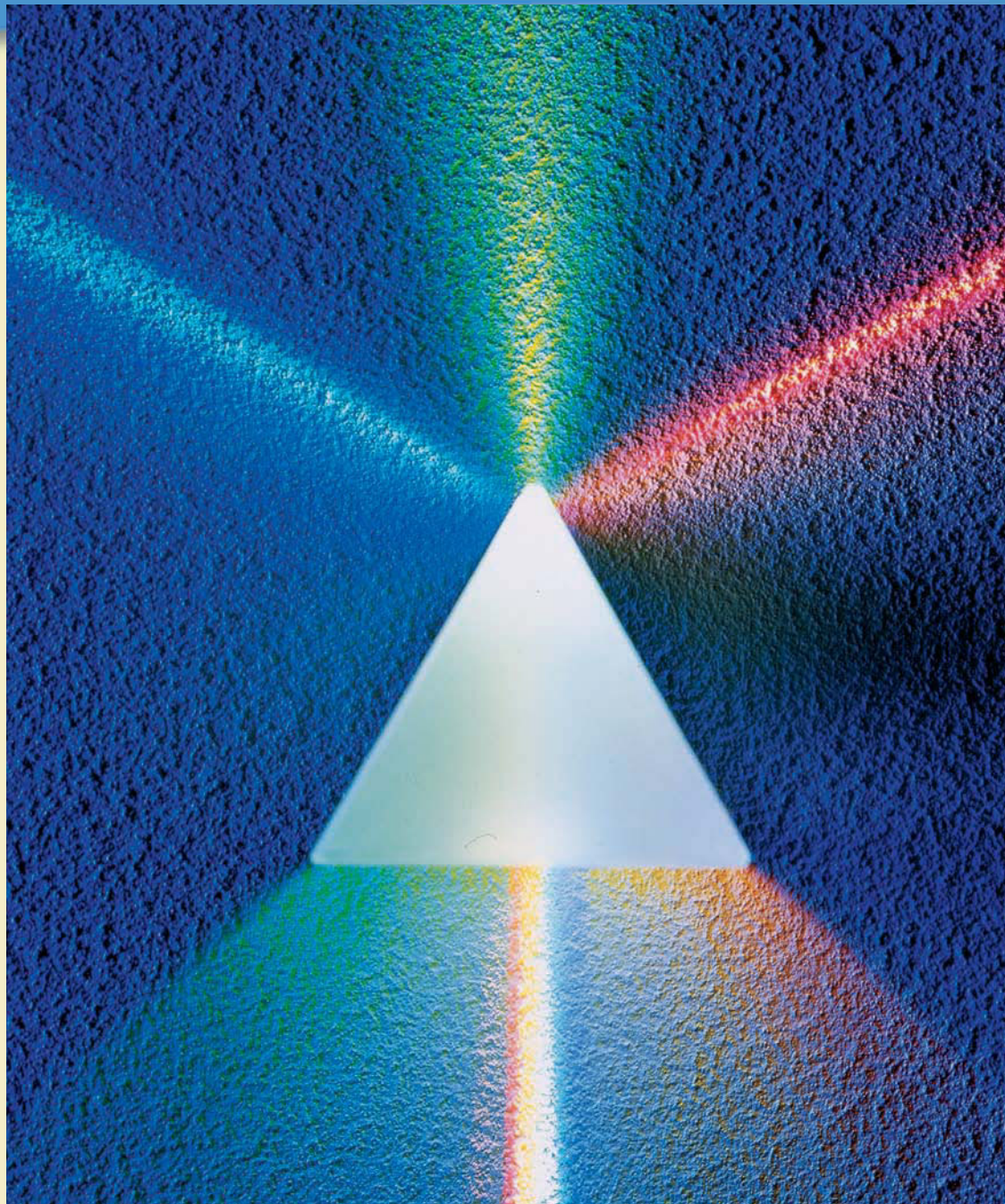


7 Atomic Structure and Periodicity

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Light refracted through a prism.



Wavelength λ and frequency ν are inversely related.

c = speed of light
= 2.9979×10^8 m/s

In the past 200 years, a great deal of experimental evidence has accumulated to support the atomic model. This theory has proved to be both extremely useful and physically reasonable. When atoms were first suggested by the Greek philosophers Democritus and Leucippus about 400 B.C., the concept was based mostly on intuition. In fact, for the following 20 centuries, no convincing experimental evidence was available to support the existence of atoms. The first real scientific data were gathered by Lavoisier and others from quantitative measurements of chemical reactions. The results of these stoichiometric experiments led John Dalton to propose the first systematic atomic theory. Dalton's theory, although crude, has stood the test of time extremely well.

Once we came to "believe in" atoms, it was logical to ask: What is the nature of an atom? Does an atom have parts, and if so, what are they? In Chapter 2 we considered some of the experiments most important for shedding light on the nature of the atom. Now we will see how the atomic theory has evolved to its present state.

One of the most striking things about the chemistry of the elements is the periodic repetition of properties. There are several groups of elements that show great similarities in chemical behavior. As we saw in Chapter 2, these similarities led to the development of the periodic table of the elements. In this chapter we will see that the modern theory of atomic structure accounts for periodicity in terms of the electron arrangements in atoms.

However, before we examine atomic structure, we must consider the revolution that took place in physics in the first 30 years of the twentieth century. During that time, experiments were carried out, the results of which could not be explained by the theories of classical physics developed by Isaac Newton and many others who followed him. A radical new theory called *quantum mechanics* was developed to account for the behavior of light and atoms. This "new physics" provides many surprises for humans who are used to the macroscopic world, but it seems to account flawlessly (within the bounds of necessary approximations) for the behavior of matter.

As the first step in our exploration of this revolution in science we will consider the properties of light, more properly called *electromagnetic radiation*.

7.1 Electromagnetic Radiation

One of the ways that energy travels through space is by **electromagnetic radiation**. The light from the sun, the energy used to cook food in a microwave oven, the X rays used by dentists, and the radiant heat from a fireplace are all examples of electromagnetic radiation. Although these forms of radiant energy seem quite different, they all exhibit the same type of wavelike behavior and travel at the speed of light in a vacuum.

Waves have three primary characteristics: wavelength, frequency, and speed. **Wavelength** (symbolized by the lowercase Greek letter lambda, λ) is the *distance between two consecutive peaks or troughs in a wave*, as shown in Fig. 7.1. The **frequency** (symbolized by the lowercase Greek letter nu, ν) is defined as the *number of waves (cycles) per second that pass a given point in space*. Since all types of electromagnetic radiation travel at the speed of light, short-wavelength radiation must have a high frequency. You can see this in Fig. 7.1, where three waves are shown traveling between two points at constant speed. Note that the wave with the shortest wavelength (λ_3) has the highest frequency and the wave with the longest wavelength (λ_1) has the lowest frequency. This implies an inverse relationship between wavelength and frequency, that is, $\lambda \propto 1/\nu$, or

$$\lambda\nu = c$$



Visualization: Electromagnetic Wave

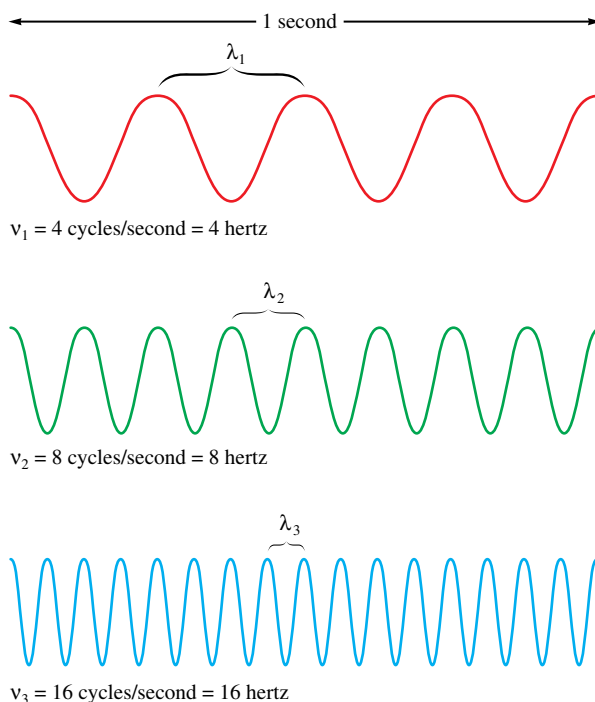


FIGURE 7.1

The nature of waves. Note that the radiation with the shortest wavelength has the highest frequency.



Although the waves associated with light are not obvious to the naked eye, ocean waves provide a familiar source of recreation.

where λ is the wavelength in meters, ν is the frequency in cycles per second, and c is the speed of light ($2.9979 \times 10^8 \text{ m/s}$). In the SI system, cycles is understood, and the unit per second becomes $1/\text{s}$, or s^{-1} , which is called the *hertz* (abbreviated Hz).

