as the nuclear charge increases. As a result, we find that orbital energies become lower (more negative) with increasing atomic number of the atom. Also, orbital energies in multielectron atoms depend on the type of orbital; the orbitals with different values of ℓ within a principal shell are not degenerate.

> **KEEP IN MIND**
>
> that orbital-wave functions extend farther out from the nucleus as n increases. Thus, an electron in a $3s$ or $3p$ orbital has a higher probability of being farther from the nucleus than does an electron in a $1s$ orbital.

Penetration and Shielding

Think about the attractive force of the atomic nucleus for one particular electron some distance from the nucleus. Electrons in orbitals closer to the nucleus *screen* or *shield* the nucleus from electrons farther away. In effect, the screening electrons reduce the effectiveness of the nucleus in attracting the particular more-distant electron. They effectively reduce the nuclear charge.

The magnitude of the reduction of the nuclear charge depends on the types of orbitals the inner electrons are in and the type of orbital that the screened electron is in. We have seen that electrons in s orbitals have a high probability density at the nucleus, whereas p and d orbitals have zero probability densities

at the nucleus. Thus, electrons in *s* orbitals are more effective at screening the nucleus from outer electrons than are electrons in *p* or *d* orbitals. This ability of electrons in *s* orbitals that allows them to get close to the nucleus is called *penetration*. An electron in an orbital with good penetration is better at screening than one with low penetration.

We must consider a different kind of probability distribution to describe the penetration to the nucleus by orbital electrons. Rather than considering the probability at a point, which we did to ascribe three-dimensional shapes to orbitals, we need to consider the probability of finding the electron anywhere in a spherical shell of radius *r* and an infinitesimal thickness. This type of probability is called a *radial probability distribution* and is found by multiplying the radial probability density, $R^2(r)$, by the factor $4\pi r^2$, the area of a sphere of radius *r*. Figure 8-34 offers a dartboard analogy that might help clarify the distinction between probability at a point and probability in a region of space.

The quantity $4\pi r^2 \times R^2(r)$ provides a different insight into the behavior of the electron. The radial probability distributions for some hydrogenic (hydrogen-like) orbitals are plotted in Figure 8-35. The radial probability density, $R^2(r)$, for a 1*s* orbital predicts that the maximum probability for a 1*s* electron is *at* the nucleus. However, because the volume of this region is vanishingly small $(r = 0)$, the radial probability distribution $[4\pi r^2 \times R^2(r)]$ is zero at the nucleus. The electron in a hydrogen atom is most likely to be found 53 pm from the nucleus; this is where the radial probability distribution reaches a maximum. This is the same radius as the first Bohr orbit. The boundary surface within which there is a 95% probability of finding an electron (see Figure 8-25, p. 329) is a much larger sphere, one with a radius of about 141 pm.

In comparing the radial probability curves for the 1*s*, 2*s*, and 3*s* orbitals, we find that a 1*s* electron has a greater probability of being close to the nucleus than a 2*s* electron does, which in turn has a greater probability than does a 3*s* electron. In comparing 2*s* and 2*p* orbitals, a 2*s* electron has a greater chance of being close to the nucleus than a 2*p* electron does. The 2*s* electron exhibits
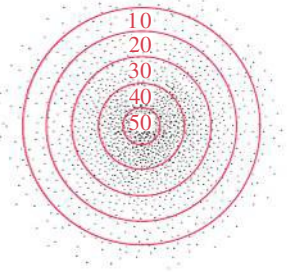
▲ FIGURE 8-34
Dartboard analogy to a 1*s* orbital
Imagine that a single dart (electron) is thrown at a dartboard 1500 times. The board contains 95% of all the holes; it is analogous to the 1*s* orbital. Where is a thrown dart most likely to hit? The number of holes per unit area is greatest in the "50" region—that is, the 50 region has the greatest probability density. The most likely score is "30," however, because the most probable area hit is in the 30 ring and not the 50 ring, which is smaller than the 30 ring. The 30 *ring* on the dartboard is analogous to a spherical *shell* of 53 pm radius within the larger sphere representing the 1*s* orbital.
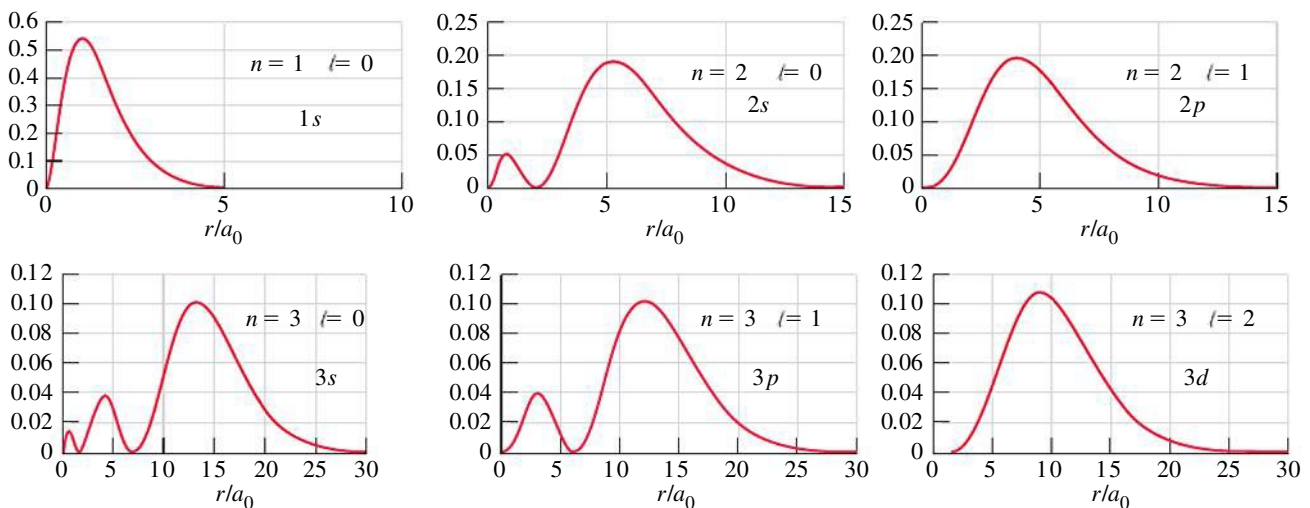
▲ FIGURE 8-35
Radial probability distributions
Graphs of the value of $4\pi r^2 R^2(r)$ as a function of *r* for the orbitals in the first three principal shells. Note that the smaller the orbital angular momentum quantum number, the more closely an electron approaches the nucleus. Thus, *s* orbital electrons penetrate more, and are less shielded from the nucleus, than electrons in other orbitals with the same value of *n*.

greater penetration than the 2*p* electron. Electrons having a high degree of penetration effectively "block the view" of an electron in an outer orbital "looking" for the nucleus.

The nuclear charge that an electron would experience if there were no intervening electrons is Z, the atomic number. The nuclear charge that an electron actually experiences is reduced by intervening electrons to a value of Z_{eff}, called the **effective nuclear charge**. The less of the nuclear charge that an outer electron "sees" (that is, the smaller the value of Z_{eff}), the smaller is the attraction of the electron to the nucleus, and hence the *higher* is the energy of the orbital in which the electron is found.
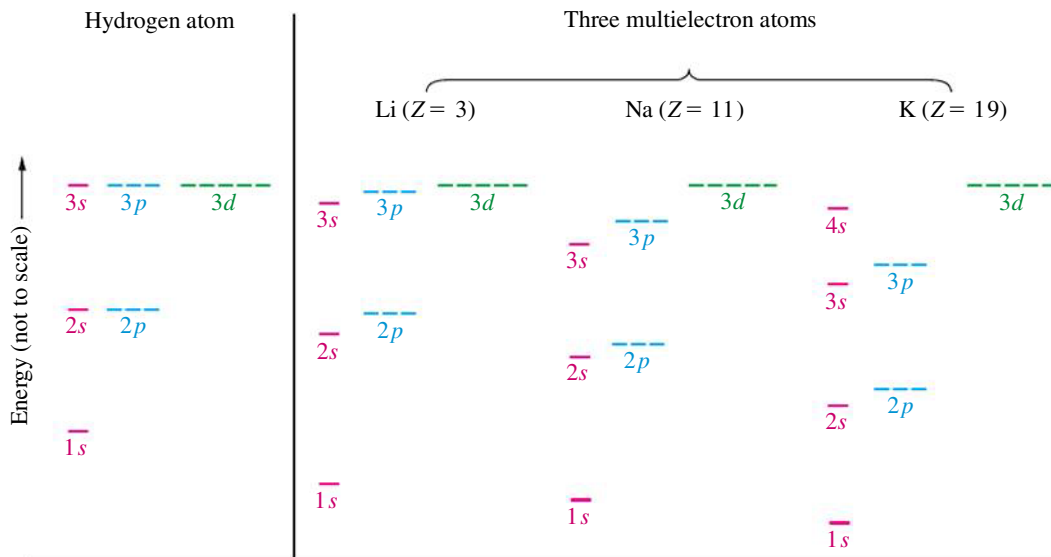
To summarize, compared with a *p* electron in the same principal shell, an *s* electron is more penetrating and not as well screened. The *s* electron experiences a higher Z_{eff}, is held more tightly, and is at a lower energy than a *p* electron. Similarly, the *p* electron is at a lower energy than a *d* electron in the same principal shell. Thus, the energy level of a principal shell is split into separate levels for its subshells. There is no further splitting of energies within a subshell, however, because all the orbitals in the subshell have the same radial characteristics and thereby experience the same effective nuclear charge, Z_{eff}. As a result, all three *p* orbitals of a principal shell have the same energy; all five *d* orbitals have the same energy; and so on.

In a few instances, the combined effect of the decreased spacing between successive energy levels at higher quantum numbers (because of the energy dependence on $1/n^2$) and the splitting of subshell energy levels (because of shielding and penetration) causes some energy levels to overlap. For example, because of the extra penetration of a 4*s* electron over that of a 3*d* electron, the 4*s* energy level is below the 3*d* level despite its higher principal quantum number *n* (Fig. 8-36). We will see some of the consequences of this energy-level splitting in the next two sections, where we consider the relationship between the electronic structures of atoms and their positions in the periodic table.

KEEP IN MIND

that, similar to the situation in equation (8.9), the energy of an orbital (E_n) is given by the proportionality

$$E_n \propto -\frac{Z_{eff}^2}{n^2}.$$

▲ FIGURE 8-36
Orbital energy-level diagram for the first three electronic shells
Energy levels are shown for a hydrogen atom (left) and three typical multielectron atoms (right). Each multielectron atom has its own energy-level diagram. Note that for the hydrogen atom, orbital energies within a principal shell—for example, 3s, 3p, 3d—are alike (degenerate), but in a multielectron atom they become rather widely separated. Another feature of the diagram is the steady decrease in all orbital energies with increasing atomic number. Finally, note that the 4s orbital is at a lower energy than 3d.

8-11   Electron Configurations

The **electron configuration** of an atom is a designation of how electrons are distributed among various orbitals in principal shells and subshells. In later chapters, we will find that many of the physical and chemical properties of elements can be correlated with electron configurations. In this section, we will see how the results of wave mechanics, expressed as a set of rules, can help us to write probable electron configurations for the elements.

Rules for Assigning Electrons to Orbitals

1. **Electrons occupy orbitals in a way that minimizes the energy of the atom.** Figure 8-36 suggests the order in which electrons occupy the subshells in the principal electronic shells; first the $1s$, then $2s, 2p$, and so on. The exact order of filling of orbitals has been established by experiment, principally through spectroscopy and magnetic studies, and it is this order based on experiment that we must follow in assigning electron configurations to the elements. With only a few exceptions, the order in which orbitals fill is

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p \qquad \textbf{(8.20)}$$

Some students find the diagram pictured in Figure 8-37 a useful way to remember this order, but the best method of establishing the order of filling of orbitals is based on the periodic table, as we will see in Section 8-12.

2. **No two electrons in an atom can have all four quantum numbers alike—the Pauli exclusion principle**. In 1926, Wolfgang Pauli explained complex features of emission spectra associated with atoms in magnetic fields by proposing that no two electrons in an atom can have all four quantum numbers alike. The first three quantum numbers, n, ℓ, and m_ℓ, determine a specific orbital. Two electrons may have these three quantum numbers alike; but if they do, they must have different values of m_s, the spin quantum number. Another way to state this result is that *only two electrons may occupy the same orbital, and these electrons must have opposing spins*.
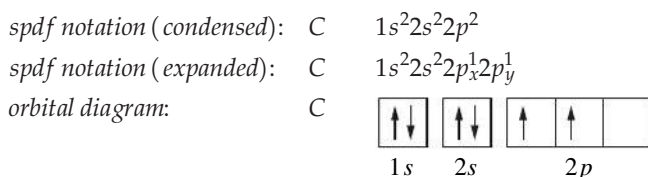
Because of this limit of two electrons per orbital, the capacity of a subshell for electrons can be obtained by doubling the number of orbitals in the subshell. Thus, the s subshell consists of *one* orbital with a capacity of *two* electrons; the p subshell consists of *three* orbitals with a total capacity of *six* electrons; and so on.

3. **When orbitals of identical energy (degenerate orbitals) are available, electrons initially occupy these orbitals singly**. In line with this rule, known as **Hund's rule**, an atom tends to have as many unpaired electrons as possible. This behavior can be rationalized by saying that electrons, because they all carry the same electric charge, try to get as far apart as possible. They do this by seeking out empty orbitals of similar energy in preference to pairing up with an electron in a half-filled orbital.
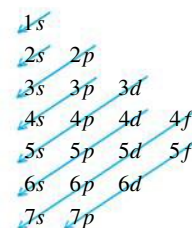
◀ This order of filling corresponds roughly to the order of increasing orbital energy, but the overriding principle governing the order of filling of orbitals is that the energy of the atom as a whole be kept at a minimum.

▲ FIGURE 8-37
The order of filling of electronic subshells
Beginning with the top line, follow the arrows, and the order obtained is the same as in expression (8.20).

Representing Electron Configurations

Before we assign electron configurations to atoms of the different elements, we need to introduce methods of representing these configurations. The electron configuration of a carbon atom is shown in three different ways:

spdf notation (condensed):	C	$1s^2 2s^2 2p^2$
spdf notation (expanded):	C	$1s^2 2s^2 2p_x^1 2p_y^1$
orbital diagram:	C	

In each of these methods we assign six electrons because the atomic number of carbon is 6. Two of these electrons are in the $1s$ subshell, two in the $2s$, and

▶ When listed in tables, as in Appendix D, electron configurations are usually written in the condensed *spd f* notation.

two in the 2*p*. The condensed ***spd f* notation** denotes only the total number of electrons in each subshell; it does not show how electrons are distributed among orbitals of equal energy. In the expanded ***spd f* notation,** Hund's rule is reflected in the assignment of electrons to the 2*p* subshell—two 2*p* orbitals are singly occupied and one remains empty. The **orbital diagram** breaks down each subshell into individual orbitals (drawn as boxes). This notation is similar to an energy-level diagram except that the direction of increasing energy is from left to right instead of vertically.

Electrons in orbitals are shown as arrows. An arrow pointing up corresponds to one type of spin $(+\frac{1}{2})$, and an arrow pointing down to the other $(-\frac{1}{2})$. Electrons in the same orbital with opposing (opposite) spins are said to be *paired* (↑↓). The electrons in the 1*s* and 2*s* orbitals of the carbon atom are paired. Electrons in different, singly occupied orbitals of the same subshell have the same, or *parallel*, spins (arrows pointing in the same direction). This is conveyed in the orbital diagram for carbon, where we write [↑][↑][ ] rather than [↑][↓][ ] for the 2*p* subshell. Both experiment and theory confirm that an electron configuration in which electrons in singly occupied orbitals have parallel spins is a better representation of the lowest energy state of an atom than any other electron configuration that we can write. The configuration represented by the orbital diagram [↑][↓][ ] is, in fact, an excited state of carbon; any orbital diagram with unpaired spins that are not parallel constitutes an excited state.

The most stable or the most energetically favorable configurations for isolated atoms, those discussed here, are called *ground-state electron configurations*. Later in the text we will briefly mention some electron configurations that are not the most stable. Atoms with such configurations are said to be in an *excited state*.

The Aufbau Process

To write electron configurations we will use the **aufbau process**. *Aufbau* is a German word that means "building up," and what we do is assign electron configurations to the elements in order of increasing atomic number. To proceed from one atom to the next, we add a proton and some neutrons to the nucleus and then describe the orbital into which the added electron goes.

Z = 1, H. The lowest energy state for the electron is the 1*s* orbital. The electron configuration is $1s^1$.

Z = 2, He. A second electron goes into the 1*s* orbital, and the two electrons have opposing spins, $1s^2$.

Z = 3, Li. The third electron cannot be accommodated in the 1*s* orbital (Pauli exclusion principle). It goes into the lowest energy orbital available, 2*s*. The electron configuration is $1s^2 2s^1$.

Z = 4, Be. The configuration is $1s^2 2s^2$.

Z = 5, B. Now the 2*p* subshell begins to fill: $1s^2 2s^2 2p^1$.

Z = 6, C. A second electron also goes into the 2*p* subshell, but into one of the remaining empty *p* orbitals (Hund's rule) with a spin parallel to the first 2*p* electron. (See figure to the left.)

Z = 7–10, N through Ne In this series of four elements, the filling of the subshell is completed. The number of unpaired electrons reaches a maximum (three) with nitrogen and then decreases to zero with neon.


1*s*   2*s*   2*p*

1*s*   2*s*   2*p*
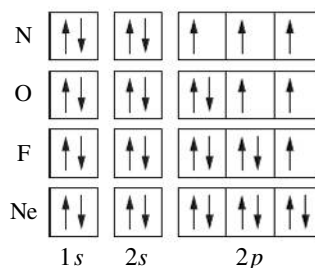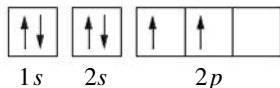
$Z = 11-18$, Na through Ar. The filling of orbitals for this series of eight elements closely parallels the eight elements from Li through Ne, except that electrons go into $3s$ and $3p$ subshells. Each element has the $1s, 2s$, and $2p$ subshells filled. Because the configuration $1s^2 2s^2 2p^6$ is that of neon, we will call this the neon core, represent it as [Ne], and concentrate on the electrons beyond the core. Electrons that are added to the electronic shell of highest principal quantum number (the outermost, or *valence shell*) are called **valence electrons**. The electron configuration of Na is written below in a form called a *noble-gas-core-abbreviated electron configuration*, consisting of [Ne] as the noble gas core and $3s^1$ as the configuration of the valence electron. For the other third-period elements, only the valence-shell electron configurations are shown.