Electromagnetic radiation is classified as shown in Fig. 7.2. Radiation provides an important means of energy transfer. For example, the energy from the sun reaches the earth mainly in the form of visible and ultraviolet radiation, whereas the glowing coals of a fireplace transmit heat energy by infrared radiation. In a microwave oven the water molecules in food absorb microwave radiation, which increases their motions. This energy is then transferred to other types of molecules via collisions, causing an increase in the food's temperature. As we proceed in the study of chemistry, we will consider many of the classes of electromagnetic radiation and the ways in which they affect matter.

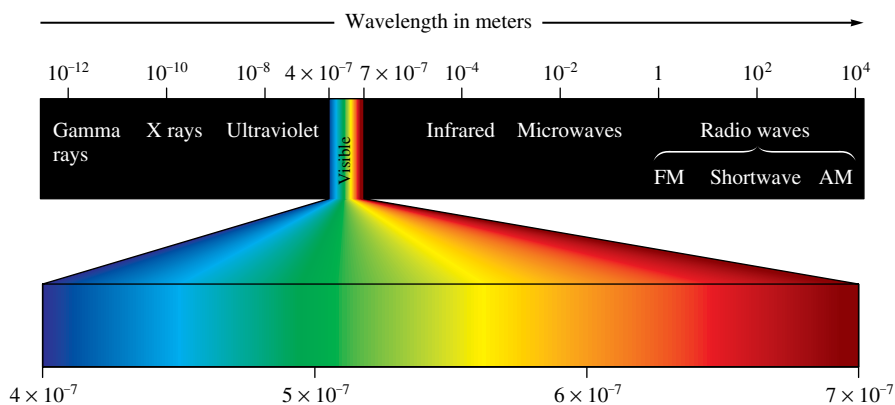


FIGURE 7.2

Classification of electromagnetic radiation.

Spectrum adapted by permission from C. W. Keenan, D. C. Kleinfelter, and J. H. Wood, *General College Chemistry*, 6th ed. (New York: Harper & Row, 1980).



CHEMICAL IMPACT

Flies That Dye

Mediterranean and Mexican fruit flies are formidable pests that have the potential to seriously damage several important fruit crops. Because of this, there have been several widely publicized sprayings of residential areas in southern California with the pesticide malathion to try to control fruit flies. Now there may be a better way to kill fruit flies—with a blend of two common dyes (red dye no. 28 and yellow dye no. 8) long used to color drugs and cosmetics. One of the most interesting things about this new pesticide is that it

is activated by light. After an insect eats the blend of dyes, the molecules absorb light (through the insect's transparent body), which causes them to generate oxidizing agents that attack the proteins and cell membranes in the bug's body. Death occurs within 12 hours.

The sunlight that turns on the dye's toxicity after the fly ingests it also degrades the dye in the environment, making it relatively safe. It appears likely that in the near future the fruit fly will "dye" with little harm to the environment.

Sample Exercise 7.1

Frequency of Electromagnetic Radiation



When a strontium salt is dissolved in methanol (with a little water) and ignited, it gives a brilliant red flame. The red color is produced by emission of light when electrons, excited by the energy of the burning methanol, fall back to their ground states.

The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $\text{Sr}(\text{NO}_3)_2$ and SrCO_3 are heated. (This can be easily demonstrated in the lab by dissolving one of these salts in methanol that contains a little water and igniting the mixture in an evaporating dish.) Calculate the frequency of red light of wavelength 6.50×10^2 nm.

Solution

We can convert wavelength to frequency using the equation

$$\lambda\nu = c \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

where $c = 2.9979 \times 10^8$ m/s. In this case $\lambda = 6.50 \times 10^2$ nm. Changing the wavelength to meters, we have

$$6.50 \times 10^2 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 6.50 \times 10^{-7} \text{ m}$$

and

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{6.50 \times 10^{-7} \text{ m}} = 4.61 \times 10^{14} \text{ s}^{-1} = 4.61 \times 10^{14} \text{ Hz}$$

See Exercises 7.31 and 7.32.

7.2 The Nature of Matter

It is probably fair to say that at the end of the nineteenth century, physicists were feeling rather smug. Theories could explain phenomena as diverse as the motions of the planets and the dispersion of visible light by a prism. Rumor has it that students were being discouraged from pursuing physics as a career because it was felt that all the major problems had been solved, or at least described in terms of the current physical theories.

At the end of the nineteenth century, the idea prevailed that matter and energy were distinct. Matter was thought to consist of particles, whereas energy in the form of light (electromagnetic radiation) was described as a wave. Particles were things that had mass and whose position in space could be specified. Waves were described as massless and delocalized; that is, their position in space could not be specified. It also was assumed that there was no intermingling of matter and light. Everything known before 1900 seemed to fit neatly into this view.



Visualization: Electrified Pickle



When alternating current at 110 volts is applied to a dill pickle, a glowing discharge occurs. The current flowing between the electrodes (forks), which is supported by the Na^+ and Cl^- ions present, apparently causes some sodium atoms to form in an excited state. When these atoms relax to the ground state, they emit visible light at 589 nm, producing the yellow glow reminiscent of sodium vapor lamps.

At the beginning of the twentieth century, however, certain experimental results suggested that this picture was incorrect. The first important advance came in 1900 from the German physicist Max Planck (1858–1947). Studying the radiation profiles emitted by solid bodies heated to incandescence, Planck found that the results could not be explained in terms of the physics of his day, which held that matter could absorb or emit any quantity of energy. Planck could account for these observations only by postulating that energy can be gained or lost only in *whole-number multiples* of the quantity $h\nu$, where h is a constant called **Planck's constant**, determined by experiment to have the value $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$. That is, the change in energy for a system ΔE can be represented by the equation

$$\Delta E = nh\nu$$

where n is an integer (1, 2, 3, . . .), h is Planck's constant, and ν is the frequency of the electromagnetic radiation absorbed or emitted.

Planck's result was a real surprise. It had always been assumed that the energy of matter was continuous, which meant that the transfer of any quantity of energy was possible. Now it seemed clear that energy is in fact **quantized** and can occur only in discrete units of size $h\nu$. Each of these small "packets" of energy is called a *quantum*. A system can transfer energy only in whole quanta. Thus energy seems to have particulate properties.

Energy can be gained or lost only in integer multiples of $h\nu$.

Planck's constant = $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$.

Sample Exercise 7.2

The Energy of a Photon

The blue color in fireworks is often achieved by heating copper(I) chloride (CuCl) to about 1200°C . Then the compound emits blue light having a wavelength of 450 nm. What is the increment of energy (the quantum) that is emitted at $4.50 \times 10^2 \text{ nm}$ by CuCl ?

Solution

The quantum of energy can be calculated from the equation

$$\Delta E = h\nu$$

The frequency ν for this case can be calculated as follows:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{4.50 \times 10^{-7} \text{ m}} = 6.66 \times 10^{14} \text{ s}^{-1}$$

So

$$\Delta E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(6.66 \times 10^{14} \text{ s}^{-1}) = 4.41 \times 10^{-19} \text{ J}$$

A sample of CuCl emitting light at 450 nm can lose energy only in increments of $4.41 \times 10^{-19} \text{ J}$, the size of the quantum in this case.

See Exercises 7.33 and 7.34.

The next important development in the knowledge of atomic structure came when Albert Einstein (see Fig. 7.3) proposed that electromagnetic radiation is itself quantized. Einstein suggested that electromagnetic radiation can be viewed as a stream of "particles" called **photons**. The energy of each photon is given by the expression

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

where h is Planck's constant, ν is the frequency of the radiation, and λ is the wavelength of the radiation.



Visualization: Photoelectric Effect

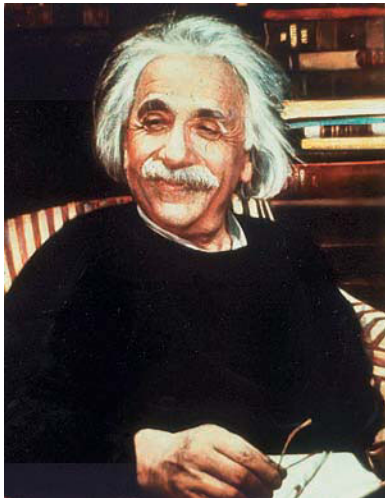


FIGURE 7.3

Albert Einstein (1879–1955) was born in Germany. Nothing in his early development suggested genius; even at the age of 9 he did not speak clearly, and his parents feared that he might be handicapped. When asked what profession Einstein should follow, his school principal replied, “It doesn’t matter; he’ll never make a success of anything.” When he was 10, Einstein entered the Luitpold Gymnasium (high school), which was typical of German schools of that time in being harshly disciplinarian. There he developed a deep suspicion of authority and a skepticism that encouraged him to question and doubt—valuable qualities in a scientist. In 1905, while a patent clerk in Switzerland, Einstein published a paper explaining the photoelectric effect via the quantum theory. For this revolutionary thinking he received a Nobel Prize in 1921. Highly regarded by this time, he worked in Germany until 1933, when Hitler’s persecution of the Jews forced him to come to the United States. He worked at the Institute for Advanced Studies in Princeton, New Jersey, until his death in 1955.