Na	Mg	Al	Si	P	S	Cl	Ar
$[Ne]3s^1$	$3s^2$	$3s^2 3p^1$	$3s^2 3p^2$	$3s^2 3p^3$	$3s^2 3p^4$	$3s^2 3p^5$	$3s^2 3p^6$

$Z = 19$ and 20, K and Ca. After argon, instead of $3d$, the next subshell to fill is $4s$. Using the symbol [Ar] to represent the noble gas core, $1s^2 2s^2 2p^6 3s^2 3p^6$, we get the electron configurations shown below for K and Ca.
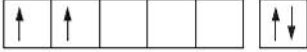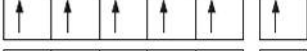
$$\text{K: } [Ar]4s^1 \quad \text{and} \quad \text{Ca: } [Ar]4s^2$$
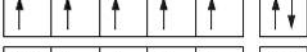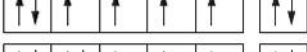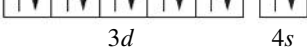
$Z = 21-30$, Sc through Zn. In this next series of elements, electrons fill the d orbitals of the third shell. The d subshell has a total capacity of ten electrons—ten elements are involved. There are two possible ways to write the electron configuration of scandium.

$$\text{(a) Sc: } [Ar]3d^1 4s^2 \quad \text{or} \quad \text{(b) Sc: } [Ar]4s^2 3d^1$$
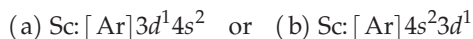
Both methods are commonly used. Method (a) groups together all the subshells of a principal shell and places subshells of the highest principal quantum level last. Method (b) lists orbitals in the apparent order in which they fill. In this text, we will use method (a).

The electron configurations of this series of ten elements are listed below in both the orbital diagram and the *spdf* notation.

◀ Although method (b) conforms better to the order in which orbitals fill, method (a) better represents the order in which electrons are lost on ionization, as we will see in the next chapter.

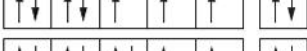|		$3d$		$4s$
Sc:	[Ar]			$[Ar]3d^1 4s^2$
Ti:	[Ar]			$[Ar]3d^2 4s^2$
V:	[Ar]			$[Ar]3d^3 4s^2$
Cr:	[Ar]			$[Ar]3d^5 4s^1$
Mn:	[Ar]			$[Ar]3d^5 4s^2$
Fe:	[Ar]			$[Ar]3d^6 4s^2$
Co:	[Ar]			$[Ar]3d^7 4s^2$
Ni:	[Ar]			$[Ar]3d^8 4s^2$
Cu:	[Ar]			$[Ar]3d^{10} 4s^1$
Zn:	[Ar]			$[Ar]3d^{10} 4s^2$

The d orbitals fill in a fairly regular fashion in this series, but there are two exceptions: chromium (Cr) and copper (Cu). These exceptions are usually

explained in terms of a special stability for configurations in which a $3d$ subshell is half-filled with electrons, as with $Cr(3d^5)$, or completely filled, as with $Cu(3d^{10})$.

$Z = 31–36$, Ga through Kr. In this series of six elements, the $4p$ subshell is filled, ending with krypton.

$$Kr: [Ar]3d^{10}4s^24p^6$$
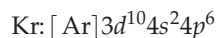
$Z = 37–54$, Rb to Xe. In this series of 18 elements, the subshells fill in the order $5s, 4d,$ and $5p$, ending with the configuration of xenon.

$$Xe: [Kr]4d^{10}5s^25p^6$$

$Z = 55–86$, Cs to Rn. In this series of 32 elements, with a few exceptions, the subshells fill in the order $6s, 4f, 5d, 6p$. The configuration of radon is

$$Rn: [Xe]4f^{14}5d^{10}6s^26p^6$$

$Z = 87–?$, Fr to ? Francium starts a series of elements in which the subshells that fill are $7s, 5f, 6d,$ and presumably $7p$, although atoms in which filling of the $7p$ subshell is expected have only recently been discovered and are not yet characterized.
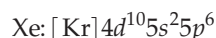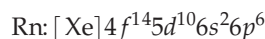
Appendix D gives a complete listing of probable electron configurations.

? 8-7 ARE YOU WONDERING...

Why chromium and copper have "anomalous" electron configurations?

First we need to recognize that the balance between electron–electron repulsions, electron–nuclear attractions, and other electron–electron interactions, due to the fact that electron motions in a multielectron atom are correlated, determines the most stable electron configuration. Next, recall Hund's rule that the subshell electron configuration with the greatest number of unpaired electrons is the most stable. On page 340, this led us to the conclusion that the ground-state electron configuration of carbon is $1s^22s^22p^2$, with two unpaired electrons in the $2p$ subshell. Calculations on simple atoms and ions have shown that, although there is a larger electron–electron repulsion in the state with the unpaired electrons, this repulsion is more than offset by a larger electron–nucleus attraction because the electrons are closer to the nucleus in the configuration with unpaired electrons. Thus, configurations with unpaired electrons are favored.

In determining the ground-state electron configuration of Cr, we have to choose between $[Ar]3d^44s^2$ and $[Ar]3d^54s^1$, because the energies of the $3d$ and $4s$ orbitals are very similar. In this case, we can use Hund's rule to decide that the most stable electron configuration is that with the most unpaired electrons, that is, $[Ar]3d^54s^1$.

For Cu we have to choose between $[Ar]3d^94s^2$ and $[Ar]3d^{10}4s^1$, and there is no difference between the number of unpaired electrons—Hund's rule is no help here. So where does the extra stability for the configuration $[Ar]3d^{10}4s^1$ come from? A filled (or half-filled) subshell has a spherically symmetrical charge density that leads to a more stable electron configuration; and the greater the number of electrons in that subshell, the greater the stabilization. The $[Ar]3d^{10}4s^1$ electron configuration is more stable than $[Ar]3d^94s^2$ because of its filled $3d$ subshell. Thus nearly all the anomalous configurations contain either filled or half-filled subshells.

## EXAMPLE 8-13   Recognizing Correct and Incorrect Ground State and Excited State Atomic Orbital Diagrams

Which of the following orbital diagrams is incorrect? Explain. Which of the correct diagrams corresponds to an excited state and which to the ground state of the neutral atom?

Analyze

When faced with a set of orbital diagrams, the best strategy is to investigate each one and apply Hund's rule and the Pauli exclusion principle, the former to decide on ground or excited states, and the latter for the correctness of the diagram.

(a)
$1s$ $2s$ $2p$ $3s$ $3p$

(b)
$1s$ $2s$ $2p$ $3s$ $3p$

(c)
$1s$ $2s$ $2p$ $3s$ $3p$

(d)
$1s$ $2s$ $2p$ $3s$ $3p$

(e)
$1s$ $2s$ $2p$ $3s$ $3p$

Solve

(a) By scanning diagram (a), we see that all the orbitals $1s, 2s, 2p$, and $3s$ are filled with two electrons of opposite spin, conforming to the Pauli exclusion principle. However, the $3p$ orbital contains three electrons, which violates this principle.

(b) In diagram (b), the orbitals $1s, 2s, 2p$, and $3s$ are filled with two electrons of opposite spin, which is correct. The $3p$ level contains three electrons in separate orbitals, conforming to Hund's rule, but two of them have opposite spin to the other; consequently, this is an excited state of the element.

(c) When we compare diagram (c) with diagram (b), we see that all the three electrons in the $3p$ subshell have the same spin, and so this is the ground state.

(d) When we compare diagram (d) with diagram (b), we see that of the three electrons in the $3p$ subshell, two are paired and one is not. Again, this is an excited state.

(e) By scanning diagram (e), we see that all the orbitals $1s, 2s$, and $2p$ are filled with two electrons of opposite spin. However, the $3p$ orbital contains two electrons with the same spin, which violates the Pauli principle. This diagram is incorrect.
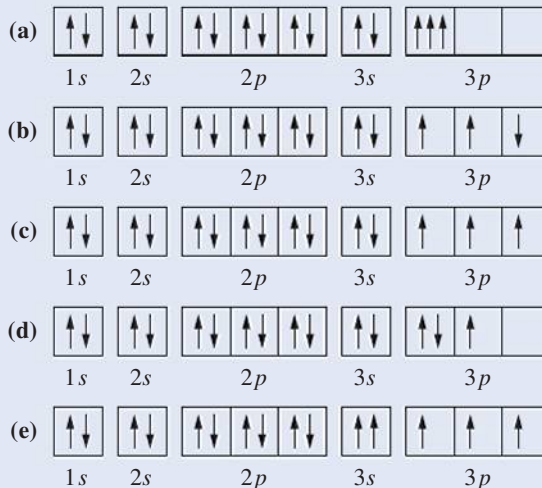
Assess

Orbital diagrams are a useful way to display electronic configurations, but we must take care to obey Hund's rule and the Pauli exclusion principle.

PRACTICE EXAMPLE A: Which two of the following orbital diagrams are equivalent?

(a)
$1s$ $2s$ $2p$

(b)
$1s$ $2s$ $2p$

(c)
$1s$ $2s$ $2p$

(d)
$1s$ $2s$ $2p$
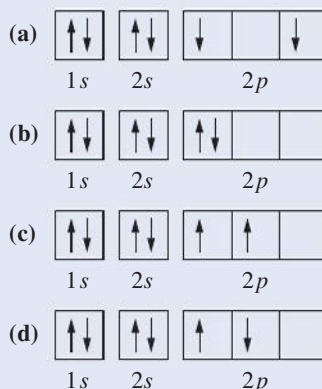
PRACTICE EXAMPLE B: Does the following orbital diagram for a neutral species correspond to the ground state or an excited state?

[Ar]
$4s$ $3d$ $4p$
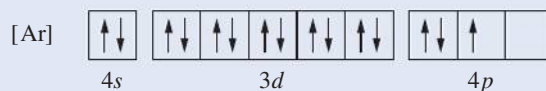
8-12   Electron Configurations and the Periodic Table

We have just described the aufbau process of making probable assignments of electrons to the orbitals in atoms. Although electron configurations may seem rather abstract, they actually lead us to a better understanding of the periodic table. Around 1920, Niels Bohr began to promote the connection between the periodic table and quantum theory. The chief link, he pointed out, is in electron configurations. *Elements in the same group o fthe table have similar electron con figurations.*

To construct Table 8.2, we have taken three groups of elements from the periodic table and written their electron configurations. The similarity in electron configuration within each group is readily apparent. If the shell of the highest principal quantum number—the outermost, or valence, shell—is labeled n, then

▶ Hydrogen is found in group 1 because of its electron configuration, $1s^1$. However, it is not an alkali metal.

- The group 1 atoms (alkali metals) have *one* outer-shell (valence) electron in an s orbital, that is, ns^1.
- The group 17 atoms (halogens) have *seven* outer-shell (valence) electrons, in the configuration ns^2np^5.
- The group 18 atoms (noble gases)—with the exception of helium, which has only two electrons—have outermost shells with *eight* electrons, in the configuration ns^2np^6.

Although it is not correct in all details, Figure 8-38 relates the aufbau process to the periodic table by dividing the table into the following four blocks of elements according to the subshells being filled:

- *s block.* The s orbital of highest principal quantum number (n) fills. The s block consists of groups 1 and 2 (plus He in group 18).
- *p block.* The p orbitals of highest quantum number (n) fill. The p block consists of groups 13, 14, 15, 16, 17, and 18 (except He).
- *d block.* The d orbitals of the electronic shell $n-1$ (the next to outermost) fill. The d block includes groups 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12.
- *f block.* The f orbitals of the electronic shell $n-2$ fill. The *f* block elements are the lanthanides and the actinides.

TABLE 8.2 Electron Configurations of Some Groups of Elements		
Group	Element	Configuration
1	H	$1s^1$
	Li	$[He]2s^1$
	Na	$[Ne]3s^1$
	K	$[Ar]4s^1$
	Rb	$[Kr]5s^1$
	Cs	$[Xe]6s^1$
	Fr	$[Rn]7s^1$
17	F	$[He]2s^22p^5$
	Cl	$[Ne]3s^23p^5$
	Br	$[Ar]3d^{10}4s^24p^5$
	I	$[Kr]4d^{10}5s^25p^5$
	At	$[Xe]4f^{14}5d^{10}6s^26p^5$
18	He	$1s^2$
	Ne	$[He]2s^22p^6$
	Ar	$[Ne]3s^23p^6$
	Kr	$[Ar]3d^{10}4s^24p^6$
	Xe	$[Kr]4d^{10}5s^25p^6$
	Rn	$[Xe]4f^{14}5d^{10}6s^26p^6$

Main-group elements

▲ FIGURE 8-38
Electron configurations and the periodic table
To use this figure as a guide to the aufbau process, locate the position of an element in the table. Subshells listed ahead of this position are filled. For example, germanium (Z = 32) is located in group 14 of the blue $4p$ row. The filled subshells are $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$, and $3d^{10}$. At (Z = 32), a second electron has entered the $4p$ subshell. The electron configuration of Ge is $[Ar]3d^{10}4s^24p^2$. Exceptions to the orderly filling of subshells suggested here are found among a few of the d-block and some of the f-block elements.

Another point to notice from Table 8.2 is that the electron configuration consists of a noble-gas core corresponding to the noble gas from the previous period plus the additional electrons required to satisfy the atomic number. Recognizing this and dividing the periodic table into blocks can simplify the task of assigning electron configurations. For example, strontium is in group 2, the second s-block group, so that its valence-shell configuration is $5s^2$ since it is in the fifth period. The remaining electrons are in the krypton core configuration (the noble gas in the previous period); thus the electron configuration of Sr is

$$\text{Sr:} [Kr]5s^2$$

For the p-block elements in groups 13 to 18, the number of valence electrons is from 1 to 6. For example, aluminum is in period 3 and group 13, its valence-shell electron configuration is $3s^23p^1$. We use $n = 3$ since Al is in the third period and we have to accommodate three electrons after the neon core, which contains 10 electrons. Thus the electron configuration of Al is

$$\text{Al:} [Ne]3s^23p^1$$

Gallium is also in group 13, but in period 4. Its valence-shell electron configuration is $4s^2 4p^1$. To write the electron configuration of Ga, we can start with the electron configuration of the noble gas that closes the third period, argon, and we add to it the subshells that fill in the fourth period: $4s$, $3d$, and $4p$. The $3d$ subshell must fill with 10 electrons before the $4p$ subshell begins to fill. Consequently, the electron configuration of gallium must be

$$\text{Ga: } [\text{Ar}] 3d^{10} 4s^2 4p^1$$
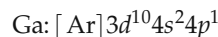
Thallium is in group 13 and period 6. Its valence-shell electron configuration is $6s^2 6p^1$. Again, we indicate the electron configuration of the noble gas that closes the fifth period as a core, and add the subshells that fill in the sixth period: $6s$, $4f$, $5d$, and $6p$.

$$\text{Tl: } [\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^1$$
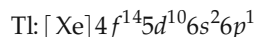
The elements in group 13 have the common valence configuration $ns^2 np^1$, again illustrating the repeating pattern of valence electron configurations down a group, which is the basis of the similar chemical properties of the elements within a group of the periodic table.

The transition elements correspond to the d block, and their electron configurations are established in a similar manner. To write the electron configuration of a transition element, start with the electron configuration of the noble gas that closes the prior period and add the subshells that fill in the period of the transition element being considered. The s subshell fills immediately after the preceding noble gas; most transition metal atoms have two electrons in the s subshell of the valence shell, but some have only one. Thus, vanadium ($Z = 23$), which has two valence electrons in the $4s$ subshell and core electrons in the configuration of the noble gas argon, must have *three* $3d$ electrons ($2 + 18 + 3 = 23$).

$$\text{V: } [\text{Ar}] 3d^3 4s^2$$
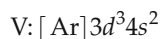
Chromium ($Z = 24$), as we have seen before, has only one valence electron in the $4s$ subshell and core electrons in the argon configuration. Consequently it must have *five* $3d$ electrons ($1 + 18 + 5 = 24$).

$$\text{Cr: } [\text{Ar}] 3d^5 4s^1$$

Copper ($Z = 29$) also has only one valence electron in the $4s$ subshell in addition to its argon core, so the copper atom must have *ten* $3d$ electrons ($1 + 18 + 10 = 29$).

$$\text{Cu: } [\text{Ar}] 3d^{10} 4s^1$$
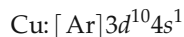
Chromium and copper are two exceptions to the straightforward filling of atomic subshells in the first d-block row. An examination of the electron configurations of the heavier elements (Appendix D) will reveal that there are other special cases that are not easily explained—for example, gadolinium has the configuration $[\text{Xe}] 4f^7 6d^1 6s^2$. Examples 8-14 through 8-16 provide several more illustrations of the assignment of electron configurations using the ideas presented here.

▶ The electron configurations for the *lower d- and f*block elements contain many exceptions that need not be memorized. Few people know all of them. Anyone needing any of these configurations can look them up when needed in tables, such as in Appendix D.

🔍 **8-8   CONCEPT ASSESSMENT**

The following orbital diagram represents an excited state of an atom. Identify the atom and give the orbital diagram corresponding to its ground state orbital diagram.

[Ar] | ↑↓ | | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | | ↑↓ | ↑↓ | |
           4s   3d   4p

EXAMPLE 8-14   Using *spd f* Notation for an Electron Configuration

(a) Identify the element having the electron configuration

$$1s^2 2s^2 2p^6 3s^2 3p^5$$

(b) Write the electron configuration of arsenic.

Analyze

The total number of electrons in a neutral atomic species is equal to the atomic number of the element. All electrons must be accounted for in an electron configuration.

Solve

(a) Add the superscript numerals $(2 + 2 + 6 + 2 + 5)$ to obtain the atomic number 17. The element with this atomic number is chlorine.

(b) Arsenic $(Z = 33)$ is in period 4 and group 15. Its valence-shell electron configuration is $4s^2 4p^3$. The noble gas that closes the third period is Ar $(Z = 18)$, and the subshells that fill in the fourth period are $4s, 3d,$ and $4p$, in that order. Note that we account for 33 electrons in the configuration

$$\text{As:} [\,\text{Ar}\,] 3d^{10} 4s^2 4p^3$$

Assess

As long as we count the number of electrons accurately and know the order of the orbitals, we should be able to interpret or write the correct electronic configuration.

PRACTICE EXAMPLE A: Identify the element having the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$.

PRACTICE EXAMPLE B: Use *spd f* notation to show the electron configuration of iodine. How many electrons does the I atom have in its $3d$ subshell? How many unpaired electrons are there in an I atom?

EXAMPLE 8-15   Representing Electron Configurations

Write **(a)** the electron configuration of mercury, and **(b)** an orbital diagram for the electron configuration of tin.

Analyze

To write the electronic configuration, we locate the element on the periodic table and then ascertain which subshells are filled. We must be careful, with high-atomic-number elements, to take into account the lanthanide and actinide elements.

Solve

(a) Mercury, in period 6 and group 12, is the transition element at the end of the third transition series, in which the $5d$ subshell fills $(5d^{10})$. The noble gas that closes period 5 is xenon, and the lanthanide series intervenes between xenon and mercury, in which the $4f$ subshell fills $(4f^{14})$. When we put all these facts together, we conclude that the electron configuration of mercury is

$$[\,\text{Xe}\,] 4f^{14} 5d^{10} 6s^2$$

(b) Tin is in period 5 and group 14. Its valence-shell electron configuration is $5s^2 5p^2$. The noble gas that closes the fourth period is Kr $(Z = 36)$, and the subshells that fill in the fifth period are $5s, 4d,$ and $5p$. Note that all subshells are filled in the orbital diagram except for $5p$. Two of the $5p$ orbitals are occupied by single electrons with parallel spins; one $5p$ orbital remains empty.