Einstein was undoubtedly the greatest physicist of our age. Even if someone else had derived the theory of relativity, his other work would have ensured his ranking as the second greatest physicist of his time. Our concepts of space and time were radically changed by ideas he first proposed when he was 26 years old. From then until the end of his life, he attempted unsuccessfully to find a single unifying theory that would explain all physical events.

The Photoelectric Effect

Einstein arrived at this conclusion through his analysis of the **photoelectric effect** (for which he later was awarded the Nobel Prize). The photoelectric effect refers to the phenomenon in which electrons are emitted from the surface of a metal when light strikes it. The following observations characterize the photoelectric effect.

1. Studies in which the frequency of the light is varied show that no electrons are emitted by a given metal below a specific threshold frequency ν_0 .
2. For light with frequency lower than the threshold frequency, no electrons are emitted regardless of the intensity of the light.
3. For light with frequency greater than the threshold frequency, the number of electrons emitted increases with the intensity of the light.
4. For light with frequency greater than the threshold frequency, the kinetic energy, of the emitted electrons increases linearly with the frequency of the light.

These observations can be explained by assuming that electromagnetic radiation is quantized (consists of photons), and that the threshold frequency represents the minimum energy required to remove the electron from the metal’s surface.

$$\text{Minimum energy required to remove an electron} = E_0 = h\nu_0$$

Because a photon with energy less than E_0 ($\nu < \nu_0$) cannot remove an electron, light with a frequency less than the threshold frequency produces no electrons. On the other hand, for light where $\nu > \nu_0$, the energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE):

$$\text{KE}_{\text{electron}} = \frac{1}{2}mv^2 = h\nu - h\nu_0$$

Mass of electron
Velocity of electron
Energy of incident photon
Energy required to remove electron from metal’s surface

Because in this picture the intensity of light is a measure of the number of photons present in a given part of the beam, a greater intensity means that more photons are available to release electrons (as long as $\nu > \nu_0$ for the radiation).

In a related development, Einstein derived the famous equation

$$E = mc^2$$

in his *special theory of relativity* published in 1905. The main significance of this equation is that *energy has mass*. This is more apparent if we rearrange the equation in the following form:

$$m = \frac{E}{c^2}$$

Mass
Energy
Speed of light



CHEMICAL IMPACT

Chemistry That Doesn't Leave You in the Dark

In the animal world, the ability to see at night provides predators with a distinct advantage over their prey. The same advantage can be gained by military forces and law enforcement agencies around the world through the use of recent advances in night vision technology.

All types of night vision equipment are electro-optical devices that amplify existing light. A lens collects light and focuses it on an image intensifier. The image intensifier is based on the photoelectric effect—materials that give off electrons when light is shined on them. Night vision intensifiers use semiconductor-based materials to produce large numbers of electrons for a given input of photons. The emitted electrons are then directed onto a screen covered with compounds that phosphoresce (glow when struck by electrons). While television tubes use various phosphors to produce color pictures, night vision devices use phosphors that appear green, because the human eye can distinguish more shades of green than any other color. The viewing screen shows an image that otherwise would be invisible to the naked eye during nighttime viewing.

Current night vision devices use gallium arsenide (GaAs)-based intensifiers that can amplify input light as much as 50,000 times. These devices are so sensitive they can use starlight to produce an image. It is also now possible to use light (infrared) that cannot be sensed with the human eye to create an image.

This technology, while developed originally for military and law enforcement applications, is now becoming available to the consumer. For example, Cadillac included night vision as an option on its cars for the year 2000. As night-imaging technology improves and costs become less prohibitive, a whole new world is opening up for the technophile—after the sun goes down.



A night vision photo of the midair refueling of a U.S. Air Force plane.

Note that the apparent mass of a photon depends on its wavelength. The mass of a photon at rest is thought to be zero, although we never observe it at rest.

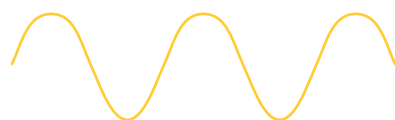
Using this form of the equation, we can calculate the mass associated with a given quantity of energy. For example, we can calculate the *apparent* mass of a photon. For electromagnetic radiation of wavelength λ , the energy of each photon is given by the expression

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

Then the apparent mass of a photon of light with wavelength λ is given by

$$m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{\lambda c}$$

Does a photon really have mass? The answer *appears to be* yes. In 1922 American physicist Arthur Compton (1892–1962) performed experiments involving collisions of X rays and electrons that showed that photons do exhibit the apparent mass calculated from the preceding equation. However, it is clear that photons do not have mass in the classical sense. A photon has mass only in a relativistic sense—it has no rest mass.



Light as a wave phenomenon



Light as a stream of photons

FIGURE 7.4

Electromagnetic radiation exhibits wave properties and particulate properties. The energy of each photon of the radiation is related to the wavelength and frequency by the equation $E_{\text{photon}} = h\nu = hc/\lambda$.

We can summarize the important conclusions from the work of Planck and Einstein as follows:

Energy is quantized. It can occur only in discrete units called quanta.

Electromagnetic radiation, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well. This phenomenon is sometimes referred to as the **dual nature of light** and is illustrated in Fig. 7.4.

Thus light, which previously was thought to be purely wavelike, was found to have certain characteristics of particulate matter. But is the opposite also true? That is, does matter that is normally assumed to be particulate exhibit wave properties? This question was raised in 1923 by a young French physicist named Louis de Broglie (1892–1987). To see how de Broglie supplied the answer to this question, recall that the relationship between mass and wavelength for electromagnetic radiation is $m = h/\lambda c$. For a particle with velocity v , the corresponding expression is

$$m = \frac{h}{\lambda v}$$

Rearranging to solve for λ , we have

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

This equation, called *de Broglie's equation*, allows us to calculate the wavelength for a particle, as shown in Sample Exercise 7.3.

Do not confuse ν (frequency) with v (velocity).

Sample Exercise 7.3

Calculations of Wavelength

Compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of 1.0×10^7 m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

Solution

We use the equation $\lambda = h/mv$, where

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \quad \text{or} \quad 6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$$

since

$$1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$$

For the electron,

$$\lambda_e = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m} \cdot \text{m}}{\text{s}}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^7 \text{ m/s})} = 7.27 \times 10^{-11} \text{ m}$$

For the ball,

$$\lambda_b = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m} \cdot \text{m}}{\text{s}}}{(0.10 \text{ kg})(35 \text{ m/s})} = 1.9 \times 10^{-34} \text{ m}$$

See Exercises 7.41 through 7.44.

Notice from Sample Exercise 7.3 that the wavelength associated with the ball is incredibly short. On the other hand, the wavelength of the electron, although still quite small, happens to be on the same order as the spacing between the atoms in a typical crystal. This is important because, as we will see presently, it provides a means for testing de Broglie's equation.



CHEMICAL IMPACT

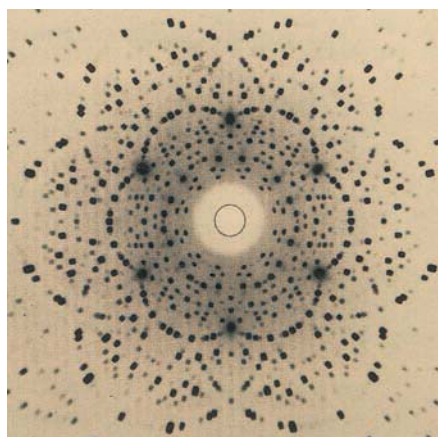
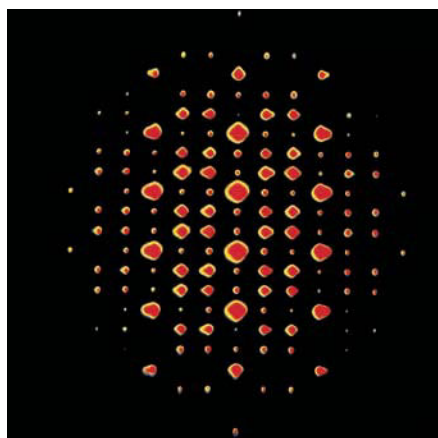
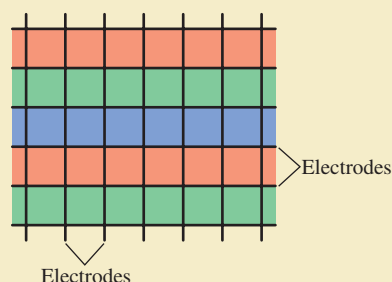
Thin Is In

Since the beginning of television about 75 years ago, TV sets have been built around cathode ray tubes (CRTs) in which a “gun” fires electrons at a screen containing phosphors (compounds that emit colored light when excited by some energy source). Although CRT televisions produce excellent pictures, big-screen TVs are very thick and very heavy. Several new technologies are now being used that reduce the bulk of color monitors. One such approach involves a plasma flat-panel display. As the name suggests, the major advantage of these screens is that they are very thin and relatively light.

All color monitors work by manipulating millions of pixels, each of which contains red, blue, and green color-producing phosphors. By combining these three fundamental colors with various weightings, all colors of the rainbow can be generated, thereby producing color images on the monitor. The various types of monitors differ in the energy source used to excite the phosphors. Whereas a CRT monitor uses an electron gun as the energy source, a plasma monitor

uses an applied voltage to produce gas-phase ions and electrons, which, when they recombine, emit ultraviolet light. This light, in turn, excites the phosphors.

Plasma monitors have pixel compartments that contain xenon and neon gas. Each pixel consists of three subpixels: one containing a red phosphor, one with a green phosphor, and one with a blue phosphor. Two perpendicular sets of electrodes define a matrix around the subpixels:



Diffraction results when light is scattered from a regular array of points or lines. You may have noticed the diffraction of light from the ridges and grooves of a compact disc. The colors result because the various wavelengths of visible light are not all scattered in the same way. The colors are “separated,” giving the same effect as light passing through a prism. Just as a regular arrangement of ridges and grooves produces diffraction, so does a regular array of atoms or ions in a crystal, as shown in the photographs below. For example, when X rays are directed onto a crystal of sodium chloride, with its regular array of Na^+ and Cl^- ions, the scattered radiation produces a **diffraction pattern** of bright spots and dark areas on a photographic plate, as shown in Fig. 7.5(a). This occurs because the scattered light can interfere constructively (the peaks and troughs of the beams are in phase) to produce a bright spot [Fig. 7.5(b)] or destructively (the peaks and troughs are out of phase) to produce a dark area [Fig. 7.5(c)].

A diffraction pattern can only be explained in terms of waves. Thus this phenomenon provides a test for the postulate that particles such as electrons have wavelengths. As we saw in Sample Exercise 7.3, an electron with a velocity of 10^7 m/s (easily achieved by acceleration of the electron in an electric field) has a wavelength of about 10^{-10} m, which is roughly the distance between the ions in a crystal such as sodium chloride. This is important because diffraction occurs most efficiently when the spacing between the scattering points is about the same as the wavelength of the wave being diffracted. Thus, if electrons really do have an associated wavelength, a crystal should diffract electrons. An experiment to test this idea was carried out in 1927 by C. J. Davisson and

(top) The pattern produced by electron diffraction of a titanium/nickel alloy. (bottom) Pattern produced by X-ray diffraction of a beryl crystal.

One set of the electrodes is above the pixels, and the perpendicular set is below the pixels. When the computer managing the image places a voltage difference across a given subpixel, electrons are removed from the xenon and neon atoms present to form a plasma (cations and electrons). When the cations recombine with the electrons, photons of light are emitted that are absorbed by the phosphor compound, which then emits red, green, or blue light. By controlling the size of the voltage on a given subpixel, a given pixel can produce a variety of colors. When all of the pixels are excited appropriately, a color image is produced.

The plasma display makes it possible to have a large, yet relatively thin screen. Since each pixel is energized individually, this display looks bright and clear from almost any angle. The main disadvantage of this technology is its relatively high cost. However, as advances are being made, the price is falling significantly. CRT monitors may soon be of interest only to antique collectors.



A plasma display from Sony.

L. H. Germer at Bell Laboratories. When they directed a beam of electrons at a nickel crystal, they observed a diffraction pattern similar to that seen from the diffraction of X rays. This result verified de Broglie's relationship, at least for electrons. Larger chunks of matter, such as balls, have such small wavelengths (see Sample Exercise 7.3) that they are impossible to verify experimentally. However, we believe that all matter obeys de Broglie's equation.

Now we have come full circle. Electromagnetic radiation, which at the turn of the twentieth century was thought to be a pure waveform, was found to possess particulate properties. Conversely, electrons, which were thought to be particles, were found to have a wavelength associated with them. The significance of these results is that matter and energy are not distinct.

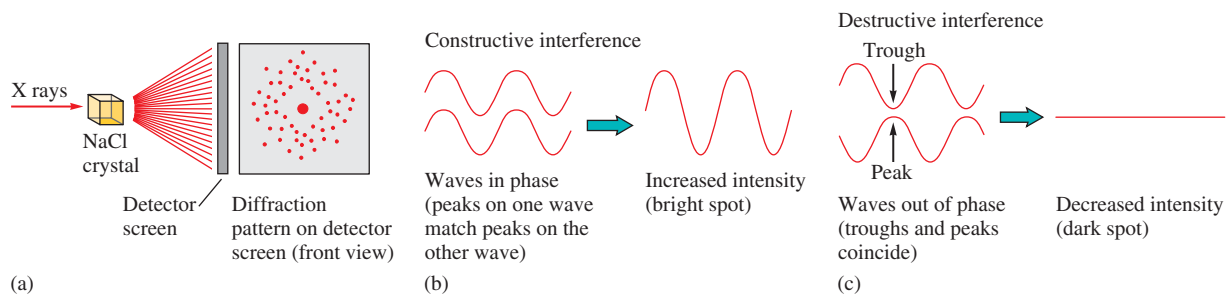


FIGURE 7.5

(a) Diffraction occurs when electromagnetic radiation is scattered from a regular array of objects, such as the ions in a crystal of sodium chloride. The large spot in the center is from the main incident beam of X rays. (b) Bright spots in the diffraction pattern result from *constructive interference* of waves. The waves are in phase; that is, their peaks match. (c) Dark areas result from *destructive interference* of waves. The waves are out of phase; the peaks of one wave coincide with the troughs of another wave.

Energy is really a form of matter, and all matter shows the same types of properties. That is, *all matter exhibits both particulate and wave properties*. Large pieces of matter, such as baseballs, exhibit predominantly particulate properties. The associated wavelength is so small that it is not observed. Very small “bits of matter,” such as photons, while showing some particulate properties, exhibit predominantly wave properties. Pieces of matter with intermediate mass, such as electrons, show clearly both the particulate and wave properties of matter.

7.3 The Atomic Spectrum of Hydrogen

As we saw in Chapter 2, key information about the atom came from several experiments carried out in the early twentieth century, in particular Thomson’s discovery of the electron and Rutherford’s discovery of the nucleus. Another important experiment was the study of the emission of light by excited hydrogen atoms. When a sample of hydrogen gas receives a high-energy spark, the H_2 molecules absorb energy, and some of the H—H bonds are broken. The resulting hydrogen atoms are *excited*; that is, they contain excess energy, which they release by emitting light of various wavelengths to produce what is called the *emission spectrum* of the hydrogen atom.

To understand the significance of the hydrogen emission spectrum, we must first describe the **continuous spectrum** that results when white light is passed through a prism, as shown in Fig. 7.6(a). This spectrum, like the rainbow produced when sunlight is



A beautiful rainbow.



Visualization: Refraction of White Light



Visualization: The Line Spectrum of Hydrogen

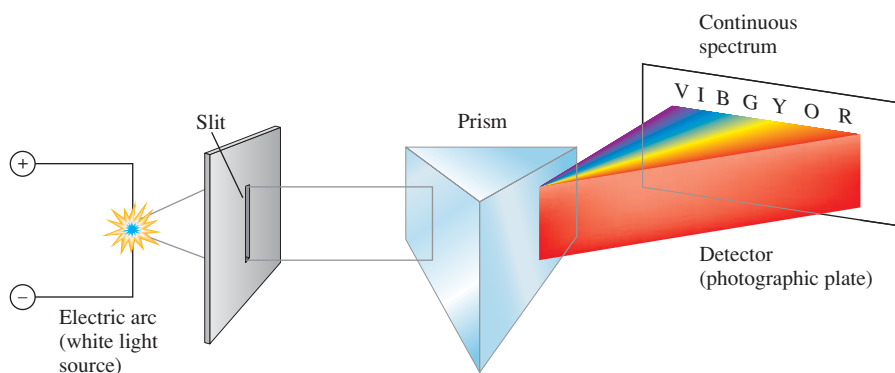


Visualization: Flame Tests

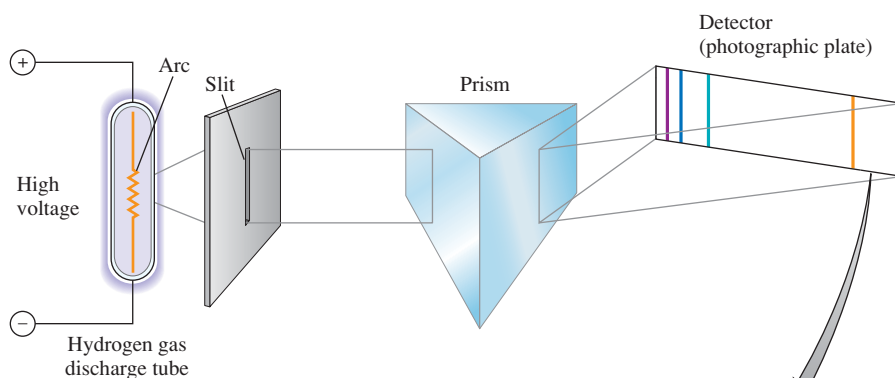
FIGURE 7.6

(a) A continuous spectrum containing all wavelengths of visible light (indicated by the initial letters of the colors of the rainbow). (b) The hydrogen line spectrum contains only a few discrete wavelengths.