Sn: [Kr] $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

$\quad\quad\quad\quad\quad\quad\quad\quad\; 4d \quad\quad\quad\quad 5s \quad\quad 5p$

Assess

Using the periodic table helps when writing electronic configurations.

PRACTICE EXAMPLE A: Represent the electron configuration of iron with an orbital diagram.

PRACTICE EXAMPLE B: Represent the electron configuration of bismuth with an orbital diagram.

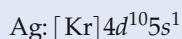**EXAMPLE 8-16** Relating Electron Configurations to the Periodic Table

Indicate the number of **(a)** valence electrons in an atom of bromine; **(b)** $5p$ electrons in an atom of tellurium; **(c)** unpaired electrons in an atom of indium; **(d)** $3d$ and $4d$ electrons in a silver atom.

Analyze

Determine the atomic number and the periodic table location of each element. Then, explain the significance of its location.

Solve

(a) Bromine ($Z = 35$) is in group 17. There are seven outer-shell, or valence, electrons in all atoms in this group.

(b) Tellurium ($Z = 52$) is in period 5 and group 16. There are six outer-shell electrons, two of them are s, and the other four are p. The valence-shell electron configuration of tellurium is $5s^2 5p^4$; the tellurium atom has four $5p$ electrons.

(c) Indium ($Z = 49$) is in period 5 and group 13. The electron configuration of its inner shells is $[Kr]4d^{10}$. All the electrons in this inner-shell configuration are paired. The valence-shell electron configuration is $5s^2 5p^1$. The two $5s$ electrons are paired, and the $5p$ electron is unpaired. The In atom has one unpaired electron.

(d) Ag ($Z = 47$) is in period 5 and group 11. The noble gas that closes period 4 is krypton, and the $4d$ subshell fills $4(d^{10})$. There is one electron in the $5s$ orbital; thus the electron configuration of silver is

$$\text{Ag: } [Kr]4d^{10}5s^1$$

There are ten $3d$ electrons and ten $4d$ electrons in a silver atom.

Assess

Again, the relationship between the periodic table and electronic configurations is evident.

PRACTICE EXAMPLE A: For an atom of Sn, indicate the number of **(a)** electronic shells that are either filled or partially filled; **(b)** $3p$ electrons; **(c)** $5d$ electrons; and **(d)** unpaired electrons.

PRACTICE EXAMPLE B: Indicate the number of **(a)** $3d$ electrons in Y atoms; **(b)** $4p$ electrons in Ge atoms; and **(c)** unpaired electrons in Au atoms.

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Laser devices are in use everywhere—in compact disc players, bar-code scanners, laboratory instruments, and in cosmetic, dental, and surgical procedures. Lasers produce light with highly desirable properties by a process called stimulated emission. For a discussion of how lasers work, go to the Focus On feature for Chapter 8, Helium-Neon Lasers, on the MasteringChemistry site.

Summary

8-1 Electromagnetic Radiation—**Electromagnetic radiation** is a type of energy transmission in the form of a **wave**. The waves of electromagnetic radiation are characterized by an **amplitude**, the maximum height of wave crests and maximum depth of wave troughs, a **wavelength**, λ, the distance between wave crests and **frequency**, ν, which signifies how often the fluctuations occur. Frequency is measured in **hertz**, **Hz** (cycles per second). Wavelength and frequency are related by the equation (8.1): $c = \lambda\nu$, where c is the **speed of light**. The wave character of electromagnetic radiation means that the waves can be dispersed into individual components of different wavelengths, a

diffraction pattern, by striking a closely grooved surface (Fig. 8-4).

8-2 Atomic Spectra—A rainbow results from the dispersion of all the wavelength components of visible light by a prism or raindrops; it is an example of a continuous spectrum (Fig. 8-7). The spectra produced by light emitted from excited atoms and ions are called **atomic spectra** or **line spectra**, because only certain frequencies are observed.

8-3 Quantum Theory—The study of electromagnetic radiation emitted from hot objects led to Planck's theory, which postulates that quantities of energy can have only

certain discrete values, with the smallest unit of energy being that of a **quantum**. The energy of a quantum is given by equation (8.3): $E = h\nu$, where h is **Planck's constant**. Einstein's interpretation of the **photoelectric effect**—the ability of light to eject electrons when striking certain surfaces (Fig. 8-12)—led to a new interpretation of electromagnetic radiation: Light has a particle-like nature in addition to its wave-like properties. Light particles are called **photons**. The energy of a photon is related to the frequency of the radiation by $E_{\text{photon}} = h\nu$.

8-4 The Bohr Atom
The first attempt to explain atomic (line) spectra was made by Niels Bohr who postulated that an electron in a hydrogen atom exists in a circular orbit designated by a **quantum number**, n, that describes the energy of the electron in the orbit. The state of the electron with the lowest quantum number, $n = 1$, is called the **ground state**. An **excited state** of a hydrogen atom corresponds to those states with $n > 1$. The Bohr theory also provided a means for constructing an **energy-level diagram** (Fig. 8-14) so that emission spectra could be understood.

8-5 Two Ideas Leading to a New Quantum Mechanics
Louis de Broglie postulated a **wave–particle duality** in which particles of matter such as protons and electrons would at times display wave-like properties (equation 8.10). Because of an inherent uncertainty of the position and momentum of a wave-like particle, Heisenberg postulated that we cannot simultaneously know a subatomic particle's precise momentum and its position, a proposition referred to as the **Heisenberg uncertainty principle** (equation 8.11).

8-6 Wave Mechanics
The application of the concept of wave–particle duality requires that we view the electron in a system through a **wave function** that corresponds to a **standing wave** within the boundary of the system (Figs. 8-18 and 8-19). Application of these ideas to a particle in a one-dimensional box shows that at the lowest energy level the energy of the particle is nonzero that is, the system has a **zero-point energy**. The solution of the **Schrödinger equation** for the hydrogen atom provides wave functions called **orbitals**, which are the product of an **angular wave function**, $Y(\theta, \phi)$, and a **radial wave function**, $R(r)$.

8-7 Quantum Numbers and Electron Orbitals
The three quantum numbers arising from the Schrödinger wave equation are the *principal quantum number*, n, the *orbital angular momentum quantum number*, ℓ, and the *magnetic quantum number*, m_ℓ. All orbitals with the same value of n are in the same **principal electronic shell** (**principal level**), and all orbitals with the same values of n and ℓ are in the same **subshell** (**sublevel**). The orbitals with different values of ℓ (0, 1, 2, 3, and so on) are designated s, p, d, f (Fig. 8-23). Orbitals in the same subshell of a hydrogen-like species have the same energy and are said to be **degenerate**.

8-8 Interpreting and Representing the Orbitals of the Hydrogen Atom
Interpreting the solutions to the Schrödinger equation for the hydrogen atom leads to a description of the shapes of the electron probability distributions for electrons in the s, p, and d orbitals. The number of nodes ($n - 1$) in an orbital increases as n increases. Nodes are where the wave function changes sign.

8-9 Electron Spin: A Fourth Quantum Number
Stern and Gerlach demonstrated that electrons possess a quality called **electron spin** (Figs. 8-32 and 8-33). The electron spin quantum number, m_s, takes the value $+\frac{1}{2}$ or $-\frac{1}{2}$.

8-10 Multielectron Atoms
In multielectron atoms, orbitals with different values of ℓ are not degenerate. The loss of degeneracy within a principal shell is a result of the different **effective nuclear charge**, Z_{eff}, experienced by electrons in different subshells.

8-11 Electron Configurations
Electron configuration describes how the electrons are distributed among the various orbitals in principal shells and subshells of an atom. Electrons fill orbitals from the lowest energy to the highest (Fig. 8-37), ensuring that the energy of the atom is at a minimum. The **Pauli exclusion principle** states that a maximum of two electrons may occupy an orbital. **Hund's rule** says that when degenerate orbitals are available, electrons initially occupy these orbitals singly. Electron configurations are represented by either expanded or condensed *spdf* **notation** or an **orbital diagram** (page 339). The **aufbau process** is used to assign electron configurations to the elements of the periodic table. Electrons added to the shell of highest quantum number in the aufbau process are called **valence electrons**.

8-12 Electron Configurations and the Periodic Table
Elements in the same group of the periodic table have similar electron configurations. Groups 1 and 2 correspond to the **s block** with filled or partially filled valence-shell s orbitals. Groups 13 through 18 correspond to the **p block** with filled or partially filled valence-shell p orbitals. The **d block** corresponds to groups 3 through 12 as the $n - 1$ energy level is being filled—that is, having filled or partially filled d orbitals. In the **ƒblock** elements, also called the lanthanides and actinides, the $n - 2$ shell fills with electrons; that is, they have filled or partially filled f orbitals.

Integrative Example

Microwave ovens have become increasingly popular in kitchens around the world. They are also useful in the chemical laboratory, particularly in drying samples for chemical analysis. A typical microwave oven uses microwave radiation with a wavelength of 12.2 cm.

Are there any electronic transitions in the hydrogen atom that could *conceivably* produce microwave radiation of wavelength 12.2 cm? Estimate the principal quantum levels between which the transition occurs.

Analyze

Use the wavelength of microwaves to calculate the frequency of the radiation. Calculate the energy of the photon that has this frequency. Estimate where in the emission spectrum for a hydrogen atom such a photon emission might be found, by using equation (8.6).

Solve

1. Calculate the frequency of the microwave radiation. Microwaves are a form of electromagnetic radiation and thus travel at the speed of light, $2.998 \times 10^8 \, \text{m s}^{-1}$. Convert the wavelength to meters, and then use the equation

$$\nu = c/\lambda$$

$$\nu = \frac{2.998 \times 10^8 \, \text{m s}^{-1}}{12.2 \, \text{cm} \times 1 \, \text{m}/100 \, \text{cm}} = 2.46 \times 10^9 \, \text{Hz}$$

2. Calculate the energy associated with one photon of the microwave radiation. This is a direct application of Planck's equation.

$$E = h\nu = 6.626 \times 10^{-34} \, \text{J s} \times 2.46 \times 10^9 \, \text{s}^{-1}$$
$$= 1.63 \times 10^{-24} \, \text{J}$$

3. Determine whether there are any electronic transitions in the hydrogen atom with an energy per photon of 1.63×10^{-24} J. Let the principal quantum number of the final state (n_f) be n, and that of the initial state (n_i) is then $n + 1$. Substitute these two values into equation (8.9).

$$E_{\text{photon}} = \Delta E = 2.179 \times 10^{-18} \, \text{J}\left(\frac{1}{(n+1)^2} - \frac{1}{n^2}\right)$$

Solving for n

$$E_{\text{photon}} = \Delta E = 2.179 \times 10^{-18} \, \text{J}\left(\frac{n^2 - (n+1)^2}{n^2(n+1)^2}\right)$$

$$= -2.179 \times 10^{-18} \, \text{J}\left(\frac{2n+1}{n^2(n+1)^2}\right)$$

4. The negative sign indicates that a photon is emitted and now can be ignored. Substitute the value for the energy of the photon and rearrange the equation

$$E_{\text{photon}} = 1.63 \times 10^{-24} \, \text{J} = 2.179 \times 10^{-18} \, \text{J}\left(\frac{2n+1}{n^2(n+1)^2}\right)$$

$$\frac{1.63 \times 10^{-24} \, \text{J}}{2.179 \times 10^{-18} \, \text{J}} = 7.48 \times 10^{-7} = \left(\frac{2n+1}{n^2(n+1)^2}\right)$$

5. Look at Figure 8-14, the *energy*-level diagram for the Bohr hydrogen atom. Energy differences between the low-lying levels are of the order 10^{-19} to 10^{-20} J. These are orders of magnitude (10^4 to 10^5 times) greater than the energy per photon of 1.63×10^{-24} J from part 2. Note, however, that the energy differences become progressively smaller for high-numbered orbits. As n approaches ∞, the energy differences approach zero, and some transitions between high-numbered orbits should correspond to microwave radiation. Thus we expect n to be large, so that to a good approximation we can neglect one with respect to n and write

$$7.48 \times 10^{-7} = \left(\frac{2n+1}{n^2(n+1)^2}\right) \simeq \left(\frac{2n}{n^2 n^2}\right) \simeq \left(\frac{2}{n^3}\right)$$

Solving for n

$$n \simeq \left(\frac{2}{7.48 \times 10^{-7}}\right)^{1/3} \simeq 138.8$$

6. We can check this result by substituting this value of $n = 139$ into the exact expression

$$7.48 \times 10^{-7} = \frac{2n+1}{n^2(n+1)^2} = \frac{2(139)+1}{139^2(139+1)^2} = 7.37 \times 10^{-7}$$

The agreement is not very good, so let's try $n = 138$

$$7.48 \times 10^{-7} = \frac{2n+1}{n^2(n+1)^2} = \frac{2(138)+1}{138^2(138+1)^2} = 7.53 \times 10^{-7}$$

This provides closer agreement. The value of the principal quantum number is $n = 138$.

Assess

Using equation (8.6) we have shown that the emission of a photon for the deexcitation of an electron from $n = 139$ to $n = 138$ produces a wavelength for that photon in the microwave region. However, we might question whether the $n = 139$ state is still a bound state or whether the energy required to create this state causes ionization (see Exercise 106).

9

The Periodic Table and Some Atomic Properties
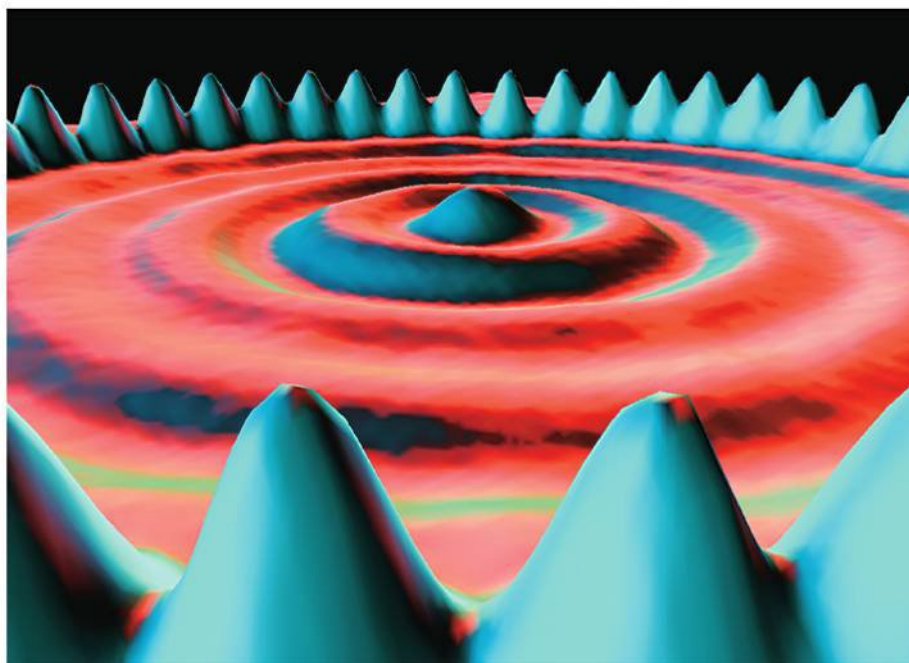
A scanning tunneling microscope image of 48 iron atoms adsorbed onto a surface of copper atoms. The iron atoms were moved into position with the tip of the scanning tunneling microscope in order to create a barrier that forced some electrons of the copper atoms into a quantum state seen here as circular rings of electron density. The colors are from the computer rendering of the image. In this chapter we discuss the periodic table and the properties of atoms and ions.

Chemists value the periodic table as a means of organizing their field, and they would have continued to use it even if they had never figured out why it works. The underlying rationale of the periodic table was discovered about 50 years after the table was proposed.

The basis of the periodic table is the electron configurations of the elements, a topic we studied in Chapter 8. In this chapter, we will use the table as a backdrop for a discussion of some properties of elements, including atomic radii, ionization energies, and electron affinities. These atomic properties also arise in the discussion of chemical bonding in the following two chapters, and the periodic table itself will be our indispensable guide throughout much of the remainder of the text.

9-1   Classifying the Elements: The Periodic Law and the Periodic Table

In 1869, Dmitri Mendeleev and Lothar Meyer independently proposed the **periodic law**:

> When the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically.

Meyer based his periodic law on the property called atomic volume—the atomic mass of an element divided by the density of its solid form. We now just call this property *molar volume*.

$$\text{atomic (molar) volume}(\text{cm}^3/\text{mol}) = \text{molar mass}(\text{g/mol}) \times 1/d\,(\text{cm}^3/\text{g})\quad\textbf{(9.1)}$$

Meyer presented his results as a graph of atomic volume against atomic mass. Now it is customary to plot his results as molar volume against atomic number, as seen in Figure 9-1. Notice how high atomic volumes recur periodically for the alkali metals Li, Na, K, Rb, and Cs. Later, Meyer examined other physical properties of the elements and their compounds, such as hardness, compressibility, and boiling points, and found that these also vary periodically.

Mendeleev's Periodic Table

As previously described, the periodic table is a tabular arrangement of the elements that groups similar elements together. Mendeleev's work attracted more attention than Meyer's for two reasons: He left blank spaces in his table for undiscovered elements, and he corrected some atomic mass values. The blanks in his table came at atomic masses 44, 68, 72, and 100 for the elements we now know as scandium, gallium, germanium, and technetium. Two of the atomic mass values he corrected were those of indium and uranium.
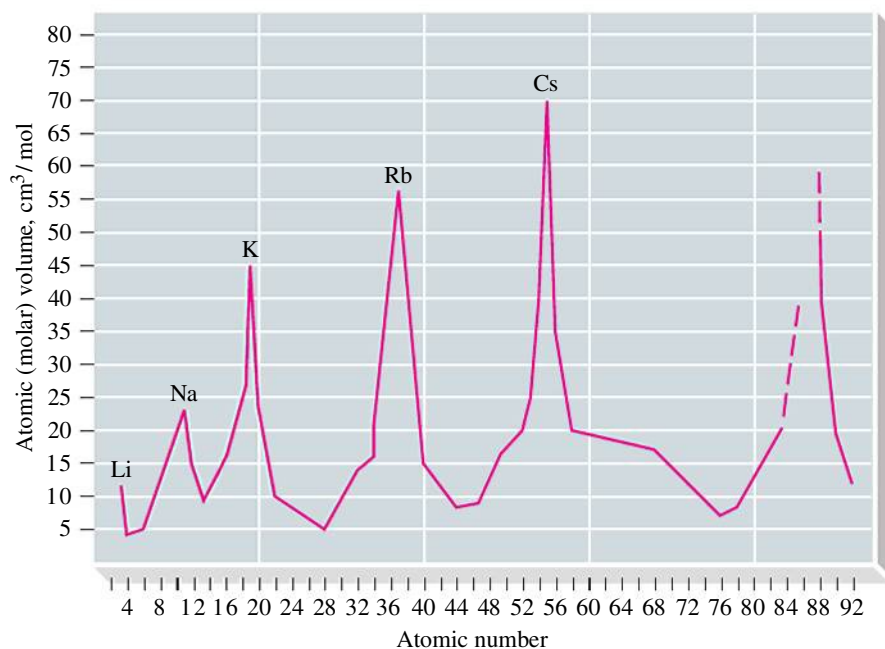
▲ FIGURE 9-1
An illustration of the periodic law—variation of atomic volume with atomic number
This adaptation of Meyer's 1870 graph plots atomic volumes against atomic numbers. Of course, a number of elements, such as the noble gases, were undiscovered in Meyer's time. The graph shows peaks at the alkali metals (Li, Na, K, and so on). Nonmetals fall on the ascending portions of the curve and metals at the peaks, on the descending portions, and in the valleys.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	– = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	– = 68	– = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	– = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	–	–	–	– – – –
9	(–)	–	–	–				
10	–	–	?Er = 178	?La = 180	Ta = 182	W = 184		Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208			
12	–	–	–	Th = 231	–	U = 240		

▲ **Dmitri Mendeleev (1834–1907)**

Mendeleev's discovery of the periodic table came from his attempts to systematize properties of the elements for presentation in a chemistry textbook. His highly influential book went through eight editions in his lifetime and five more after his death.