Spectrum adapted by permission from C. W. Keenan, D. C. Kleinfelter, and J. H. Wood, *General College Chemistry*, 6th ed. (New York: Harper & Row, 1980).



(a)



(b)

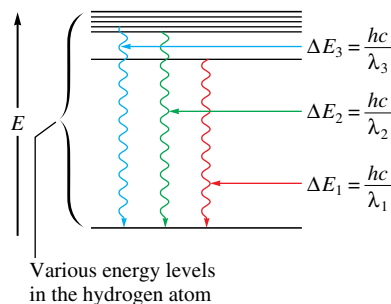


FIGURE 7.7
A change between two discrete energy levels emits a photon of light.

dispersed by raindrops, contains *all* the wavelengths of visible light. In contrast, when the hydrogen emission spectrum in the visible region is passed through a prism, as shown in Fig. 7.6(b), we see only a few lines, each of which corresponds to a discrete wavelength. The hydrogen emission spectrum is called a **line spectrum**.

What is the significance of the line spectrum of hydrogen? It indicates that *only certain energies are allowed for the electron in the hydrogen atom*. In other words, the energy of the electron in the hydrogen atom is *quantized*. This observation ties in perfectly with the postulates of Max Planck discussed in Section 7.2. Changes in energy between discrete energy levels in hydrogen will produce only certain wavelengths of emitted light, as shown in Fig. 7.7. For example, a given change in energy from a high to a lower level would give a wavelength of light that can be calculated from Planck's equation:

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

Change in energy
Frequency of light emitted
Wavelength of light emitted

The discrete line spectrum of hydrogen shows that only certain energies are possible; that is, the electron energy levels are quantized. In contrast, if any energy level were allowed, the emission spectrum would be continuous.

7.4 The Bohr Model

In 1913, a Danish physicist named Niels Bohr (1885–1962), aware of the experimental results we have just discussed, developed a **quantum model** for the hydrogen atom. Bohr proposed that the *electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits*. He calculated the radii for these allowed orbits by using the theories of classical physics and by making some new assumptions.

From classical physics Bohr knew that a particle in motion tends to move in a straight line and can be made to travel in a circle only by application of a force toward the center of the circle. Thus Bohr reasoned that the tendency of the revolving electron to fly off the atom must be just balanced by its attraction for the positively charged nucleus. But classical physics also decreed that a charged particle under acceleration should radiate energy. Since an electron revolving around the nucleus constantly changes its direction, it is constantly accelerating. Therefore, the electron should emit light and lose energy—and thus be drawn into the nucleus. This, of course, does not correlate with the existence of stable atoms.

Clearly, an atomic model based solely on the theories of classical physics was untenable. Bohr also knew that the correct model had to account for the experimental spectrum of hydrogen, which showed that only certain electron energies were allowed. The experimental data were absolutely clear on this point. Bohr found that his model would fit the experimental results if he assumed that the angular momentum of the electron (angular momentum equals the product of mass, velocity, and orbital radius) could occur only in certain increments. It was not clear why this should be true, but with this assumption, Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum. The model is represented pictorially in Fig. 7.8.

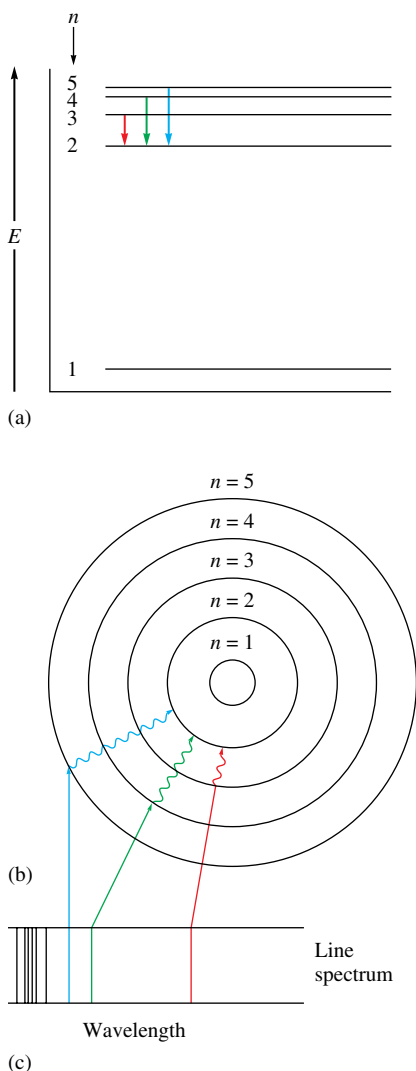
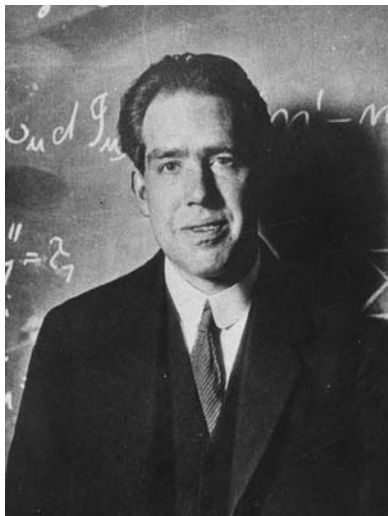


FIGURE 7.8
Electronic transitions in the Bohr model for the hydrogen atom. (a) An energy-level diagram for electronic transitions. (b) An orbit-transition diagram, which accounts for the experimental spectrum. (Note that the orbits shown are schematic. They are not drawn to scale.) (c) The resulting line spectrum on a photographic plate. Note that the lines in the visible region of the spectrum correspond to transitions from higher levels to the $n = 2$ level.

The J in Equation (7.1) stands for joules.



Niels Hendrik David Bohr (1885–1962) as a boy lived in the shadow of his younger brother Harald, who played on the 1908 Danish Olympic Soccer Team and later became a distinguished mathematician. In school, Bohr received his poorest marks in composition and struggled with writing during his entire life. In fact, he wrote so poorly that he was forced to dictate his Ph.D. thesis to his mother. Nevertheless, Bohr was a brilliant physicist. After receiving his Ph.D. in Denmark, he constructed a quantum model for the hydrogen atom by the time he was 27. Even though his model later proved to be incorrect, Bohr remained a central figure in the drive to understand the atom. He was awarded the Nobel Prize in physics in 1922.

Although we will not show the derivation here, the most important equation to come from Bohr's model is the expression for the *energy levels available to the electron in the hydrogen atom*:

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right) \quad (7.1)$$

in which n is an integer (the larger the value of n , the larger is the orbit radius) and Z is the nuclear charge. Using Equation (7.1), Bohr was able to calculate hydrogen atom energy levels that exactly matched the values obtained by experiment.

The negative sign in Equation (7.1) simply means that the energy of the electron bound to the nucleus is lower than it would be if the electron were at an infinite distance ($n = \infty$) from the nucleus, where there is no interaction and the energy is zero:

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{\infty} \right) = 0$$

The energy of the electron in any orbit is negative relative to this reference state.

Equation (7.1) can be used to calculate the change in energy of an electron when the electron changes orbits. For example, suppose an electron in level $n = 6$ of an excited hydrogen atom falls back to level $n = 1$ as the hydrogen atom returns to its lowest possible energy state, its **ground state**. We use Equation (7.1) with $Z = 1$, since the hydrogen nucleus contains a single proton. The energies corresponding to the two states are as follows:

$$\text{For } n = 6: \quad E_6 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{6^2} \right) = -6.050 \times 10^{-20} \text{ J}$$

$$\text{For } n = 1: \quad E_1 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{1^2} \right) = -2.178 \times 10^{-18} \text{ J}$$

Note that for $n = 1$ the electron has a more negative energy than it does for $n = 6$, which means that the electron is more tightly bound in the smallest allowed orbit.

The change in energy ΔE when the electron falls from $n = 6$ to $n = 1$ is

$$\begin{aligned} \Delta E &= \text{energy of final state} - \text{energy of initial state} \\ &= E_1 - E_6 = (-2.178 \times 10^{-18} \text{ J}) - (-6.050 \times 10^{-20} \text{ J}) \\ &= -2.117 \times 10^{-18} \text{ J} \end{aligned}$$

The negative sign for the *change* in energy indicates that the atom has *lost* energy and is now in a more stable state. The energy is carried away from the atom by the production (emission) of a photon.

The wavelength of the emitted photon can be calculated from the equation

$$\Delta E = h \left(\frac{c}{\lambda} \right) \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}$$

where ΔE represents the change in energy of the atom, which equals the energy of the emitted photon. We have

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{2.117 \times 10^{-18} \text{ J}} = 9.383 \times 10^{-8} \text{ m}$$

Note that for this calculation the absolute value of ΔE is used (we have not included the negative sign). In this case we indicate the direction of energy flow by saying that a photon

of wavelength 9.383×10^{-8} m has been *emitted* from the hydrogen atom. Simply plugging the negative value of ΔE into the equation would produce a negative value for λ , which is physically meaningless.

Sample Exercise 7.4

Energy Quantization in Hydrogen

Calculate the energy required to excite the hydrogen electron from level $n = 1$ to level $n = 2$. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.*

Solution

Using Equation (7.1) with $Z = 1$, we have

$$E_1 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{1^2} \right) = -2.178 \times 10^{-18} \text{ J}$$

$$E_2 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1^2}{2^2} \right) = -5.445 \times 10^{-19} \text{ J}$$

$$\Delta E = E_2 - E_1 = (-5.445 \times 10^{-19} \text{ J}) - (-2.178 \times 10^{-18} \text{ J}) = 1.633 \times 10^{-18} \text{ J}$$

The positive value for ΔE indicates that the system has gained energy. The wavelength of light that must be *absorbed* to produce this change is

$$\begin{aligned} \lambda &= \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{1.633 \times 10^{-18} \text{ J}} \\ &= 1.216 \times 10^{-7} \text{ m} \end{aligned}$$

Note from Fig. 7.2 that the light required to produce the transition from the $n = 1$ to $n = 2$ level in hydrogen lies in the ultraviolet region.

See Exercises 7.45 and 7.46.

At this time we must emphasize two important points about the Bohr model:

1. The model correctly fits the quantized energy levels of the hydrogen atom and postulates only certain allowed circular orbits for the electron.
2. As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state (corresponding to the electron being at infinite distance from the nucleus). As the electron is brought closer to the nucleus, energy is released from the system.

Using Equation (7.1), we can derive a general equation for the electron moving from one level (n_{initial}) to another level (n_{final}):

$$\begin{aligned} \Delta E &= \text{energy of level } n_{\text{final}} - \text{energy of level } n_{\text{initial}} \\ &= E_{\text{final}} - E_{\text{initial}} \\ &= (-2.178 \times 10^{-18} \text{ J}) \left(\frac{1^2}{n_{\text{final}}^2} \right) - (-2.178 \times 10^{-18} \text{ J}) \left(\frac{1^2}{n_{\text{initial}}^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \end{aligned} \quad (7.2)$$

Equation (7.2) can be used to calculate the energy change between *any* two energy levels in a hydrogen atom, as shown in Sample Exercise 7.5.

*After this exercise we will no longer show cancellation marks. However, the same process for canceling units applies throughout this text.



CHEMICAL IMPACT

Fireworks

The art of using mixtures of chemicals to produce explosives is an ancient one. Black powder—a mixture of potassium nitrate, charcoal, and sulfur—was being used in China well before 1000 A.D. and has been used subsequently through the centuries in military explosives, in construction blasting, and for fireworks. The DuPont Company, now a major chemical manufacturer, started out as a manufacturer of black powder. In fact, the founder, Eleuthère duPont, learned the manufacturing technique from none other than Lavoisier.

Before the nineteenth century, fireworks were confined mainly to rockets and loud bangs. Orange and yellow colors came from the presence of charcoal and iron filings. However, with the great advances in chemistry in the nineteenth century, new compounds found their way into fireworks. Salts of copper, strontium, and barium added brilliant colors. Magnesium and aluminum metals gave a dazzling white light. Fireworks, in fact, have changed very little since then.

How do fireworks produce their brilliant colors and loud bangs? Actually, only a handful of different chemicals are responsible for most of the spectacular effects. To produce the noise and flashes, an oxidizer (an oxidizing agent) and a fuel (a reducing agent) are used. A common mixture involves potassium perchlorate (KClO_4) as the oxidizer and aluminum and sulfur as the fuel. The perchlorate oxidizes the fuel in a very exothermic reaction, which produces a brilliant flash, due to the aluminum, and a loud report from the rapidly expanding gases produced. For a color effect, an element with a colored emission spectrum is included. Recall that the electrons in atoms can be raised to higher-energy orbitals when the atoms absorb energy. The excited atoms can then release this excess energy by emitting light of specific wavelengths, often in the visible region. In fireworks, the energy to excite the electrons comes from the reaction between the oxidizer and fuel.

Yellow colors in fireworks are due to the 589-nm emission of sodium ions. Red colors come from strontium salts emitting at 606 nm and from 636 to 688 nm. This red color is familiar from highway safety flares. Barium salts give a green color in fireworks, due to a series of emission lines

between 505 and 535 nm. A really good blue color, however, is hard to obtain. Copper salts give a blue color, emitting in the 420- to 460-nm region. But difficulties occur because the oxidizing agent, potassium chlorate (KClO_3), reacts with copper salts to form copper chlorate, a highly explosive compound that is dangerous to store. (The use of KClO_3 in fireworks has been largely abandoned because of its explosive hazards.) Paris green, a copper salt containing arsenic, was once used extensively but is now considered to be too toxic.

In recent years the colors produced by fireworks have become more intense because of the formation of metal chlorides during the burning process. These gaseous metal chloride molecules produce colors much more brilliant than do the metal atoms by themselves. For example, strontium chloride produces a much brighter red than do strontium atoms.



Fireworks in Washington, D.C.

Thus, chlorine-donating compounds are now included in many fireworks shells.

A typical aerial shell is shown in the diagram. The shell is launched from a mortar (a steel cylinder) using black powder as the propellant. Time-delayed fuses are used to fire the shell in stages. A list of chemicals commonly used in fireworks is given in the table.

Although you might think that the chemistry of fireworks is simple, the achievement of the vivid white flashes and the brilliant colors requires complex combinations of chemicals. For example, because the white flashes produce high flame temperatures, the colors tend to wash out. Thus oxidizers such as KClO_4 are commonly used with fuels that produce relatively low flame temperatures. An added difficulty, however, is that perchlorates are very sensitive to accidental ignition and are therefore quite hazardous. Another problem arises from the use of sodium salts. Because sodium produces an extremely bright yellow emission, sodium salts cannot be used when other colors are desired. Carbon-based fuels also give a yellow flame that masks other colors, and this limits the use of organic compounds as fuels. You can see that the manufacture of fireworks that produce the desired effects and are also safe to handle requires careful selection of chemicals. And, of course, there is still the dream of a deep blue flame.

Chemicals Commonly Used in the Manufacture of Fireworks

| Oxidizers | Fuels | Special Effects |
|-----------------------|--------------------|---|
| Potassium nitrate | Aluminum | Red flame: strontium nitrate, strontium carbonate |
| Potassium chlorate | Magnesium | Green flame: barium nitrate, barium chlorate |
| Potassium perchlorate | Titanium | Blue flame: copper carbonate, copper sulfate, copper oxide |
| Ammonium perchlorate | Charcoal | Yellow flame: sodium oxalate, cryolite (Na_3AlF_6) |
| Barium nitrate | Sulfur | White flame: magnesium, aluminum |
| Barium chlorate | Antimony sulfide | Gold sparks: iron filings, charcoal |
| Strontium nitrate | Dextrin | White sparks: aluminum, magnesium, aluminum–magnesium alloy, titanium |
| | Red gum | Whistle effect: potassium benzoate or sodium salicylate |
| | Polyvinyl chloride | White smoke: mixture of potassium nitrate and sulfur |
| | | Colored smoke: mixture of potassium chlorate, sulfur, and organic dye |

Sample Exercise 7.5

Electron Energies

Calculate the energy required to remove the electron from a hydrogen atom in its ground state.

Solution

Removing the electron from a hydrogen atom in its ground state corresponds to taking the electron from $n_{\text{initial}} = 1$ to $n_{\text{final}} = \infty$. Thus

$$\begin{aligned}\Delta E &= -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{\infty} - \frac{1}{1^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J}(0 - 1) = 2.178 \times 10^{-18} \text{ J}\end{aligned}$$

The energy required to remove the electron from a hydrogen atom in its ground state is $2.178 \times 10^{-18} \text{ J}$.

See Exercises 7.51 and 7.52.



Visualization: Flame Tests

Although Bohr's model fits the energy levels for hydrogen, it is a fundamentally incorrect model for the hydrogen atom.

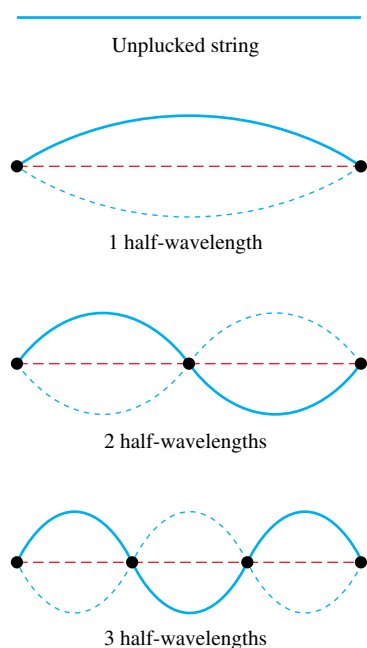


FIGURE 7.9
The standing waves caused by the vibration of a guitar string fastened at both ends. Each dot represents a node (a point of zero displacement).