In his periodic table Mendeleev arranged the elements into eight groups (Gruppe) and twelve rows (Reihen). The formulas are written as Mendeleev wrote them. R^2O, RO, and so on, are formulas of the element oxides (such as Li_2O, MgO, . . .); RH^4, RH^3, and so forth, are formulas of the element hydrides (such as CH_4, NH_3, . . .).

▶ Other properties of the alkali metals are discussed in Section 9-7.

In Mendeleev's table, similar elements fall in vertical groups, and the properties of the elements change gradually from top to bottom in the group. As an example, we have seen that the alkali metals (Mendeleev's group I) have high molar volumes (Fig. 9-1). They also have low melting points, which decrease in the order

$$\text{Li}\,(174\,°\text{C}) > \text{Na}\,(97.8\,°\text{C}) > \text{K}\,(63.7\,°\text{C}) > \text{Rb}\,(38.9\,°\text{C}) > \text{Cs}\,(28.5\,°\text{C})$$

In their compounds, the alkali metals exhibit the oxidation state +1, forming ionic compounds, such as NaCl, KBr, CsI, Li_2O, and so on.

Discovery of New Elements

Three elements predicted by Mendeleev were discovered shortly after the appearance of his 1871 periodic table (gallium, 1875; scandium, 1879; germanium, 1886). Table 9.1 illustrates how closely Mendeleev's predictions for eka-silicon agree with the observed properties of the element germanium, discovered in 1886. Often, new ideas in science take hold slowly, but the success of Mendeleev's predictions stimulated chemists to adopt his table fairly quickly.

▶ The term *eka* is derived from Sanskrit and means "first." That is, eka-silicon means, literally, "first comes silicon" (and then comes the unknown element).

TABLE 9.1   Properties of Germanium: Predicted and Observed

Property	Predicted Eka-silicon (1871)	Observed Germanium (1886)
Atomic mass	72	72.6
Density, g/cm^3	5.5	5.47
Color	dirty gray	grayish white
Density of oxide, g/cm^3	EsO_2: 4.7	GeO_2: 4.703
Boiling point of chloride	$EsCl_4$: below 100 °C	$GeCl_4$: 86 °C
Density of chloride, g/cm^3	$EsCl_4$: 1.9	$GeCl_4$: 1.887

One group of elements that Mendeleev did not anticipate was the noble gases. He left no blanks for them. William Ramsay, their discoverer, proposed placing them in a separate group of the table. Because argon, the first noble gas discovered (1894), had an atomic mass greater than that of chlorine and comparable to that of potassium, Ramsay placed the new group, which he called group 0, between the halogen elements (group VII) and the alkali metals (group I).

Atomic Number as the Basis for the Periodic Law

Mendeleev placed certain elements out of the order of increasing atomic mass to get them into the proper groups of his periodic table. He assumed this was because of errors in atomic masses. With improved methods of determining atomic masses and with the discovery of argon (group 0, atomic mass 39.9), which was placed ahead of potassium (group I, atomic mass 39.1), it became clear that a few elements might always remain "out of order." At the time, these out-of-order placements were justified by chemical evidence. Elements were placed in the groups that their chemical behavior dictated. There was no theoretical explanation for this reordering. Matters changed in 1913 as a result of some research by Henry G. J. Moseley on the X-ray spectra of the elements.

As we learned in Chapter 2, X-rays are a high-frequency form of electromagnetic radiation produced when a cathode-ray (electron) beam strikes the anode of a cathode-ray tube (see Figure 9-2a). The anode is called the *target*. Moseley was familiar with Bohr's atomic model, and explained X-ray emission in the following way. If the bombarding electrons have sufficient energy, they can eject electrons from the inner orbitals of target metal atoms. Electrons from higher orbitals then drop down to fill the vacancies, emitting X-ray photons with energies corresponding to the difference in energy between the originating level and the vacancy level (see Figure 8-13). Moseley reasoned that because the energies of electron orbitals depend on the nuclear charge, the frequencies of emitted X-rays should depend on the nuclear charges of atoms in the target. Using techniques newly developed by the father–son team of W. Henry Bragg and W. Lawrence Bragg, Moseley obtained photographic images of X-ray spectra and assigned frequencies to the spectral lines. His spectra for the elements from Ca to Zn are reproduced in Figure 9-2(b).

Moseley was able to correlate X-ray frequencies to numbers equal to the nuclear charges and corresponding to the positions of elements in Mendeleev's periodic table. For example, aluminum, the thirteenth element in the table, was assigned an *atomic number* of 13. Moseley's equation is $\nu = A(Z - b)^2$, where ν is the X-ray frequency, Z is the atomic number, and A and b are constants. Moseley used this relationship to predict three new elements ($Z = 43, 61$, and 75), which were discovered in 1937, 1945, and 1925, respectively. Also, he proved that in the portion of the periodic table with which he worked (from $Z = 13$ to $Z = 79$), there could be no additional new elements beyond those three. All available atomic numbers had been assigned. From the standpoint of Moseley's work, then, we should restate the periodic law.

▲ **Henry G. J. Moseley (1887–1915)**
Moseley was one of a group of brilliant scientists whose careers were launched under Ernest Rutherford. He was tragically killed at Gallipoli, in Turkey, during World War I.

> Similar properties recur periodically when elements are arranged according to increasing atomic number.

Description of a Modern Periodic Table: The Long Form

Mendeleev's periodic table consisted of 8 groups, but most modern periodic tables are arranged in 18 groups of elements. Let us briefly review the description of the periodic table given in Section 2-6.
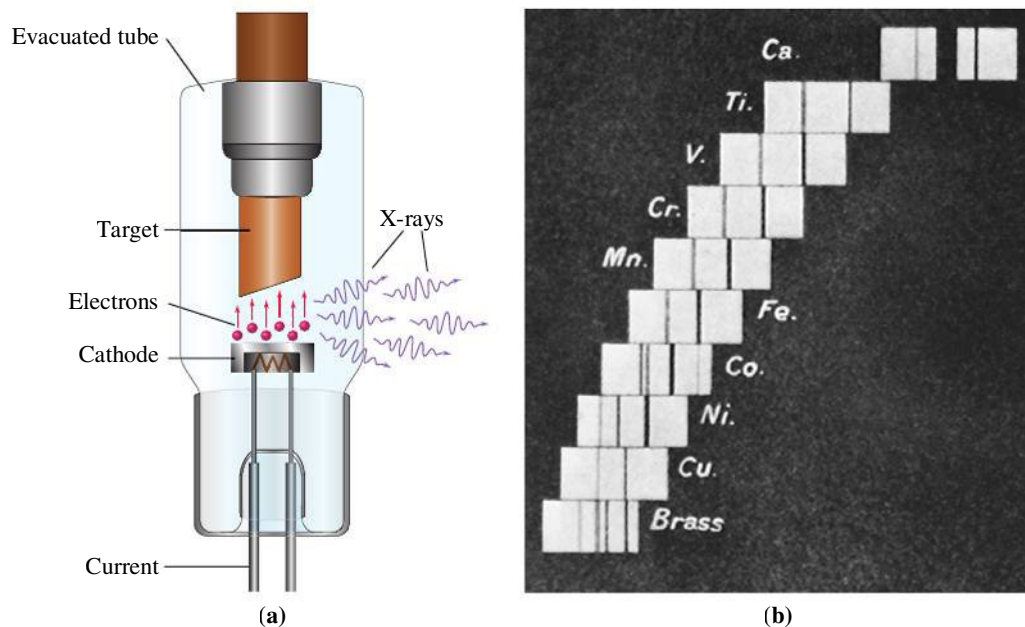
▲ FIGURE 9-2
Schematic of an X-ray tube and Moseley's X-ray spectra of several elements
(a) A heated filament emits electrons by a process called thermionic emission. The electrons are accelerated by a high voltage, and collide with the metal target. The highly energetic electrons ionize electrons from the inner shells of the metal atoms of the target. Subsequently, electrons from higher orbitals drop down to occupy the vacancies and in doing so, emit X-ray photons that correspond to the energy difference between the two orbitals. (b) In this photograph from Moseley's 1913 paper, you can see two lines for each element, beginning with Ca at the top. With each successive element, the lines are displaced to the left, the direction of increasing X-ray frequency in these experiments. Where more than two lines appear, the sample contained one or more other elements, or impurities. Notice, for example, that one line in the Co spectrum matches a line in the Fe spectrum, and another matches a line in the Ni spectrum. Brass, which is an alloy of copper and zinc, shows two lines for Cu and two for Zn.

In the periodic table (see inside front cover), the vertical groups bring together elements with similar properties. The horizontal periods of the table are arranged in order of increasing atomic number from left to right. The groups are numbered at the top, and the periods at the extreme left. The first two groups—the *s* block—and the last six groups—the *p* block—together constitute the *main-group elements*. Because they come between the *s* block and the *p* block, the *d* block elements are known as the *transition elements*. The *f* block elements, sometimes called the *inner transition elements*, would extend the table to a width of 32 members if incorporated in the main body of the table. The table would generally be too wide to fit on a printed page, and so the *f* block elements are extracted from the table and placed at the bottom. The 15 elements following barium ($Z = 56$) are called the *lanthanides*, and the 15 following radon ($Z = 88$) are called the *actinides*.

9-2   Metals and Nonmetals and Their Ions

In Section 2-6, we established two categories of elements, *metals* and *nonmetals*, and described them in terms of physical properties. Most metals are good conductors of heat and electricity, are malleable and ductile, and have moderate to high melting points. In general, nonmetals are nonconductors of heat and

electricity and are nonmalleable (brittle) solids, though a number of non-metals are gases at room temperature.

Through the color scheme of the periodic table on the inside front cover, we see that the majority of the elements are metals (orange) and that non-metals (blue) are confined to the right side of the table. The noble gases (purple) are treated as a special group of nonmetals. Metals and nonmetals are often separated by a stairstep diagonal line, and several elements near this line are often called metalloids (green). **Metalloids** are elements that look like metals and in some ways behave like metals but also have some nonmetallic properties.

In the original periodic table, the positions of the elements were based on readily observable physical and chemical properties. In Chapter 8, we learned of the close correlation between electron configurations and the positions of the elements in the table. Thus, it appears that the physical and chemical properties of an element are determined largely by its electron configuration, particularly that of the *valence* (outermost) electronic shell. Adjacent members of a series of main-group elements in the same period (such as P, S, and Cl) have significantly different properties because they differ in their valence-electron configurations. Within a transition series, differences in electron configurations are mostly in inner shells, and so a transition element has some similarities to neighboring transition elements in the same period. In particular we find many similar properties for adjacent members of the same period within the *f* block. In fact, the strong similarities among the lanthanide elements presented a particular challenge to the nineteenth-century chemists who tried to separate and identify them.

Let's now briefly explore a few of the links between electron configurations and some other observations about the elements, starting with the noble gases.

◄ Metalloids (such as silicon) are semiconductors and materials composed of metalloids play an important role in microcomputer technology.

Noble Gases

Atoms of the noble gases have the maximum number of electrons permitted in the valence shell of an atom, two in helium ($1s^2$) and eight in the other noble gas atoms (ns^2np^6). These electron configurations are very difficult to alter and seem to confer a high degree of chemical inertness to the noble gases. It is interesting to note, then, that the *s*-block metals, together with Al in group 13, tend to lose enough electrons to acquire the electron configurations of the noble gases. Conversely, nonmetals tend to gain enough electrons to achieve the same configurations.

◄ Compounds containing radon, xenon and krypton have been prepared. Recently, compounds containing argon have also been prepared.

Main-Group Metal Ions

The atoms of elements of groups 1 and 2—the most active metals—have electron configurations that differ from those of the noble gas of the preceding period by only one and two electrons in the *s* orbital of a new electron shell. If a K atom is stripped of its outer-shell electron, it becomes the *positive ion* K$^+$ with the electron configuration [Ar]. A Ca atom acquires the [Ar] configuration following the removal of two electrons.

$$K([Ar]4s^1) \longrightarrow K^+([Ar]) + e^-$$
$$Ca([Ar]4s^2) \longrightarrow Ca^{2+}([Ar]) + 2e^-$$
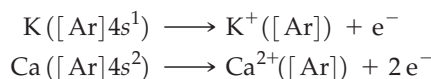
Although metal atoms do not lose electrons spontaneously, the energy required to bring about ionization is often provided by other processes occurring at the same time (such as an attraction between positive and negative ions). Aluminum is the only *p*-block metal that forms an ion with a noble gas electron configuration—Al^{3+}. This is because all other *p*-block elements would have to remove 10 *d* electrons to attain the electron configuration of the previous noble gas. The electron configurations of the other *p*-block metal ions are summarized in Table 9.2.

▲ Metals tend to lose electrons to attain noble gas electron configurations.

TABLE 9.2 Electron Configurations of Some Metal Ions[a]

"Noble Gas"		"Pseudo-Noble Gas"[b]	"18 + 2"[c]	Other
Li^+	Be^{2+}	Ga^{3+}	In^+	Cr^{2+}, Cr^{3+}
Na^+	Mg^{2+}	Tl^{3+}	Tl^+	Mn^{2+}, Fe^{2+}
K^+	Ca^{2+}	Cu^+	Sn^{2+}	Fe^{3+}, Co^{2+}
Rb^+	Sr^{2+}	Ag^+, Au^+	Pb^{2+}	Ni^{2+}, Cu^{2+}
Cs^+	Ba^{2+}	Zn^{2+}	Sb^{3+}	
Fr^+	Ra^{2+}		Bi^{3+}	
Al^{3+}				

[a]Main-group metal ions are printed in black and transition metal ions in blue.
[b]In the configuration labeled "pseudo-noble gas," all electrons of the outermost shell have been lost. The next-to-outermost electron shell of the atom becomes the outermost shell of the ion and contains 18 electrons, for example, Ga^{3+}: $[Ne]3s^23p^63d^{10}$.
[c]In the configuration labeled "18 + 2" all outer-shell electrons except the two s electrons are lost, producing an ion with 18 electrons in the next-to-outermost shell and 2 electrons in the outermost, for example, Sn^{2+}: $[Ar]3d^{10}4s^24p^64d^{10}5s^2$.

Main-Group Nonmetal Ions

The atoms of groups 17 and 16—the most active nonmetals—have one and two electrons fewer than the noble gas at the end of the period. Groups 17 and 16 atoms can acquire the electron configurations of noble gas atoms by *gaining* the appropriate numbers of electrons.

$$Cl([Ne]3s^23p^5) + e^- \longrightarrow Cl^-([Ar])$$
$$S([Ne]3s^23p^4) + 2e^- \longrightarrow S^{2-}([Ar])$$

▲ Nonmetals tend to gain electrons to attain noble-gas electron configurations.
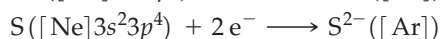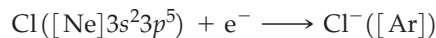
In most cases, a nonmetal atom will gain a single electron spontaneously, but energy is required to force it to accept more than one. The necessary energy is often supplied by other processes that occur simultaneously (such as an attraction between positive and negative ions). Nonmetal ions with a charge of 3− are rare. However, some metal nitrides containing the nitride ion, N^{3-}, and some metal phosphides containing the phosphide ion, P^{3-}, are known.

Transition Metal Ions

In the aufbau process, the *ns* subshell fills before electrons enter the $(n - 1)d$ subshell (page 340), but the energy levels of these two subshells are nearly the same (Fig. 8-36). Thus, it is not surprising that when transition metal atoms ionize, the *ns* subshell is emptied. For example, the electron configuration of Ti is $[Ar]3d^24s^2$, and that of Ti^{2+} is $[Ar]3d^2$. Moreover, in some cases one or more $(n - 1)d$ electrons might be lost together with the *ns* electrons. This happens in the formation of Ti^{4+}, which has the electron configuration [Ar].

▶ A useful mnemonic is that the electron configuration of a cation can be obtained from the electron configuration of the parent atom by removing those electrons in orbitals with the *highest* quantum number first.

A few transition metal atoms acquire noble-gas electron configurations when forming cations, as do Sc in Sc^{3+} and Ti in Ti^{4+}, but most transition metal atoms do not (see Table 9.2). An iron atom does not acquire a noble-gas electron configuration when it loses its $4s^2$ electrons to form the ion Fe^{2+},

$$Fe([Ar]3d^64s^2) \longrightarrow Fe^{2+}([Ar]3d^6) + 2e^-$$
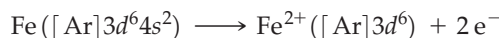
nor does it with the loss of an additional 3d electron to form the ion Fe^{3+}.

$$Fe([Ar]3d^64s^2) \longrightarrow Fe^{3+}([Ar]3d^5) + 3e^-$$
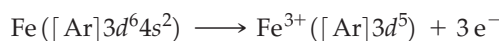
The 3d subshell in Fe^{3+} is half-filled, a fact that helps to account for the observed ease of oxidation of iron(II) to iron(III) compounds. Electron configurations with half-filled or filled d or f subshells have a special stability, and a number of transition metal ions have such configurations.

Hydrogen

Although all the other elements have a definite place in the periodic table, hydrogen does not. Its uniqueness stems from the fact that its atoms have only one electron, in the configuration $1s^1$. This single electron is the reason that we put hydrogen in group 1, even though we classify it as a nonmetal. Hydrogen does appear to become metallic when subjected to pressures of about 2 million bar, but these are hardly ordinary laboratory conditions. Because hydrogen, like the halogens, is one electron short of having a noble-gas electron configuration, it is sometimes placed in group 17; however, hydrogen does not resemble the halogens very much. For example, F_2 and Cl_2 are excellent oxidizing agents, but H_2 is a reducing agent. Still another alternative places hydrogen by itself at the top of the periodic table and near the center.

🔍 9-1   CONCEPT ASSESSMENT

On the blank periodic table in the margin, indicate where elements that satisfy the following descriptions occur.

(a) A noble gas having the same electron configuration as the Na^+ cation

(b) An anion of a nonmetal with a charge of $3-$ that has a noble-gas electron configuration

(c) A transition metal ion with a charge of $2+$ and no valence shell s and p electrons

---

9-3   Sizes of Atoms and Ions

In earlier chapters we discovered the importance of atomic masses in matters relating to stoichiometry. To understand certain physical and chemical properties, we need to know something about atomic sizes. In this section we describe atomic radius, the first of a group of atomic properties that we will examine in this chapter.
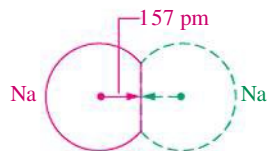
Atomic Radius

Unfortunately, atomic radius is hard to define. The probability of finding an electron decreases with increasing distance from the nucleus, but nowhere does the probability fall to zero, so there is no precise outer boundary to an atom. We might describe an *effective* atomic radius as, say, the distance from the nucleus within which 95% of all the electron charge density is found, but in fact, all that we can measure is the distance between the nuclei of adjacent atoms (internuclear distance). Even though it varies, depending on whether atoms are chemically bonded or merely in contact without forming a bond, we define atomic radius in terms of internuclear distance.

Because we are primarily interested in bonded atoms, we will emphasize an atomic radius based on the distance between the nuclei of two atoms joined by a chemical bond. The **covalent radius** is one-half the distance between the nuclei of two identical atoms joined by a single covalent bond. The **ionic radius** is based on the distance between the nuclei of ions joined by an ionic bond. Because the ions are not identical in size, this distance must be properly apportioned between the cation and anion. One way to apportion the electron density between the ions is to define the radius of one ion and then infer the radius of the other ion. The convention we have chosen to use is to assign O^{2-} an ionic radius of 140 pm. An alternative apportioning scheme is to use F^- as the reference ionic radius. When using ionic radii data, one should carefully note which convention is used and not mix radii from the different conventions. Starting with a radius of 140 pm for O^{2-}, the radius of Mg^{2+} can be obtained

▶ Despite the SI convention, the angstrom unit, Å, is still widely used by X-ray crystallographers and others who work with atomic and molecular dimensions.
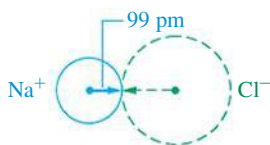
Covalent radius:

Metallic radius:
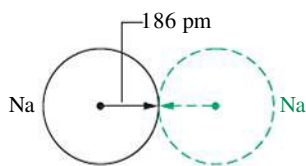
Ionic radius:

▲ **FIGURE 9-3**
Covalent, metallic, and ionic radii compared
Atomic radii are represented by the solid arrows. The covalent radius is based on the diatomic molecule $Na_2(g)$, found only in gaseous sodium. The metallic radius is based on adjacent atoms in solid sodium, $Na(s)$. The value of the ionic radius of Na^+ is obtained by the comparative method described in the text.

from the internuclear distance in MgO, the radius of Cl^- from the internuclear distance in $MgCl_2$, and the radius of Na^+ from the internuclear distance in NaCl. For metals, we define a **metallic radius** as one-half the distance between the nuclei of two atoms in contact in the crystalline solid metal. Similarly in a solid sample of a noble gas the distance between the centers of neighboring atoms is called the **van der Waals radius**. There is much debate about the values of the atomic radii of noble gases because the experimental determination of the van der Waals radii is difficult; consequently, the atomic radii of noble gases are left out of the discussion of trends in atomic radii.

The angstrom unit, Å, has long been used for atomic dimensions $(1 \text{ Å} = 10^{-10} \text{ m})$. The angstrom, however, is not a recognized SI unit. The SI units are the nanometer (nm) and picometer (pm).

$$1 \text{ nm} = 1 \times 10^{-9} \text{ m}; 1 \text{ pm} = 1 \times 10^{-12} \text{ m}; 1 \text{ nm} = 1000 \text{ pm} \qquad (9.2)$$

Figure 9-3 illustrates the definitions of covalent, ionic, and metallic radii by comparing these three radii for sodium. Figure 9-4 is a plot of atomic radius against atomic number for a large number of elements. In this plot metallic radii are used for metals and covalent radii for nonmetals. Figure 9-4 suggests certain trends in atomic radii, for example, large radii for group 1, decreasing across the periods to smaller radii for group 17. To interpret these trends, let us first return to a topic introduced in Chapter 8.

Screening and Penetration

In Section 8-10, penetration was described as a gauge of how close an electron gets to the nucleus. When interpreting the radial probability distributions, we saw that s electrons, by virtue of their extra humps of probability close to the nucleus (Fig. 8-35), penetrate better than p electrons, which in turn penetrate better than d electrons. Screening, or shielding, reflects how an outer electron is blocked from the nuclear charge by inner electrons.
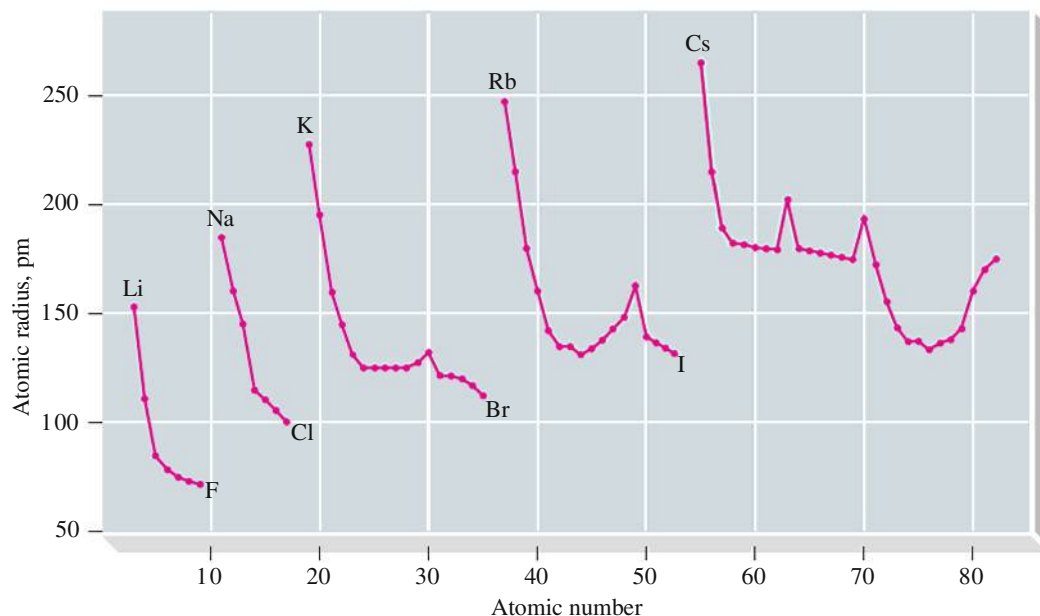
▲ FIGURE 9-4
Atomic radii
The values plotted are metallic radii for metals and covalent radii for nonmetals. Data for the noble gases are not included because of the difficulty of measuring covalent radii for these elements (only Kr and Xe compounds are known). The explanations usually given for the several small peaks in the middle of some periods are beyond the scope of this discussion.
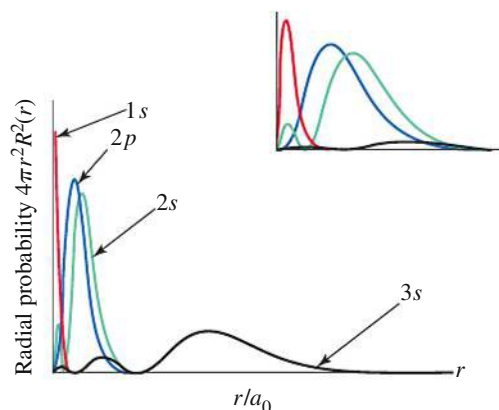
◀ FIGURE 9-5
Radial probability distributions for magnesium
Graphs of $4\pi r^2 R^2(r)$ as a function of r for the 1s, 2s, and 3s orbitals of magnesium. The graphs were obtained by using the radial functions from Table 8.1 with $Z_{eff} = 11.61$ (for 1s); $Z_{eff} = 7.39$ (for 2s); $Z_{eff} = 7.83$ (for 2p); and $Z_{eff} = 3.31$ (for 3s). The inset plot has a smaller range of r values in order to highlight the behavior of the probability functions closer to $r = 0$.

Consider the hypothetical process of building up each atom in the third period from the atom preceding it, beginning with sodium. In this process, the number of inner-shell, or core, electrons is fixed at ten in the configuration $1s^2 2s^2 2p^6$. As a first approximation, let us *assume* that the core electrons completely cancel an equivalent charge on the nucleus. In this way, the core electrons shield, or screen, the outer-shell electrons from the full attractive force of the nucleus. Let us also assume that the outer-shell electrons do not screen one another. Finally, let us redefine an **effective nuclear charge**, Z_{eff}, first introduced in Section 8-10, as the true nuclear charge minus the charge that is screened out by electrons.
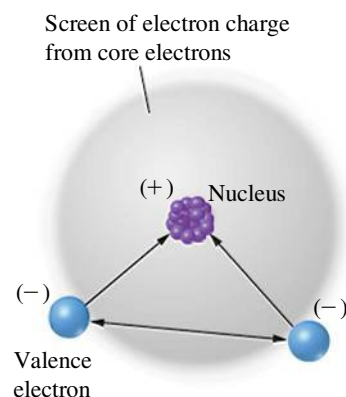
$$Z_{eff} = Z - S \qquad (9.3)$$

Think of S as representing the number of inner electrons that appear to screen or shield an outer electron. Based on the two assumptions just stated, in sodium ($Z = 11$) the ten core electrons would screen out 10 units of nuclear charge (that is, $S = 10$), leaving an effective nuclear charge of $11 - 10 = +1$. In magnesium ($Z = 12$), Z_{eff} would be $+2$. In aluminum, Z_{eff} would be $+3$, and so on across the period.

Actually, neither assumption we made above—full screening by inner-shell electrons and no screening by outer-shell electrons—is correct. These assumptions ignore the fact that the electrons, both inner and outer, occupy orbitals with different radial probability distributions and, consequently, different degrees of penetration (Fig. 9-5). Thus, an s electron, with its greater penetration, will be screened by inner electrons less than will a p electron. Similarly a p electron is shielded less than a d electron, which has a much lower penetration. In sodium, the 10 core electrons cancel only about 8.5 units of charge; thus, Z_{eff} is about $2.5+$, not $1+$. Also, outer-shell electrons do screen one another somewhat because of penetration effects. Each outer-shell electron is about one-third effective in screening the other outer-shell electrons. Thus, the Z_{eff} experienced by each of the two outer-shell electrons in magnesium is about $12 - 8.5 - \frac{1}{3} = 3.2+$, not $2+$ (Fig. 9-6). As we will see, trends in properties of atoms and ions in the periodic table are largely governed by the effective nuclear charge, Z_{eff}.

Screen of electron charge from core electrons

(+) Nucleus

(−) (−)

Valence electron

▲ FIGURE 9-6
The shielding effect and effective nuclear charge, Z_{eff}
Two valence electrons (blue) are attracted to the nucleus of a Mg atom. The atom's 12+ nuclear charge is screened by the 10 core electrons (gray), but not perfectly. The valence electrons also screen each other somewhat. The result is an *effective* nuclear charge, Z_{eff}, closer to 3+ than to 2+.

The Effects of Penetration and Screening The wave function of a multielectron atom provides a qualitative understanding of the effects of penetration and screening. In this simplified picture, the nuclear charge is replaced by Z_{eff}, so that the orbital energy is approximated by

$$E_n = -R_H \frac{Z_{eff}^2}{n^2} \qquad (9.4)$$

where Z_{eff} is the effective nuclear charge in the shell corresponding to the value of n. All other symbols have their usual meaning (see Chapter 8). Equation (9.4) has the same form as the energy of the hydrogen atom obtained as a solution to the Schrödinger equation. The multielectron atom has been

▶ The leading term of equation (9.5) is the Bohr radius of the nth Bohr orbit. The corresponding formula for the orbitals of the H atom can be obtained by setting $Z_{eff} = 1$.

reduced to a one-electron approximation, a great oversimplification, but useful nevertheless. The average size of an orbital is taken to be the average value of the distance, $\bar{r}_{nl}$, of the electron in that orbital from the nucleus.

$$\bar{r}_{nl} = \frac{n^2 a_0}{Z_{eff}} \left\{ 1 + \frac{1}{2} \left[1 - \frac{\ell(\ell + 1)}{n^2} \right] \right\} \tag{9.5}$$

9-1 ARE YOU WONDERING...

Where estimates of the screening by electrons come from?

These estimates come from an analysis of the wave functions of multielectron atoms. An exact solution of the Schrödinger equation can be obtained for the H atom, but for multielectron atoms, only approximate solutions are possible. The principle of the calculation is to assume each electron in the atom occupies an orbital much like those of the hydrogen atom. However, the functional form of the orbital is based on another assumption: that the electron moves in an effective or average field dictated by all the other electrons. With this assumption, the complicated multielectron Schrödinger equation is converted into a set of simultaneous equations—one for each electron. Each equation contains the unknown effective field and the unknown functional form of the orbital for the electron. The approach to solving such a set of equations is to guess at the functional forms of the orbitals, calculate an average potential for each electron to move in, and then solve for a new set of orbitals—one for each electron. The expectation is that the new orbitals are better than the initial guess. The new orbitals are then used to calculate a new effective field for the electrons, and the whole process is repeated until the calculated orbitals do not change much.

This iterative procedure, called the *self-consistent field* (*SCF*) *method*, was devised by Douglas Hartree in 1936, before the advent of computers. Currently, the wave functions of atoms and molecules are obtained by implementing the SCF procedures on computers. The use of computers to calculate molecular properties from a wave function by the SCF procedure has lead to the term molecular modeling. Molecular modeling has become a tool in modern chemical research.

The atomic orbitals obtained from SCF calculations closely resemble the atomic orbitals of the hydrogen atom in many ways. The angular dependence of the orbitals is identical, so that we can identify s, p, d, f orbitals by their characteristic shapes. The radial functions of the orbitals are different because the effective field is different from the one in the hydrogen atom, but the principal quantum number can still be defined. Thus, each electron in a multielectron atom has associated with it the four quantum numbers n, ℓ, m_ℓ, and m_s. Estimates of screening constants are based on an analysis of the radial functions obtained from SCF calculations.

In equation (9.5), all the symbols have their usual meaning. Again, equation (9.5) is the equation for the hydrogen atom or hydrogen-like ions with the nuclear charge replaced by Z_{eff} to approximate multielectron effects. Equations (9.4) and (9.5) are approximate but provide for a very useful semiquantitative interpretation of atomic properties. We consider next the three most important trends among atomic radii in relation to the periodic table.

KEEP IN MIND

that s- and p-valence electrons have some probability of being near the nucleus (Fig. 8-35). These electrons penetrate the inner core of electrons and experience a greater attraction to the nucleus than otherwise expected.

1. **Variation of Atomic Radii Within a Group of the Periodic Table.** Radial probability densities extend farther out from the nucleus as n increases, a fact seen both in Figure 8-35 and in equation (9.5). Thus, we should expect that the more electron shells occupied by electrons, the larger the atom. This idea works for the group members of lower atomic numbers, where the increase in radius from one period to the next is large (as from Li to Na to K in group 1). At higher atomic numbers, the increase in radius is smaller (as from K to Rb to Cs in group 1). In these elements of higher atomic number, outer-shell electrons are held somewhat more tightly than

expected because inner-shell electrons in d and f subshells are less effective than s and p electrons in screening outer-shell electrons from the nucleus; that is, Z_{eff} is larger than expected. Nevertheless, in general, the following is true.

> The more electronic shells in an atom, the larger is the atom. Atomic radius increases from top to bottom through a group of elements.

2. **Variation of Atomic Radii Within a Period of the Periodic Table.** From Figure 9-4, we see that, in general, atomic radius decreases from left to right across a period. A careful look at the figure suggests that this trend does not apply to the transition elements. Let us look first at the general trend of decreasing radii and then at what is special about the transition elements.

   Across a period, the atomic number increases by one for each succeeding element. For the main-group elements, each increase in atomic number is accompanied by the addition of one electron to the valence shell. The valence-shell electrons, being in the same shell, shield each other poorly from the increasing nuclear charge. The Z_{eff} for the $2s$ electron of Li is 1.3, and that for Be is 1.9; thus, Z_{eff} increases as Z increases across the main-group portions of a period. Across a period, the principal quantum number stays constant, so that whether we use Z_{eff} or just the nuclear charge Z in equation (9.5), the result is as follows.

◄ Values of Z_{eff} can be estimated using the rules set out in Feature Problem 73.

> The atomic radius decreases from left to right through a period of elements.

3. **Variation in Atomic Radius Within a Transition Series.** With the transition elements, the situation is a little different from that described above. In Figure 9-4, it is apparent that the atomic radii of transition elements tend to be about the same across a period but with a few unusual peaks. It is beyond the scope of this text to explain the exceptions; however, the general trend is not difficult to understand. In a series of transition elements, additional electrons go into an *inner* electron shell, where they participate in shielding outer-shell electrons from the nucleus. At the same time, the number of electrons in the *outer* shell tends to remain constant. Thus, the outer-shell electrons experience a roughly comparable force of attraction to the nucleus throughout a transition series. Consider Fe, Co, and Ni. Fe has 26 protons in the nucleus and 24 inner-shell electrons. In Co ($Z = 27$), there are 25 inner-shell electrons, and in Ni ($Z = 28$), there are 26. In each case, the two outer-shell electrons are under the influence of about the same net charge (about +2). That is, Z_{eff} for the $4s$ electrons of the first transition series is approximately constant. Thus, atomic radii do not change very much for this series of three elements, namely, 124 pm for Fe and 125 pm for Co and Ni.

🔍 **9-2   CONCEPT ASSESSMENT**
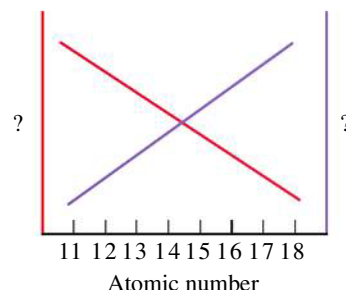
The graph in the margin represents the variation of Z_{eff} and atomic radius with atomic number. Which axis and correspondingly colored line corresponds to Z_{eff} and which to atomic radius?

11 12 13 14 15 16 17 18
Atomic number

EXAMPLE 9-1   **Relating Atomic Size to Position in the Periodic Table**

Refer only to the periodic table on the inside front cover, and determine which is the largest atom: Sc, Ba, or Se.

Analyze

We first place the element in the periodic table and decide whether or not the elements are in the same period and whether they are on the right or left of the periodic table. We can then use the rules noted above to decide on the relative sizes of atoms (or ions).
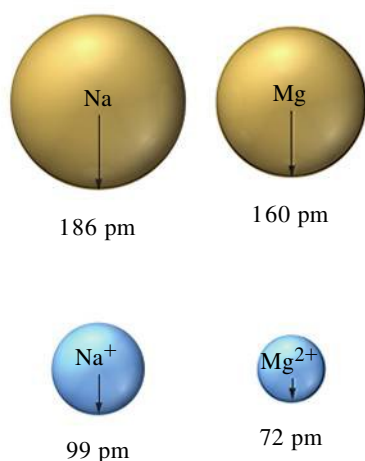
Solve

Sc and Se are both in the fourth period, and we would expect Sc to be larger than Se because atomic sizes decrease from left to right in a period. Ba is in the sixth period and so has more electronic shells than either Sc or Se. Furthermore, it lies even closer to the left side of the table (group 2) than does Sc (group 3). We can say with confidence that the Ba atom should be the largest of the three.