Wave-generating apparatus.

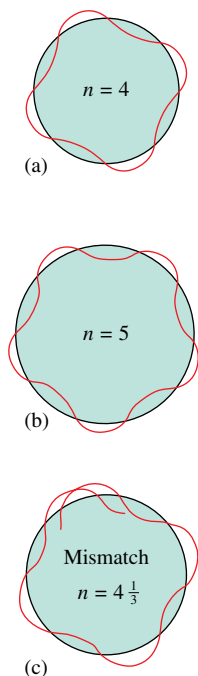
At first Bohr's model appeared to be very promising. The energy levels calculated by Bohr closely agreed with the values obtained from the hydrogen emission spectrum. However, when Bohr's model was applied to atoms other than hydrogen, it did not work at all. Although some attempts were made to adapt the model using elliptical orbits, it was concluded that Bohr's model is fundamentally incorrect. The model is, however, very important historically, because it showed that the observed quantization of energy in atoms could be explained by making rather simple assumptions. Bohr's model paved the way for later theories. It is important to realize, however, that the current theory of atomic structure is in no way derived from the Bohr model. Electrons do *not* move around the nucleus in circular orbits, as we shall see later in this chapter.

7.5 The Quantum Mechanical Model of the Atom

By the mid-1920s it had become apparent that the Bohr model could not be made to work. A totally new approach was needed. Three physicists were at the forefront of this effort: Werner Heisenberg (1901–1976), Louis de Broglie (1892–1987), and Erwin Schrödinger (1887–1961). The approach they developed became known as *wave mechanics* or, more commonly, *quantum mechanics*. As we have already seen, de Broglie originated the idea that the electron, previously considered to be a particle, also shows wave properties. Pursuing this line of reasoning, Schrödinger, an Austrian physicist, decided to attack the problem of atomic structure by giving emphasis to the wave properties of the electron. To Schrödinger and de Broglie, the electron bound to the nucleus seemed similar to a **standing wave**, and they began research on a wave mechanical description of the atom.

The most familiar example of standing waves occurs in association with musical instruments such as guitars or violins, where a string attached at both ends vibrates to produce a musical tone. The waves are described as “standing” because they are stationary;



**FIGURE 7.10**

The hydrogen electron visualized as a standing wave around the nucleus. The circumference of a particular circular orbit would have to correspond to a whole number of wavelengths, as shown in (a) and (b), or else destructive interference occurs, as shown in (c). This is consistent with the fact that only certain electron energies are allowed; the atom is quantized. (Although this idea encouraged scientists to use a wave theory, it does not mean that the electron really travels in circular orbits.)

the waves do not travel along the length of the string. The motions of the string can be explained as a combination of simple waves of the type shown in Fig. 7.9. The dots in this figure indicate the nodes, or points of zero lateral (sideways) displacement, for a given wave. Note that there are limitations on the allowed wavelengths of the standing wave. Each end of the string is fixed, so there is always a node at each end. This means that there must be a whole number of *half* wavelengths in any of the allowed motions of the string (see Fig. 7.9). Standing waves can be illustrated using the wave generator shown in the photo below.

A similar situation results when the electron in the hydrogen atom is imagined to be a standing wave. As shown in Fig. 7.10, only certain circular orbits have a circumference into which a whole number of wavelengths of the standing electron wave will “fit.” All other orbits would produce destructive interference of the standing electron wave and are not allowed. This seemed like a possible explanation for the observed quantization of the hydrogen atom, so Schrödinger worked out a model for the hydrogen atom in which the electron was assumed to behave as a standing wave.

It is important to recognize that Schrödinger could not be sure that this idea would work. The test had to be whether or not the model would correctly fit the experimental data on hydrogen and other atoms. The physical principles for describing standing waves were well known in 1925 when Schrödinger decided to treat the electron in this way. His mathematical treatment is too complicated to be detailed here. However, the form of Schrödinger’s equation is

$$\hat{H}\psi = E\psi$$

where ψ , called the **wave function**, is a function of the coordinates (x , y , and z) of the electron’s position in three-dimensional space and \hat{H} represents a set of mathematical instructions called an *operator*. In this case, the operator contains mathematical terms that produce the total energy of the atom when they are applied to the wave function. E represents the total energy of the atom (the sum of the potential energy due to the attraction between the proton and electron and the kinetic energy of the moving electron). When this equation is analyzed, many solutions are found. Each solution consists of a wave function ψ that is characterized by a particular value of E . A specific wave function is often called an **orbital**.

To illustrate the most important ideas of the **quantum (wave) mechanical model** of the atom, we will first concentrate on the wave function corresponding to the lowest energy for the hydrogen atom. This wave function is called the $1s$ orbital. The first point of interest is to explore the meaning of the word *orbital*. As we will see, this is not a trivial matter. One thing is clear: An orbital is *not* a Bohr orbit. The electron in the hydrogen $1s$ orbital is not moving around the nucleus in a circular orbit. How, then, is the electron moving? The answer is quite surprising: *We do not know*. The wave function gives us no information about the detailed pathway of the electron. This is somewhat disturbing. When we solve problems involving the motions of particles in the macroscopic world, we are able to predict their pathways. For example, when two billiard balls with known velocities collide, we can predict their motions after the collision. However, we cannot predict the electron’s motion from the $1s$ orbital function. Does this mean that the theory is wrong? Not necessarily: We have already learned that an electron does not behave much like a billiard ball, so we must examine the situation closely before we discard the theory.

To help us understand the nature of an orbital, we need to consider a principle discovered by Werner Heisenberg, one of the primary developers of quantum mechanics. Heisenberg’s mathematical analysis led him to a surprising conclusion: *There is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time*. This is a statement of the **Heisenberg uncertainty principle**. Stated mathematically, the uncertainty principle is

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

where Δx is the uncertainty in a particle's position, $\Delta(mv)$ is the uncertainty in a particle's momentum, and h is Planck's constant. Thus the minimum uncertainty in the product $\Delta \cdot \Delta(mv)$ is $h/4\pi$. What this equation really says is that the more accurately we know a particle's position, the less accurately we can know its momentum, and vice versa. This limitation is so small for large particles such as baseballs or billiard balls that it is unnoticed. However, for a small particle such as the electron, the limitation becomes quite important. Applied to the electron, the uncertainty principle implies that we cannot know the exact motion of the electron as it moves around the nucleus. It is therefore not appropriate to assume that the electron is moving around the nucleus in a well-defined orbit, as in the Bohr model.

The Physical Meaning of a Wave Function

Given the limitations indicated by the uncertainty principle, what then is the physical meaning of a wave function for an electron? That is, what is an atomic orbital? Although the wave function itself has no easily visualized meaning, the square of the function does have a definite physical significance. *The square of the function indicates the probability of finding an electron near a particular point in space.* For example, suppose we have two positions in space, one defined by the coordinates $x_1, y_1,$ and z_1 and the other by the coordinates $x_2, y_2,$ and z_2 . The relative probability of finding the electron at positions 1 and 2 is given by substituting the values of $x, y,$ and z for the two positions into the wave function, squaring the function value, and computing the following ratio:

$$\frac{[\psi(x_1, y_1, z_1)]^2}{[\psi(x_2, y_2, z_2)]^2} = \frac{N_1}{N_2}$$

The quotient N_1/N_2 is the ratio of the probabilities of finding the electron at positions 1 and 2. For example, if the value of the ratio N_1/N_2 is 100, the electron is 100 times more likely to be found at position 1 than at position 2. The model gives no information concerning when the electron will be at either position or how it moves between the positions. This vagueness is consistent with the concept of the Heisenberg uncertainty principle.

The square of the wave function is most conveniently represented as a **probability distribution**, in which the intensity of color is used to indicate the probability value near a given point in space. The probability distribution for the hydrogen 1s wave function (orbital) is shown in Fig. 7.11(a). The best way to think about this diagram is as a three-dimensional time exposure with the electron as a tiny moving light. The more times the electron visits a particular point, the darker the negative becomes. Thus the darkness of a point indicates the probability of finding an electron at that position. This diagram is also known as an *electron density map*; *electron density* and *electron probability* mean the same thing. When a chemist uses the term *atomic orbital*, he or she is probably picturing an electron density map of this type.

Another way of representing the electron probability distribution for the 1s wave function is to calculate the probability at points along a line drawn outward in any direction from the nucleus. The result is shown in Fig. 7.11(b). Note that the probability of finding the electron at a particular position is greatest close to the nucleus and drops off rapidly as the distance from the nucleus increases. We are also interested in knowing the *total* probability of finding the electron in the hydrogen atom at a particular *distance* from the nucleus. Imagine that the space around the hydrogen nucleus is made up of a series of thin spherical shells (rather like layers in an onion), as shown in Fig. 7.12(a). When the total probability of finding the electron in each spherical shell is plotted versus the distance from the nucleus, the plot in Fig. 7.12(b) is obtained. This graph is called the **radial probability distribution**.