Assess

By using the procedure outlined above, we have been able to show that $r_{Ba} > r_{Sc} > r_{Se}$. The actual atomic radii are Se, 117 pm; Sc, 161 pm; and Ba, 217 pm.

PRACTICE EXAMPLE A: Use the periodic table on the inside front cover to predict which is the smallest atom: As, I, or S.

PRACTICE EXAMPLE B: Which of the following atoms do you think is closest in size to the Na atom: Br, Ca, K, or Al? Explain your reasoning, and do not use any tabulated data from the chapter in reaching your conclusion.

Ionic Radius

When a metal atom loses one or more electrons to form a positive ion, the positive nuclear charge exceeds the negative charge of the electrons in the resulting cation. The nucleus draws the electrons in closer, and, as a consequence, the following holds true.

> Cations are smaller than the atoms from which they are formed.

Na
186 pm

Mg
160 pm

Na$^+$
99 pm

Mg^{2+}
72 pm

▲ FIGURE 9-7
A comparison of atomic and ionic sizes
Metallic radii are shown for Na and Mg and ionic radii for Na$^+$ and Mg^{2+}.

Figure 9-7 compares four species: the atoms Na and Mg and the ions Na$^+$ and Mg^{2+}. As expected, the Mg atom is smaller than the Na atom, and the cations are smaller than the corresponding atoms. Na$^+$ and Mg^{2+} are **isoelectronic**—they have equal numbers of electrons (10) in identical configurations, $1s^2 2s^2 2p^6$. Mg^{2+} is smaller than Na$^+$ because its nuclear charge is larger ($+12$, compared with $+11$ for Na).

> For isoelectronic cations, the more positive the ionic charge, the smaller the ionic radius.

When a nonmetal atom gains one or more electrons to form a negative ion (anion), the nuclear charge remains constant, but Z_{eff} is reduced because of the additional electron(s). The electrons are not held as tightly. Repulsions among the electrons increase. The electrons spread out more, and the size of the atom increases, as suggested in Figure 9-8.

> Anions are larger than the atoms from which they are formed. For isoelectronic anions, the more negative the charge, the larger the ionic radius.

Knowledge of atomic and ionic radii can be used to vary certain physical properties. One example concerns strengthening glass. Normal window glass contains Na^+ and Ca^{2+} ions. The glass is brittle and shatters easily when struck a hard blow. One way to strengthen the glass is to replace the Na^+ ions at the surface with K^+ ions. The K^+ ions are larger and fill up the surface sites, leaving less opportunity for cracking than with the smaller Na^+ ions. The result is a shatter-resistant glass.

Another example is the striking result when Cr^{3+} ions replace about 1% of the Al^{3+} ions in aluminum oxide, Al_2O_3. This substitution is possible because Cr^{3+} ions are only slightly larger (by 9 pm) than Al^{3+} ions. Pure aluminum oxide is colorless, but with this small amount of chromium(III) ion, it is a beautiful red color. This impure Al_2O_3 is the gem known as a ruby. Rubies and other gemstones can be made artificially and are used as jewelry and in devices such as lasers. The color of the ruby is further discussed in Chapter 24.

Figure 9-9, arranged in the format of the periodic table, shows relative sizes of typical atoms and ions, and summarizes the generalizations described in this section.

Covalent radius	Ionic radius
99 pm	181 pm
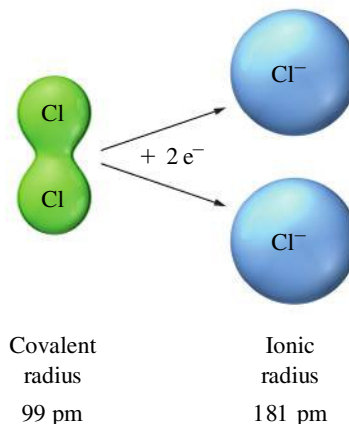
▲ FIGURE 9-8
Covalent and anionic radii compared
The two Cl atoms in a Cl_2 molecule gain one electron each to form two Cl^- ions.

EXAMPLE 9-2   Comparing the Sizes of Cations and Anions

Refer only to the periodic table on the inside front cover, and arrange the following species in order of increasing size: K^+, Cl^-, S^{2-}, and Ca^{2+}.

Analyze

The key lies in recognizing that the four species are *isoelectronic*, having the electron configuration of argon: $1s^2 2s^2 2p^6 3s^2 3p^6$. When considering isoelectronic cations, the higher the charge on the ion, the smaller the ion.

Solve

The larger charge on the calcium ion means that Ca^{2+} is smaller than K^+. Because K^+ has a higher nuclear charge than Cl^- ($Z = 19$, compared with $Z = 17$), it is smaller than Cl^-. For isoelectronic anions, the higher the charge, the larger the ion. S^{2-} is larger than Cl^-. The order of increasing size is

$$Ca^{2+} < K^+ < Cl^- < S^{2-}$$

Assess

We can summarize the generalizations about isoelectronic atoms and ions into a single statement: Among isoelectronic species, the greater the atomic number, the smaller the size.

PRACTICE EXAMPLE A: Refer only to the periodic table on the inside front cover, and arrange the following species in order of increasing size: $Ti^{2+}, V^{3+}, Ca^{2+}, Br^-$, and Sr^{2+}.

PRACTICE EXAMPLE B: Refer only to the periodic table on the inside front cover, and determine which species is in the *middle* position when the following five are ranked according to size: the atoms N, Cs, and As and the ions Mg^{2+} and Br^-.

🔍 **9-3   CONCEPT ASSESSMENT**

On the blank periodic table in the margin, locate the following:

(a) The smallest group 13 atom

(b) The smallest period 3 atom

(c) The largest anion of a nonmetal in period 3

(d) The largest group 13 cation

▲ FIGURE 9-9
A comparison of some atomic and ionic radii
The values given, in picometers (pm), are metallic radii for metals, single covalent radii for nonmetals, and ionic radii for the ions indicated.

9-4   Ionization Energy

In discussing metals, we talked about metal atoms losing electrons and thereby altering their electron configurations. But atoms do not eject electrons spontaneously. Electrons are attracted to the positive charge on the nucleus of an atom, and energy is needed to overcome that attraction. The more easily its electrons are lost, the more metallic an atom is considered to be. The **ionization energy**, *I*, is the quantity of energy a *gaseous* atom must absorb to be able to expel an electron. The electron that is lost is the one that is most loosely held.

Ionization energies are usually measured through experiments based on the photoelectric effect in which gaseous atoms at low pressures are bombarded with photons of sufficient energy to eject an electron from the atom. Here are two typical values.

$$Mg(g) \longrightarrow Mg^+(g) + e^- \qquad I_1 = 738 \text{ kJ/mol}$$
$$Mg^+(g) \longrightarrow Mg^{2+}(g) + e^- \qquad I_2 = 1451 \text{ kJ/mol}$$

The symbol I_1 stands for the *first* ionization energy—the energy required to strip one electron from a neutral gaseous atom.* I_2 is the *second* ionization energy—the energy to strip an electron from a gaseous ion with a charge of 1+. Further ionization energies are I_3, I_4, and so on. Each succeeding ionization energy is invariably larger than the preceding one. In the case of magnesium, for example, in the second ionization, the electron, once freed, has to move away from an ion with a charge of 2+ (Mg^{2+}). More energy must be invested than for a freed electron to move away from an ion with a charge of 1+ (Mg^+). This is a direct consequence of Coulomb's law, which states, in part, that the force of attraction between oppositely charged particles is directly proportional to the magnitudes of the charges.

First ionization energies (I_1) for many of the elements are plotted in Figure 9-10. In general, the farther an electron is from the nucleus, the more easily it can be extracted.

◀ A distinction between valence electrons and core electrons can be made based on the ionization energies for removing electrons one by one. The ionization energies of valence electrons are much smaller and show a big jump when the first core electron is removed.

Ionization energies decrease as atomic radii increase.
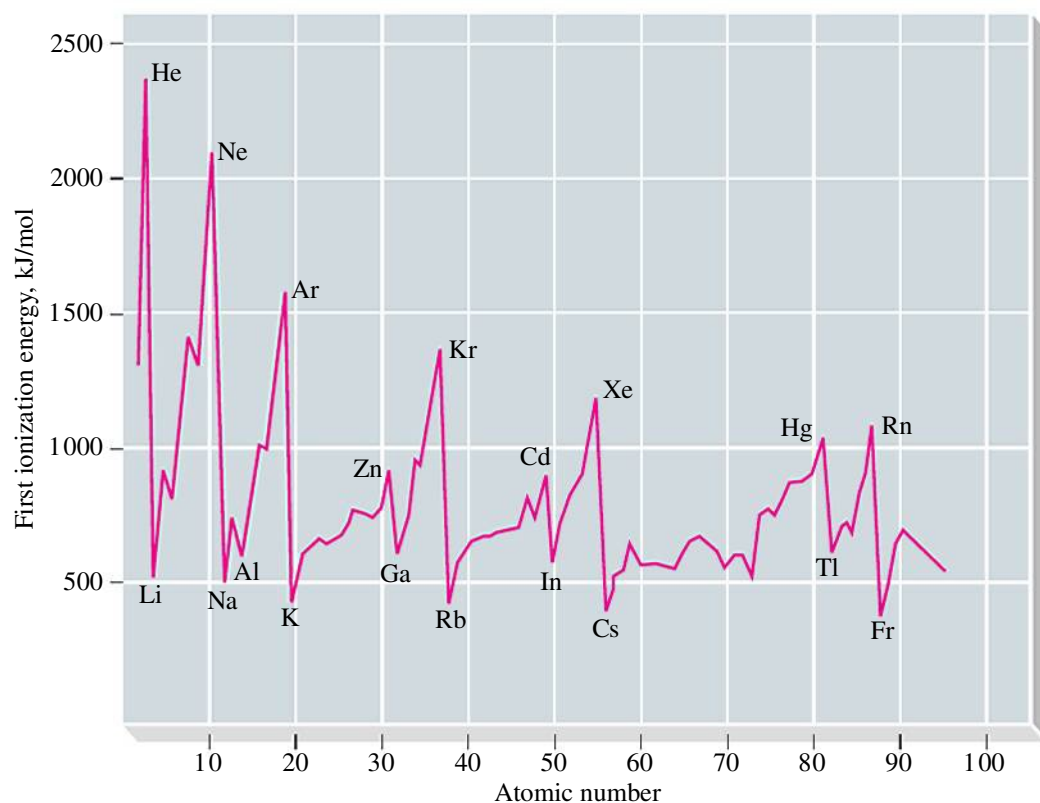
▲ FIGURE 9-10
First ionization energies as a function of atomic number
Because their electron configurations are so stable, more energy is required to ionize noble gas atoms than to ionize atoms of the elements immediately preceding or following them. The maxima on the graph come at the atomic numbers of the noble gases. The alkali metals are the most easily ionized of all groups. The minima in the graph come at their atomic numbers.

---

*Ionization energies are sometimes expressed in the unit electron-volt (eV). One electron-volt is the energy acquired by an electron as it falls through an electric potential difference of 1 volt. It is a very small energy unit, especially suited to describing processes involving individual atoms. When ionization is based on a *mole* of atoms, kJ/mol is the preferred unit (1 eV/atom = 96.49 kJ/mol). Sometimes the term *ionization potential* is used instead of ionization energy. Further, the quantities I_1, I_2, ..., may be replaced by enthalpy changes, ΔH_1, ΔH_2, and so on.

▶ This generalization works well for main-group elements but less so for transition elements, where there are several exceptions.

This observation that ionization energies decrease as atomic radii increase reflects the effect of n and Z_{eff} on the ionization energy (I). Equation (9.4) suggests that the ionization energy is given by

$$I = R_H \times \frac{Z_{eff}^2}{n^2} \tag{9.6}$$

so that across a period, as Z_{eff} increases and the valence-shell principal quantum number n remains constant, the ionization energy should increase. And down a group, as n increases and Z_{eff} increases only slightly, the ionization energy should decrease. Thus, atoms lose electrons more easily (become more metallic) as we move from top to bottom in a group of the periodic table. The decreases in ionization energy and the parallel increases in atomic radii are outlined in Table 9.3 for group 1.

Table 9.4 lists ionization energies for the third-period elements. With minor exceptions, the trend in moving across a period (follow the colored stripe) is that atomic radii decrease, ionization energies increase, and the elements become less metallic, or more nonmetallic, in character. Table 9.4 lists stepwise ionization energies (I_1, I_2, and so forth.). Note particularly the large breaks that occur along the zigzag diagonal line. Consider magnesium as an example. To remove a third electron, as measured by I_3, requires breaking into the especially stable noble-gas inner-shell electron configuration $2s^2 2p^6$. I_3 is *much* larger than I_2—so much larger that Mg^{3+} cannot be produced in ordinary chemical processes. Similarly, we do not encounter the ions Na^{2+} or Al^{4+} in chemical processes.

Now let us turn to the obvious exceptions to the regular trend in I_1 values for the third-period elements and ask, Why is I_1 of Al smaller than that of Mg and I_1 of S smaller than that of P?

TABLE 9.3   Atomic Radii and First Ionization Energies of the Alkali Metal (Group 1) Elements

	Atomic Radius, pm	Ionization Energy (I_1), kJ/mol
Li	152	520.2
Na	186	495.8
K	227	418.8
Rb	248	403.0
Cs	265	375.7

TABLE 9.4   Ionization Energies of the Third-Period Elements (in kJ/mol)

	Na	Mg	Al	Si	P	S	Cl	Ar
I_1	495.8	737.7	577.6	786.5	1,012	999.6	1,251.1	1,520.5
I_2	4,562	1,451	1,817	1,577	1,903	2,251	2,297	2,666
I_3		7,733	2,745	3,232	2,912	3,361	3,822	3,931
I_4			11,580	4,356	4,957	4,564	5,158	5,771
I_5				16,090	6,274	7,013	6,542	7,238
I_6					21,270	8,496	9,362	8,781
I_7						27,110	11,020	12,000

?   9-2   ARE YOU WONDERING...

If ionization energies can be used to estimate the effective nuclear charge?

One of the earliest estimates of effective nuclear charge was obtained by analyzing ionization energies in terms of equation (9.6). Thus, for example, the ionization energy of Li in its ground state is $519 \, kJ \, mol^{-1}$ and from equation (9.6), we have

$$I_1 = 1312.1 \frac{Z_{eff}^2}{n^2} \, kJ \, mol^{-1}$$

so that

$$519 \, \text{kJ} \, \text{mol}^{-1} = 1312.1 \frac{Z_{\text{eff}}^2}{2^2} \, \text{kJ} \, \text{mol}^{-1}$$

and we get

$$Z_{\text{eff}} = 1.26$$

The Z_{eff} obtained from the ionization energy of the first excited state of $\text{Li}(1s^2 2p)$, $339 \, \text{kJ} \, \text{mol}^{-1}$, is 1.02. The value of Z_{eff} is very close to one because the inner $1s^2$ core almost perfectly screens the $2p$ electron. By contrast, the penetration of the $2s$ electron leads to the somewhat larger $Z_{\text{eff}} = 1.26$ for the ground state.

Consider the orbital diagrams for Mg, Al, P, and S shown in the margin. We expect I_1 of Al to be larger than for Mg. The reversal occurs because of the particular electrons lost. Mg loses a $3s$ electron, while Al loses a $3p$ electron. We expect that *more* energy is required to strip an electron from the lower energy $3s$ orbital in $\text{Mg}([\text{Ne}]3s^2)$ than from a half-filled $3p$ orbital in $\text{Al}([\text{Ne}]3s^2 3p^1)$. I_1 for S is slightly lower than for P for a different reason. Although the orbitals in the $3p$ subshell are degenerate, we can think of repulsion between electrons in the filled $3p$ orbital of a S atom $([\text{Ne}]3s^2 3p^4)$ as making it easier to remove one of those electrons than an electron from the half-filled $3p$ subshell of a P atom $([\text{Ne}]3s^2 3p^3)$.

$3s$ $3p$
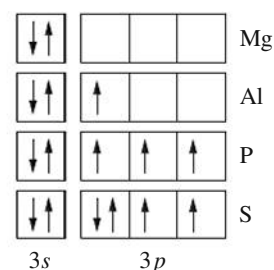
▲ Orbital diagram showing the valence electron configuration of magnesium, aluminum, phosphorus, and sulfur.

EXAMPLE 9-3   Relating Ionization Energies

Refer to the periodic table on the inside front cover, and arrange the following in the expected order of increasing first ionization energy, I_1: As, Sn, Br, Sr.

Analyze

Ionization energies decrease as atomic radii increase. Thus, if we arrange these four atoms according to decreasing radius, we will likely have arranged them according to increasing ionization energy. The largest atoms are to the left and the bottom of the periodic table. The smallest atoms are to the right and toward the top of the periodic table.

Solve

Of the four atoms, the one that best fits the large-atom category is Sr. Although none of the four atoms is particularly close to the top of the table, Br is the farthest to the right. This fixes the two extremes: Sr with the lowest ionization energy and Br with the highest. A tin atom should be larger than an arsenic atom, and thus Sn should have a lower ionization energy than As. The expected order of *increasing* ionization energies is Sr < Sn < As < Br.

Assess

The generalization that ionization energies decrease as atomic radii increase ignores the exceptions that occur when making comparisons between atoms of groups 2 and 13, as well as atoms of groups 15 and 16.

PRACTICE EXAMPLE A: Refer to the periodic table on the inside front cover, and arrange the following in the expected order of increasing first ionization energy, I_1: Cl, K, Mg, S.

PRACTICE EXAMPLE B: Refer to the periodic table on the inside front cover, and determine which element is most likely in the *middle* position when the following five elements are arranged according to first ionization energy, I_1. Rb, As, Sb, Br, Sr.

9-4 CONCEPT ASSESSMENT

On the blank periodic table in the margin, locate the following:

(a) The group 14 element with the highest first ionization energy

(b) The element with the greatest first ionization energy in period 4

(c) A *p*-block element in period 4 that has a lower first ionization energy than the element immediately preceding it and the element directly following it

9-5 Electron Affinity

Ionization energy is the energy change for the removal of an electron. Let's consider the energy change associated with the addition of an electron. The thermochemical equation for the addition of an electron to a fluorine atom is

$$F(g) + e^- \rightarrow F^-(g) \qquad \Delta H_{ea} = -328 \text{ kJ mol}^{-1}$$

Notice that the process above is *exothermic*, meaning that energy is given off when an F atom gains an electron. **Electron affinity**, *EA*, can be defined as the enthalpy change, ΔH_{ea}, that occurs when an atom in the gas phase gains an electron. According to this definition, the electron affinity of fluorine is a negative quantity.

We have defined electron affinity to reflect the tendency for a neutral atom to gain an electron. An alternative definition refers to the energy change in the process: $X^-(g) \longrightarrow X(g) + e^-$; that is, reflecting the tendency of an anion to lose an electron. This alternative definition leads to the opposite signs for *EA* values from those written in this text. You should be prepared to see electron affinities expressed in both ways in the chemical literature.

Some representative electron affinities are listed in Figure 9-11. It is more difficult to make generalizations about electron affinities than about ionization energies. The smaller atoms to the right of the periodic table (for example, group 17) tend to have large, negative electron affinities.* Electron affinities

▶ FIGURE 9-11
Electron affinities of main-group elements
Values are in kilojoules per mole for the process $X(g) + e^- \longrightarrow X^-(g)$.

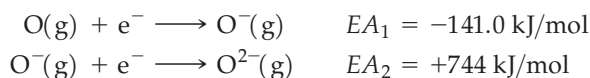| 1	2	13	14	15	16	17	18
H −72.8							**He** >0
Li −59.6	**Be** >0	**B** −26.7	**C** −121.8	**N** +7	**O** −141.0	**F** −328.0	**Ne** >0
Na −52.9	**Mg** >0	**Al** −42.5	**Si** −133.6	**P** −72	**S** −200.4	**Cl** −349.0	**Ar** >0
K −48.4	**Ca** −2.37	**Ga** −28.9	**Ge** −119.0	**As** −78	**Se** −195.0	**Br** −324.6	**Kr** >0
Rb −46.9	**Sr** −5.03	**In** −28.9	**Sn** −107.3	**Sb** −103.2	**Te** −190.2	**I** −295.2	**Xe** >0
Cs −45.5	**Ba** −13.95	**Tl** −19.2	**Pb** −35.1	**Bi** −91.2	**Po** −186	**At** −270	**Rn** >0

*It is somewhat awkward to speak of larger and smaller with the term *electron affinity*. A strong tendency to gain an electron, which implies a high "affinity" for an electron, as with F and Cl, is reflected through a *low* value of *EA*—a large *negative* value.

tend to become less negative in progressing toward the bottom of a group, with the notable exception of the second-period members of groups 15, 16, and 17 (namely, N, O, and F). It is likely that for these small atoms, an incoming electron encounters strong repulsive forces from other electrons in the atom and is thereby not as tightly bound as we might otherwise expect.

Some atoms have no tendency to gain an electron. This is the case with the noble gases, where an added electron would have to enter the empty s orbital of the next electronic shell. Other cases include the groups 2 and 12 elements, where the electron would have to enter the p subshell of the valence shell and a few other elements, such as Mn, where the electron would have to enter either the p subshell of the valence shell or a half-filled $3d$ subshell.

In considering the gain of a second electron by a nonmetal atom, we encounter positive electron affinities. Here the electron to be added is approaching not a neutral atom, but a negative ion. There is a strong repulsive force between the electron and the ion, and the energy of the system increases. Thus, for an element like oxygen, the first electron affinity is negative and the second is positive.

$$O(g) + e^- \longrightarrow O^-(g) \qquad EA_1 = -141.0 \text{ kJ/mol}$$
$$O^-(g) + e^- \longrightarrow O^{2-}(g) \qquad EA_2 = +744 \text{ kJ/mol}$$

The high positive value of EA_2 makes the formation of *gaseous* O^{2-} seem very unlikely. The ion O^{2-} can exist, however, in ionic compounds, such as $MgO(s)$, where formation of the ion is accompanied by other energetically favorable processes.

9-5   CONCEPT ASSESSMENT

On the blank periodic table in the margin locate the group expected to have:

(a) the most negative electron affinities in each period
(b) the least negative electron affinities in each period
(c) all positive electron affinities in each period
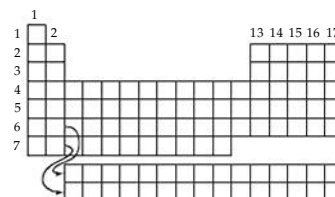
9-6   Magnetic Properties

An important property related to the electron configurations of atoms and ions is their behavior in a magnetic field. A spinning electron is an electric charge in motion. It induces a magnetic field (recall the discussion on page 334). In a **diamagnetic** atom or ion, all electrons are paired and the individual magnetic effects cancel out. A diamagnetic species is weakly repelled by a magnetic field. A **paramagnetic** atom or ion has unpaired electrons, and the individual magnetic effects do not cancel out. The unpaired electrons possess a magnetic moment that causes the atom or ion to be attracted to an external magnetic field. The more unpaired electrons present, the stronger is this attraction.
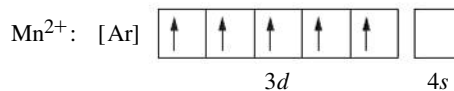
Manganese has a paramagnetism corresponding to five unpaired electrons, which is consistent with the electron configuration

Mn: [Ar] ↑ ↑ ↑ ↑ ↑   ↑↓
              $3d$ $4s$
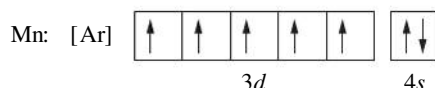
KEEP IN MIND

that it was the effect of the magnetic moments associated with the two different possibilities for an electron spin quantum number (equal in magnitude and opposite in sign) that allowed Stern and Gerlach to detect the presence of electron spin by using a magnetic field.

When a manganese atom loses two electrons, it becomes the ion Mn^{2+}, which is paramagnetic, and the strength of its paramagnetism corresponds to five unpaired electrons.

$$Mn^{2+}: \quad [Ar] \quad \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{}$$
$$3d \qquad\qquad\qquad 4s$$

When a third electron is lost to produce Mn^{3+}, the ion has a paramagnetism corresponding to four unpaired electrons. The third electron lost is one of the unpaired $3d$ electrons.

$$Mn^{3+}: \quad [Ar] \quad \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{}\ \boxed{}$$
$$3d \qquad\qquad\qquad 4s$$
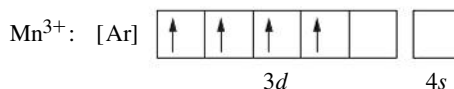
EXAMPLE 9-4   Determining the Magnetic Properties of an Atom or Ion

Which of the following would you expect to be diamagnetic and which paramagnetic?

    (a) Na atom   **(b)** Mg atom   **(c)** Cl^- ion   **(d)** Ag atom

Analyze

To determine whether or not an atom or ion is paramagnetic, we need to determine the electronic configuration of the species.

Solve

    (a) Paramagnetic. The Na atom has a single $3s$ electron outside the Ne core. This electron is unpaired.

    (b) Diamagnetic. The Mg atom has *two* $3s$ electrons outside the Ne core. They must be paired, as are all the other electrons in the Ne core.

    (c) Diamagnetic. Cl^- is isoelectronic with Ar, and Ar has all electrons paired ($1s^2 2s^2 2p^6 3s^2 3p^6$).

    (d) Paramagnetic. We do not need to work out the exact electron configuration of Ag. Because the atom has 47 electrons—an odd number—at least one of the electrons must be unpaired (recall the Stern–Gerlach experiment, page 334).

Assess

We see that a quick method of determining the magnetic properties of an atom or an ion is to use that atomic number and add or subtract for anions and cations. If the resultant number is odd, then the species is paramagnetic. However, if the number is even, the species may or may not be diamagnetic, depending on the electronic configuration—for example, consider Ti.

PRACTICE EXAMPLE A: Which of the following are paramagnetic and which are diamagnetic: Zn, Cl, K^+, O^{2-}, and Al?

PRACTICE EXAMPLE B: Which has the greater number of unpaired electrons, Cr^{2+} or Cr^{3+}? Explain.

🔍   **9-6**   **CONCEPT ASSESSMENT**

On the blank periodic table in the margin locate the following:

(a) The period 4 transition element having a cation in the +3 oxidation state that is diamagnetic

(b) The period 5 element existing in the −2 oxidation state as an anion that is diamagnetic

(c) The period 4 transition element having a 2+ cation that is paramagnetic and has a half-filled d subshell

9-7   Periodic Properties of the Elements

As we noted at the beginning of the chapter, we can use the periodic law and the periodic table to predict some of the atomic, physical, and chemical properties of elements and compounds.
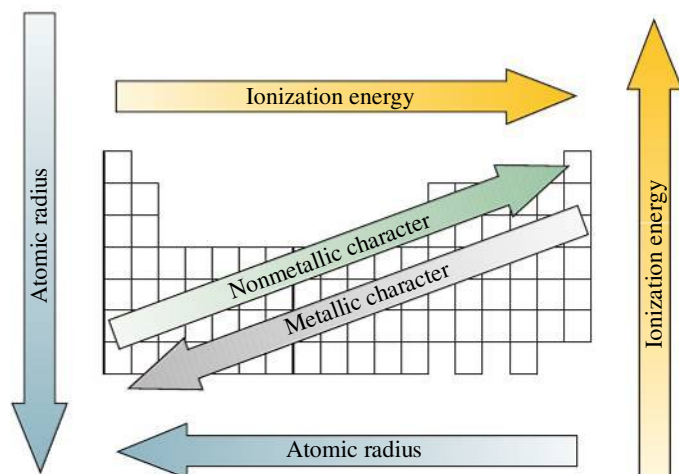
Atomic Properties

In this chapter we have learned how some atomic properties—atomic radius and ionization energy—vary within groups and periods of elements. We summarize these trends in relation to the periodic table in Figure 9-12. Trends are generally easy to apply within a group: The atomic radius of Sr is greater than that of Mg; both elements are in group 2. Usually, there is no difficulty in applying trends within a period either: The first ionization energy of P is greater than that of Mg; both elements are in the third period. However, comparing elements that are not within the same group or period can be difficult. The atomic radius of Sr is greater than that of P. Sr is farther down in its group of the periodic table and much farther to the left in its period than is P. Each of these directions is that of increasing atomic radius. We cannot, however, easily predict whether Mg or I has the larger atomic radius. The position of Mg to the left in its period suggests that Mg should have the larger radius, but the position of I toward the bottom of its group argues for I. Despite this limitation, you should find Figure 9-12 helpful in most cases.

Variation of Physical Properties Within a Group Table 9.5 lists some properties of three of the halogens (group 17). The table has two blank spaces for bromine. We fill in these blanks in Example 9-5 by making an assumption that works often enough to make it useful:

> The value of a property often changes uniformly from the top to the bottom of a group of elements in the periodic table.

TABLE 9.5   Some Properties of Three Halogen (Group 17) Elements

	Atomic Number	Atomic Mass, u	Molecular Form	Melting Point, K	Boiling Point, K
Cl	17	35.45	Cl_2	172	239
Br	35	79.90	Br_2	?	?
I	53	126.90	I_2	387	458

◀ FIGURE 9-12
Atomic properties and the periodic table—a summary
Atomic radius refers to metallic radius for metals and covalent radius for nonmetals. Ionization energies refer to first ionization energy. Metallic character relates generally to the ability to lose electrons, and nonmetallic character to the ability to gain electrons.

EXAMPLE 9-5   Using the Periodic Table to Estimate Physical Properties

Use data from Table 9.5 to estimate the boiling point of bromine.

Analyze

Remember that boiling points increase going down a group. As an initial guess we can consider the average between two elements.

Solve

The atomic number of bromine (35) is between the atomic numbers of chlorine (17) and iodine (53). Its atomic mass (79.90 u) is also intermediate to those of chlorine and iodine. (The average of the atomic masses of Cl and I is 81.18 u.) It is reasonable to expect that the boiling point of liquid bromine might also be intermediate to the boiling points of chlorine and iodine.

$$\text{bp Br}_2 \approx \frac{239 \text{ K } + \text{ } 458 \text{ K}}{2} = 349 \text{ K}$$

Assess

The observed boiling point is 332 K, which is close to the calculated result. A better estimate of the boiling point could possibly be made by plotting the known boiling points as a function of atomic mass, and then fitting the data.

PRACTICE EXAMPLE A: Estimate the melting point of bromine.

PRACTICE EXAMPLE B: Estimate the boiling point of astatine, At.

▲ FIGURE 9-13
Three halogen elements
Chlorine is a yellow-green gas.
Bromine is a dark red liquid.
Iodine is a grayish black solid.

**TABLE 9.6   Melting Points of Two Series of Compounds**

	Molecular Mass, u	Melting Point, °C
CF_4	88.0	−183.7
CCl_4	153.8	−22.9
CBr_4	331.6	90.1
CI_4	519.6	171
HF	20.0	−83.6
HCl	36.5	−114.2
HBr	80.9	−86.8
HI	127.9	−50.8

First, let us make some predictions about fluorine, the halogen not listed in Table 9.5. Its closest neighbor in group 17 is chlorine, which has a boiling point of 239 K (−34 °C); chlorine is a *gas* at room temperature (about 298 K). The other halogens are *liquid* bromine and *solid* iodine (Fig. 9-13). We would expect fluorine to have a lower melting point (mp) and lower boiling point (bp) than chlorine and also to be a gas at room temperature. (Observed values for F_2: mp = 53 K; bp = 85 K.)

The generalization that a property varies uniformly within a group of the periodic table can work for compounds as well as for elements. Table 9.6 lists the melting points of two sets of compounds, binary carbon–halogen compounds and the *hydrogen halides*, HX (where X = F, Cl, Br, or I). We see that the melting points increase fairly uniformly with increasing molecular mass for the carbon–halogen compounds. This trend between melting point (and boiling point) and molecular mass can be explained in terms of intermolecular forces, as we will see in Chapter 12. Based on the melting points of HCl, HBr, and HI, the melting point of HF should be about −145 °C, but the observed value is −83.6 °C. Some factor other than molecular mass must be involved here. In Chapter 12, we will find that in HF there is a special intermolecular force of attraction that is missing or unimportant in the other compounds in Table 9.6.

Variation of Physical Properties Across a Period   A few properties vary regularly across a period. The ability to conduct heat and electricity are two that do. Thus, among the third-period elements, the metals Na, Mg, and Al have good thermal and electrical conductivities. The metalloid Si is only a fair conductor of heat and electricity, while the nonmetals P, S, Cl, and Ar are poor conductors.

In some cases, the trend in a property reverses direction in the period (similar to the trend in melting points of the hydrogen halides reversing direction
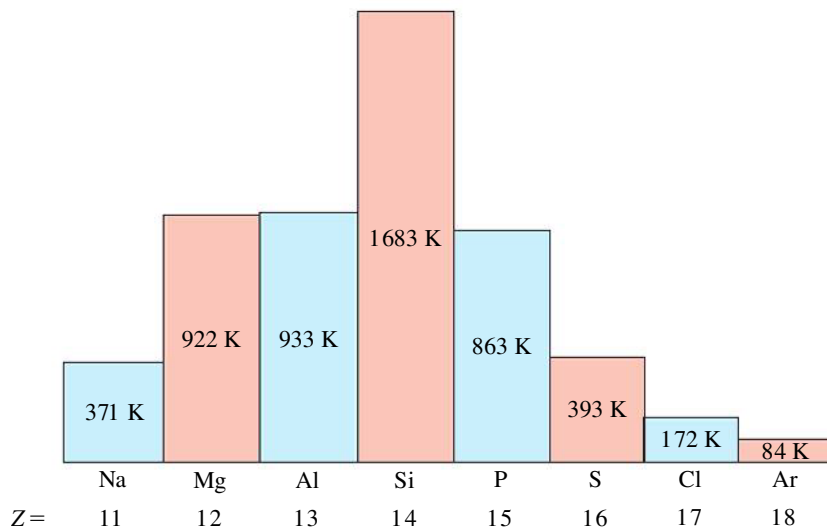
◄ FIGURE 9-14
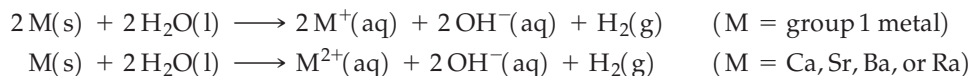**Melting points of the third-period elements**
Sometimes the trend in a property reverses direction within a period, as illustrated by this bar graph.

within a group). Consider, for example, the melting points of the third-period elements shown in a bar graph in Figure 9-14. Melting involves destruction of the orderly arrangement of the atoms or molecules in a crystalline solid. The amount of thermal energy needed for melting to occur, and hence the melting-point temperature, depends on the strength of the attractive forces between the atoms or molecules in the solid. For the metals Na, Mg, and Al, these forces are *metallic bonds*, which, roughly speaking, become stronger as the number of electrons available to participate in the bonding increases. Sodium, therefore, has the lowest melting point (371 K) of the third-period metals. With silicon, the forces between atoms are strong *covalent bonds* extending throughout the crystalline solid. Silicon has the highest melting point (1683 K) of the third-period elements. Phosphorus, sulfur, and chlorine exist as discrete molecules (P_4, S_8, and Cl_2). The bonds between atoms within molecules are strong, but *intermolecular forces*, the attractive forces between molecules, become progressively weaker across the period, and the melting points decrease. Argon atoms do not form molecules, and the forces between Ar atoms in solid argon are especially weak. Argon's melting point is the lowest for the entire period (84 K). The property of hardness also depends on forces between atoms and molecules in a solid. So the hardness of the solid third-period elements varies in much the same way as their melting points. Thus, on a 10-point scale in which solids are rated according to their abilities to scratch or abrade one another, sodium has a hardness of about 0.5; magnesium, 2; aluminum, 3; silicon, 7; and phosphorus and sulfur 1 to 2. Silicon has the greatest hardness.

◄ When evaluating trends, it is often useful to sketch a graph showing the variation of the property.

◄ Metallic bonds are described in Section 11-7, covalent bonding in substances like silicon is discussed in Section 12-7, and the topic of intermolecular forces is examined throughout Chapter 12.

Reducing Abilities of Group 1 and 2 Metals   We learned in Chapter 5 that a reducing agent makes possible a reduction half-reaction. The reducing agent itself, by losing electrons, is oxidized. In the following reactions, M, a group 1 or 2 metal, is the reducing agent and H_2O is the substance that is reduced.

$$2\,M(s) + 2\,H_2O(l) \longrightarrow 2\,M^+(aq) + 2\,OH^-(aq) + H_2(g) \qquad (M = \text{group 1 metal})$$
$$M(s) + 2\,H_2O(l) \longrightarrow M^{2+}(aq) + 2\,OH^-(aq) + H_2(g) \qquad (M = \text{Ca, Sr, Ba, or Ra})$$

At first guess, we might think that the lower the energy requirement for extracting electrons—the lower the ionization energy—the better the metal is as a reducing agent and the more vigorous its reaction with water. Potassium, for instance, has a lower ionization energy ($I_1 = 419\,\text{kJ/mol}$) than does the next member of the fourth period, calcium ($I_1 = 590; I_2 = 1145\,\text{kJ/mol}$). Our expectation is that potassium should react more vigorously with water than

(a)

(b)

▶ FIGURE 9-15
A comparison of the reactions of potassium and calcium with water
(a) Potassium, a group 1 metal, reacts so rapidly that the hydrogen evolved bursts into flame. Notice that the metal is less dense than water.
(b) Calcium, a group 2 metal, reacts more slowly than does potassium. Also, calcium is denser than water. The pink color of the acid–base indicator phenolphthalein signals the buildup of OH^- ions.
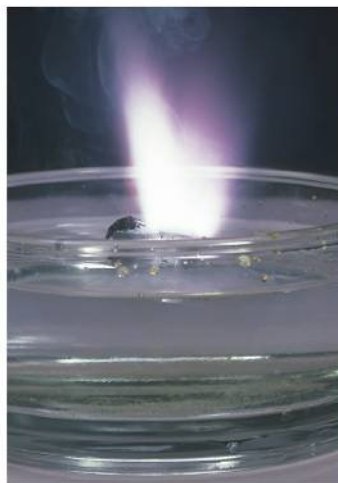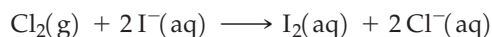
calcium does. This, indeed, is the case (Fig. 9-15). Mg and Be do not react with cold water as do the other alkaline earth metals. This might be explained in terms of the higher ionization energies for those two metals (Mg: $I_1 = 738$, $I_2 = 1451$ kJ/mol; Be: $I_1 = 900$, $I_2 = 1757$ kJ/mol).

Attributing the reactivity of these group 1 and 2 metals just to their ionization energies is an oversimplification, however. As long as the differences in ionization energies are very large, it is possible to make comparisons by considering only this factor. Where differences in ionization energies are smaller, though, other factors must also be considered, as we will see elsewhere in the text.
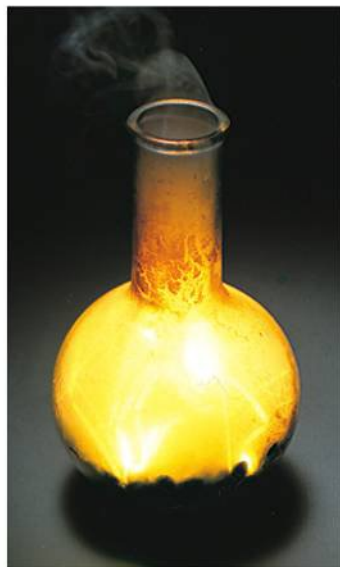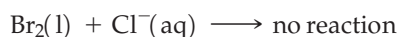
Oxidizing Abilities of the Halogen Elements (Group 17) An oxidizing agent gains the electrons that are lost in an oxidation half-reaction. The oxidizing agent, by gaining electrons, is itself reduced. Electron affinity is the atomic property introduced in this chapter that is related to the gain of electrons. We might expect an atom with a strong tendency to gain electrons (a large *negative* electron affinity) to take electrons away from atoms with low ionization energies—metals. In these terms, it is understandable that active metals form ionic compounds with active nonmetals. If M is a group 1 metal and X a group 17 nonmetal (halogen), this exchange of an electron leads to the formation of M^+ and X^- ions. In some cases, the reaction is especially vigorous (Fig. 9-16).

$$2\,M + X_2 \longrightarrow 2\,MX \qquad [e.g., 2\,Na(s) + Cl_2(g) \longrightarrow 2\,NaCl(s)]$$

Another interesting oxidation–reduction reaction involving the halogens is a *displacement reaction*. Two halogens, one in molecular form and the other in ionic form, exchange places, as in this reaction (Fig. 9-17).

$$Cl_2(g) + 2\,I^-(aq) \longrightarrow I_2(aq) + 2\,Cl^-(aq)$$

▲ FIGURE 9-16
Reaction of sodium metal and chlorine gas
The contents of the flask glow in this exothermic reaction between Na(s) and $Cl_2(g)$. The product is the ionic solid NaCl(s).

We might think of this reaction as involving a competition between Cl and I atoms for an extra electron that only the I atoms (as I^-) have initially. The Cl atoms win out because they have a more negative electron affinity. (This is an oversimplified explanation, however, because strictly speaking electron affinities apply only to the behavior of isolated gaseous atoms and not to atoms in molecules or ions in solution.) By similar reasoning, can you see why no reaction occurs for this combination?

$$Br_2(l) + Cl^-(aq) \longrightarrow \text{no reaction}$$

Such predictions as those in the preceding paragraph work well for the halogens Cl_2, Br_2, and I_2, but not for F_2. We cannot account for the observed fact that F_2 is the strongest oxidizing agent among all chemical substances, just by considering electron affinities.

Acid–Base Nature of Element Oxides.
Some metal oxides, such as Li_2O, react with water to produce the metal hydroxide.

$$\underset{\text{A basic oxide}}{Li_2O(s)} + H_2O(l) \longrightarrow \underset{\text{Lithium hydroxide}}{2\,Li^+(aq) + 2\,OH^-(aq)}$$
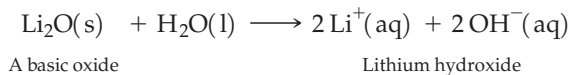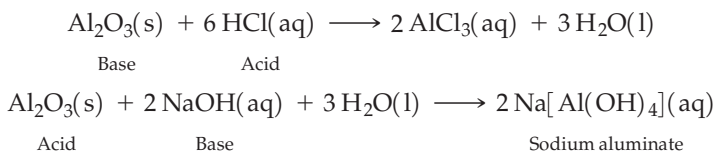
These metal oxides are called *basic oxides* or *base anhydrides*. The term **anhydride** means "without water." A "base without water" becomes a base when the water is added. Thus, the base anhydride Li_2O becomes the base LiOH, and BaO becomes $Ba(OH)_2$ after reaction with water. Moving from top to bottom down a group, the elements become more metallic, and their oxides become more basic.

Some nonmetal oxides react with water to produce an acidic solution. These are *acidic oxides* or *acid anhydrides*. $SO_2(g)$ reacts with water to produce H_2SO_3, a weak acid.

$$\underset{\text{An acidic oxide}}{SO_2(g)} + H_2O(l) \longrightarrow \underset{\text{Sulfurous acid}}{H_2SO_3(aq)}$$
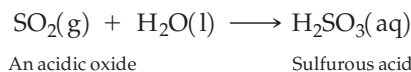
Now let us examine the acid–base properties of the oxides of the third-period elements. We expect the metal oxides at the left of the period to be basic and the nonmetal oxides at the right to be acidic, but where and how does the changeover occur? Na_2O and MgO yield basic solutions in water. Cl_2O, SO_2, and P_4O_{10} produce acidic solutions. SiO_2 (quartz) does not dissolve in water. However, it does dissolve slightly in strongly basic solutions to produce silicates (similar to the carbonates formed by CO_2 in basic solutions). For this reason, we consider SiO_2 to be an acidic oxide.

Aluminum, a good conductor of heat and electricity, is clearly metallic in its physical properties. Al_2O_3, however, can act as either an acidic or a basic oxide. Oxides with this ability are called **amphoteric** (from the Greek word *amphos*, meaning "both"). Al_2O_3 is insoluble in water but exhibits its amphoterism by reacting with both acidic and basic solutions.

$$\underset{\text{Base}}{Al_2O_3(s)} + \underset{\text{Acid}}{6\,HCl(aq)} \longrightarrow 2\,AlCl_3(aq) + 3\,H_2O(l)$$

$$\underset{\text{Acid}}{Al_2O_3(s)} + \underset{\text{Base}}{2\,NaOH(aq)} + 3\,H_2O(l) \longrightarrow \underset{\text{Sodium aluminate}}{2\,Na[Al(OH)_4](aq)}$$

The amphoterism of Al_2O_3 signifies the point at which a changeover from basic to acidic oxides occurs in the third period of elements. Figure 9-18 summarizes the acid–base properties of the oxides of the main-group elements.

(a)   (b)

▲ FIGURE 9-17
Displacement of $I^-(aq)$ by $Cl_2(g)$
(a) $Cl_2(g)$ is bubbled through colorless, dilute $I^-(aq)$. (b) The I_2 produced is extracted into $CCl_4(l)$, in which it is much more soluble (purple layer).

1	2	13	14	15	16	17
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I
Cs	Ba	Tl	Pb	Bi	Po	At

▲ FIGURE 9-18
**Acidic, basic, and amphoteric oxides of the *s*- and *p*-block elements**
The acidic oxides are pink, the basic oxides are blue, and the amphoteric oxides are tan.

🔍 **9-7   CONCEPT ASSESSMENT**

On the blank periodic table in the margin locate the following:

(a) The group 13 element that is expected to form the most basic oxide

(b) The group 15 element that is expected to form the most acidic oxide

(c) The period 5 element that is expected to form the most basic oxide

(d) The period 5 element that is expected to form the most acidic oxide

(e) The period 3 element that exhibits amphoteric behavior
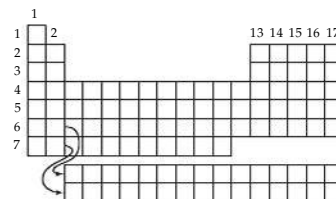
Summary

9-1 Classifying the Elements: The Periodic Law and the Periodic Table—The experimental basis of the periodic table of the elements is the **periodic law**: Certain properties recur periodically when the elements are arranged by increasing atomic number. The theoretical basis is that the properties of an element are related to the electron configuration of its atoms, and elements in the same group of the periodic table have similar electron configurations.

9-2 Metals and Nonmetals and Their Ions— The three classes of elements of the periodic table are the *nonmetals, metals,* and *metalloids*. **Metalloids** have some properties characteristic of metals and some characteristics of nonmetals. The nonmetals are further divided into the noble gases and the remainder of the main-group nonmetals, while the metals include the main-group metals and transition elements.

9-3 Sizes of Atoms and Ions—Types of atomic radii include **covalent radii**, **metallic radii**, and **van der Waals radii** (Fig. 9-3). In general, atomic radii decrease across a period and increase down a group of the periodic table (Figs. 9-4 and 9-9), mirroring the variation in **effective nuclear charge**, Z_{eff}, (equation 9.3) across a period and down a group. The **ionic radii** of positive ions are smaller than the neutral atom, whereas negative ions are larger than the parent atom (Figs. 9-7 and 9-8). Ionic radii exhibit adherence to the periodic law similar to that of atomic radii. When atoms or ions have the same number of electrons, they are said to be **isoelectronic**. When the radii of isoelectronic species are compared, the more negative the charge, the larger the radius of the ion or atom.

9-4 Ionization Energy—A study of **ionization energies**, *I*, shows that the periodic relationship observed is governed by the variation of Z_{eff}—that is, the ionization energy decreases down a group and increases across a period (Fig. 9-10, Tables 9.3 and 9.4).

9-5 Electron Affinity—**Electron affinity**, EA, is the energy change when an electron is added to a gaseous atom. Electron affinity does not exhibit clear-cut trends (Fig. 9-11).

9-6 Magnetic Properties—The magnetic properties of an atom or ion stem from the presence or absence of unpaired electrons. **Paramagnetic** atoms and ions have one or more unpaired electrons. In **diamagnetic** atoms and ions, all electrons are paired.

9-7 Periodic Properties of the Elements—The metallic, nonmetallic, and metalloid characteristics of atoms can be related to a set of atomic properties. In general, large atomic radii and low ionization energies are associated with metals; small atomic radii, high ionization energies, and large negative electron affinities are associated with nonmetals. Metalloids occur first in the third row (at Si) where the break between acid–base properties becomes less defined. Metals usually form oxides that give basic solutions, whereas nonmetal oxides form acidic solutions. The nonmetal oxide is called an **anhydride** since the addition of water gives an acid. At the break between clearly basic and acidic properties, some metals and metalloids exhibit **amphoteric** behavior because they react with both acids and bases (Fig. 9-18).

Integrative Example

When the ionization energies of a series of isoelectronic atoms and ions are compared, an interesting relationship is observed for some of them. In particular, if the square root of the ionization energy (in $kJ\,mol^{-1}$) for the series $Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}$, and F^{6+} is plotted against the atomic number (Z) of the species, a linear relationship is obtained. The corresponding graph for the series $Na, Mg^+, Al^{2+}, Si^{3+}, P^{4+}, S^{5+}$, and Cl^{6+}, is also linear. The graph is shown on page 387.

The equations for the two lines joining the points are

Second-row elements:	$\sqrt{I} = 18.4Z - 32.0$	**(9.7)**
Third-row elements:	$\sqrt{I} = 13.5Z - 124$	**(9.8)**

Explain the origin of these relationships and the differences in the numerical coefficients.

Analyze

We first notice that the electron configuration of the second-row atoms and ions is $1s^2 2s^1$, that is, a single electron ($2s^1$) beyond the helium core ($1s^2$). Similarly, for the third-row atoms and ions the electron configuration is $1s^2 2s^2 2p^6 3s^1$, that is, a single electron ($3s^1$) beyond the neon core ($1s^2 2s^2 2p^6$).
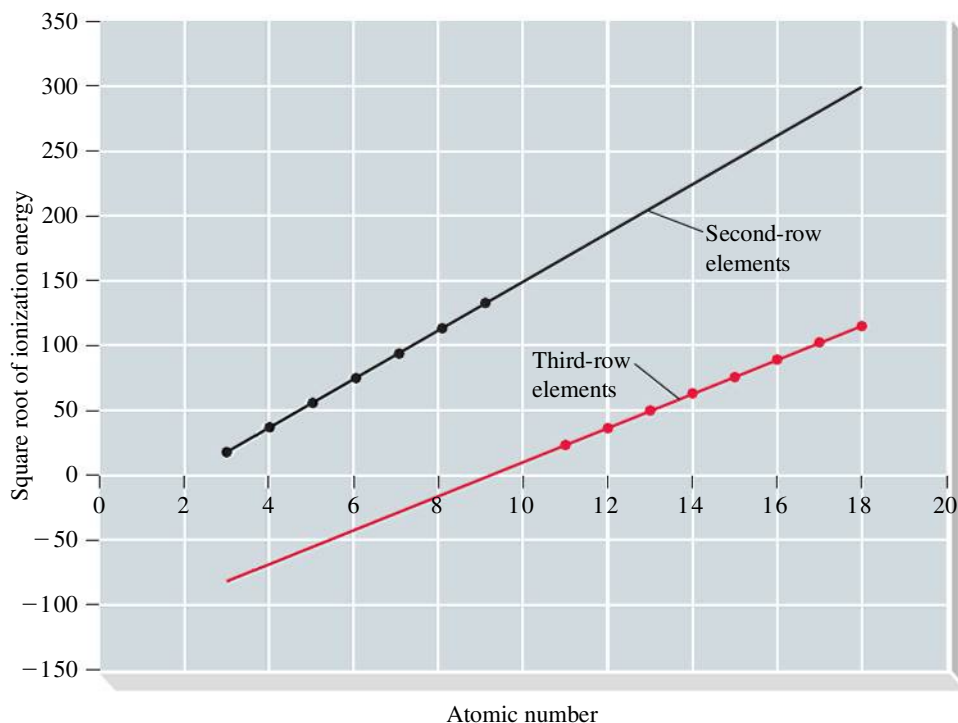
◄ Variation of $\sqrt{I}$ with atomic number for the second-row elements (black line) and the third-row elements (red line).

In both series of atoms and ions, the inner-core electrons screen the single valence-shell electron from the nucleus. These species are all reminiscent of the Bohr atom so that as an approximation we can use the expression for the energy levels for hydrogen-like atoms or hydrogen-like ions (equation 8.9). Specifically, we should be able to use equation (8.9) to derive equations for the energy required to remove the electron from the valence shells of a hydrogen-like species, that is, the ionization energy (I). Once we have these equations, we can compare them with the equations for the two straight-line graphs.

Solve

Equation (8.9), with the substitution $Z = Z_{eff}$, produces equation (9.4); and with the further substitution $R_H = 2.178 \times 10^{-18}$ J, we have

$$E_n = -2.178 \times 10^{-18}\left(\frac{Z_{eff}^2}{n^2}\right) \text{J}$$

E_n in equations (8.9) and (9.4) has the unit J atom^{-1}, which must be converted to kJ mol^{-1}—the unit of I in the two straight-line equations given to us.

$$E_n = -2.178 \times 10^{-18}\frac{\text{J}}{\text{atom}} \times 6.022 \times 10^{23}\frac{\text{atom}}{\text{mol}} \times \frac{Z_{eff}^2}{n^2}$$

$$= -1.3116 \times 10^6 \frac{Z_{eff}^2}{n^2}\text{J mol}^{-1} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

The energy required to remove an electron from an orbital with principal quantum number n in a hydrogen-like species—the ionization energy—is the *negative* of that shown above, that is,

$$I = -E_n = 1311.6 \times \frac{Z_{eff}^2}{n^2}\text{kJ mol}^{-1} \qquad \textbf{(9.9)}$$

Equation (9.9) shows that the ionization energy (I) is a linear function of $(Z_{eff})^2$ and the straight-line graphs (equations 9.7 and 9.8) show that $\sqrt{I}$ is a linear function of Z. We are on the right track. However, we must now take into account that we are considering one-electron systems with a nucleus shielded by a closed shell.

First consider the second-row series ($Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}$, and F^{6+}), all members of which have the electron configuration $1s^22s^1$. If we assume that the closed shell $1s^2$ perfectly screens the outer electron $2s^1$, the value of Z_{eff} for this series will be $Z - 2$. Thus we

should substitute $Z_{eff} = Z - 2$ into equation (9.9), and also $n = 2$ since ionization occurs from the $2s$ orbital, to obtain

$$I = 1311.6 \times \frac{(Z-2)^2}{n^2} = 1311.6 \times \frac{(Z-2)^2}{2^2}$$

Taking the square root of both sides and clearing the fraction gives

$$\sqrt{I} = 36.22 \times \left(\frac{Z-2}{2}\right) = 18.11Z - 36.22 \qquad \textbf{(9.10)}$$

Let us now look at the third-row series. In this case the configuration of the isoelectronic series is $1s^2 2s^2 2p^6 3s^1$ so that if we assume perfect screening of the $3s^1$ electron by the ten inner-core electrons we have

$$Z_{eff} = Z - 10$$

Proceeding as before and remembering that ionization occurs from the $n = 3$ level, we obtain

$$I = 1311.6 \times \frac{(Z-10)^2}{n^2} = 1311.6 \times \frac{(Z-10)^2}{3^2}$$

and

$$\sqrt{I} = 36.22 \times \left(\frac{Z-10}{3}\right) = 12.07Z - 120.7 \qquad \textbf{(9.11)}$$

Assess

In comparing equations (9.10) and (9.11), we find that the difference in the slope (coefficient for Z) is due to the difference in the principal quantum number of the orbital from which the ionization occurs. The difference in the intercepts is due both to the principal quantum number from which the ionization occurs and to the number of electrons screening the valence-shell electron.

Equation (9.10) for the second-row elements is in remarkable agreement with the empirically observed equation (9.7) at the beginning of this example, especially considering our use of the modified Bohr model.

Although the general form of equation (9.11) is correct for the third-row series, the agreement between the numerical constants is not as good. This is to be expected because we have assumed perfect screening by the core electrons, which completely ignores the different characteristics of the electrons composing the inner core. The intricate, correlated motions of the electrons in the core leads to a complicated combination of screening and penetration that cannot be accounted for with our simple model.

PRACTICE EXAMPLE A: Francium ($Z = 87$) is an extremely rare radioactive element formed when actinium ($Z = 89$) undergoes alphaparticle emission. Francium occurs in natural uranium minerals, but estimates are that little more than 15 g of francium exists in the top 1 km of Earth's crust. Few of francium's properties have been measured, but some can be inferred from its position in the periodic table. Estimate the melting point, density, and atomic (metallic) radius of francium.

PRACTICE EXAMPLE B: Discuss the likelihood that element 168, should it ever be synthesized in sufficient quantity, would be a "noble liquid" at 298 K and 1 bar. Some data that might be useful appear in the table below. Could element 168 be a "noble solid" at 298 K and 1 bar? Use $spdf$ notation to show the electron configuration you would expect for element 168.

Element	Atomic Mass, u	mp, K	bp, K
Argon	39.948	83.95	87.45
Helium	4.0026		4.25
Krypton	83.80	116.5	120.9
Neon	20.179	24.48	27.3
Radon	222	202	211.4
Xenon	131.29	161.3	166.1