The maximum in the curve occurs because of two opposing effects. The probability of finding an electron at a particular position is greatest near the nucleus, but the volume

Probability is the likelihood, or odds, that something will occur.

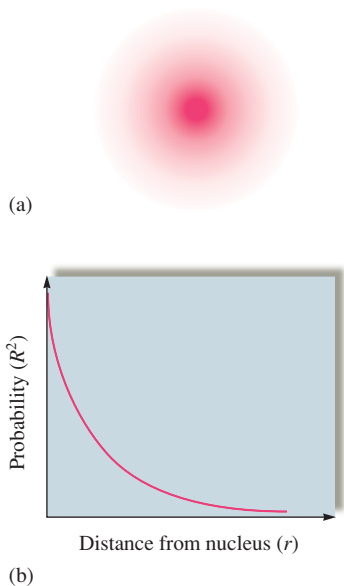
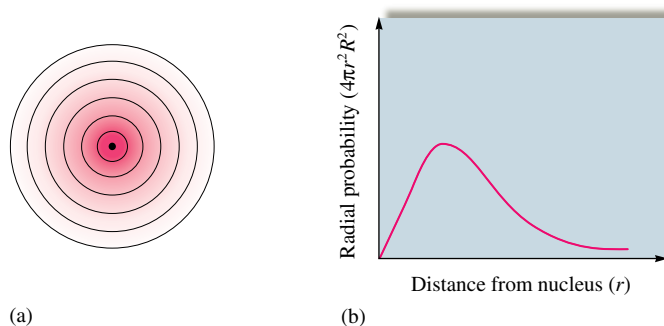


FIGURE 7.11
(a) The probability distribution for the hydrogen 1s orbital in three-dimensional space. (b) The probability of finding the electron at points along a line drawn from the nucleus outward in any direction for the hydrogen 1s orbital.

FIGURE 7.12

(a) Cross section of the hydrogen 1s orbital probability distribution divided into successive thin spherical shells. (b) The radial probability distribution. A plot of the total probability of finding the electron in each thin spherical shell as a function of distance from the nucleus.



$1 \text{ \AA} = 10^{-10} \text{ m}$; the angstrom is most often used as the unit for atomic radius because of its convenient size. Another convenient unit is the picometer:

$$1 \text{ pm} = 10^{-12} \text{ m}$$



Visualization: 1s Orbital

of the spherical shell increases with distance from the nucleus. Therefore, as we move away from the nucleus, the probability of finding the electron at a given position decreases, but we are summing more positions. Thus the total probability increases to a certain radius and then decreases as the electron probability at each position becomes very small. For the hydrogen 1s orbital, the maximum radial probability (the distance at which the electron is most likely to be found) occurs at a distance of $5.29 \times 10^{-2} \text{ nm}$ or 0.529 \AA from the nucleus. Interestingly, this is exactly the radius of the innermost orbit in the Bohr model. Note that in Bohr's model the electron is assumed to have a circular path and so is *always* found at this distance. In the quantum mechanical model, the specific electron motions are unknown, and this is the *most probable* distance at which the electron is found.

One more characteristic of the hydrogen 1s orbital that we must consider is its size. As we can see from Fig. 7.11, the size of this orbital cannot be defined precisely, since the probability never becomes zero (although it drops to an extremely small value at large values of r). So, in fact, the hydrogen 1s orbital has no distinct size. However, it is useful to have a definition of relative orbital size. *The definition most often used by chemists to describe the size of the hydrogen 1s orbital is the radius of the sphere that encloses 90% of the total electron probability.* That is, 90% of the time the electron is inside this sphere.

So far we have described only the lowest-energy wave function in the hydrogen atom, the 1s orbital. Hydrogen has many other orbitals, which we will describe in the next section. However, before we proceed, we should summarize what we have said about the meaning of an atomic orbital. An orbital is difficult to define precisely at an introductory level. Technically, an orbital is a wave function. However, it is usually most helpful to picture an orbital as a three-dimensional electron density map. That is, an electron “in” a particular atomic orbital is assumed to exhibit the electron probability indicated by the orbital map.

7.6 Quantum Numbers

When we solve the Schrödinger equation for the hydrogen atom, we find many wave functions (orbitals) that satisfy it. Each of these orbitals is characterized by a series of numbers called **quantum numbers**, which describe various properties of the orbital:

The **principal quantum number** (n) has integral values: 1, 2, 3, The principal quantum number is related to the size and energy of the orbital. As n increases, the orbital becomes larger and the electron spends more time farther from the nucleus. An increase in n also means higher energy, because the electron is less tightly bound to the nucleus, and the energy is less negative.

The **angular momentum quantum number** (ℓ) has integral values from 0 to $n - 1$ for each value of n . This quantum number is related to the shape of atomic orbitals. The value of ℓ for a particular orbital is commonly assigned a letter: $\ell = 0$ is called s ;

TABLE 7.1 The Angular Momentum Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals

| | | | | | |
|-----------------|----------|----------|----------|----------|----------|
| Value of ℓ | 0 | 1 | 2 | 3 | 4 |
| Letter Used | <i>s</i> | <i>p</i> | <i>d</i> | <i>f</i> | <i>g</i> |

Number of Orbitals per Subshell

$$s = 1$$

$$p = 3$$

$$d = 5$$

$$f = 7$$

$$g = 9$$

TABLE 7.2 Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

| <i>n</i> | ℓ | Orbital Designation | m_ℓ | Number of Orbitals |
|----------|--------|---------------------|------------------------|--------------------|
| 1 | 0 | 1 <i>s</i> | 0 | 1 |
| 2 | 0 | 2 <i>s</i> | 0 | 1 |
| | 1 | 2 <i>p</i> | -1, 0, +1 | 3 |
| 3 | 0 | 3 <i>s</i> | 0 | 1 |
| | 1 | 3 <i>p</i> | -1, 0, 1 | 3 |
| | 2 | 3 <i>d</i> | -2, -1, 0, 1, 2 | 5 |
| 4 | 0 | 4 <i>s</i> | 0 | 1 |
| | 1 | 4 <i>p</i> | -1, 0, 1 | 3 |
| | 2 | 4 <i>d</i> | -2, -1, 0, 1, 2 | 5 |
| | 3 | 4 <i>f</i> | -3, -2, -1, 0, 1, 2, 3 | 7 |

$\ell = 1$ is called *p*; $\ell = 2$ is called *d*; $\ell = 3$ is called *f*. This system arises from early spectral studies and is summarized in Table 7.1.

The **magnetic quantum number** (m_ℓ) has integral values between ℓ and $-\ell$, including zero. The value of m_ℓ is related to the orientation of the orbital in space relative to the other orbitals in the atom.

The first four levels of orbitals in the hydrogen atom are listed with their quantum numbers in Table 7.2. Note that each set of orbitals with a given value of ℓ (sometimes called a **subshell**) is designated by giving the value of n and the letter for ℓ . Thus an orbital where $n = 2$ and $\ell = 1$ is symbolized as $2p$. There are three $2p$ orbitals, which have different orientations in space. We will describe these orbitals in the next section.

$$n = 1, 2, 3, \dots$$

$$\ell = 0, 1, \dots, (n - 1)$$

$$m_\ell = -\ell, \dots, 0, \dots, +\ell$$

Sample Exercise 7.6

Electron Subshells

For principal quantum level $n = 5$, determine the number of allowed subshells (different values of ℓ), and give the designation of each.

Solution

For $n = 5$, the allowed values of ℓ run from 0 to 4 ($n - 1 = 5 - 1$). Thus the subshells and their designations are

$$\begin{array}{ccccc} \ell = 0 & \ell = 1 & \ell = 2 & \ell = 3 & \ell = 4 \\ 5s & 5p & 5d & 5f & 5g \end{array}$$

See Exercises 7.57 through 7.59.

7.7 Orbital Shapes and Energies

We have seen that the meaning of an orbital is represented most clearly by a probability distribution. Each orbital in the hydrogen atom has a unique probability distribution. We also saw that another means of representing an orbital is by the surface that surrounds 90% of the total electron probability. These two types of representations for the hydrogen $1s$, $2s$, and $3s$ orbitals are shown in Fig. 7.13. Note the characteristic spherical shape of each of the s orbitals. Note also that the $2s$ and $3s$ orbitals contain areas of high probability separated by areas of zero probability. These latter areas are called **nodal surfaces**, or simply **nodes**. The number of nodes increases as n increases. For s orbitals, the number of nodes is given by $n - 1$. For our purposes, however, we will think of s orbitals only in terms of their overall spherical shape, which becomes larger as the value of n increases.



Visualization: Orbital Energies



Visualization: $2p_x$, $2p_y$, $2p_z$ Orbitals

n value



$2p_x$ ← orientation in space



ℓ value



Visualization:
 $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{z^2}$ Orbitals

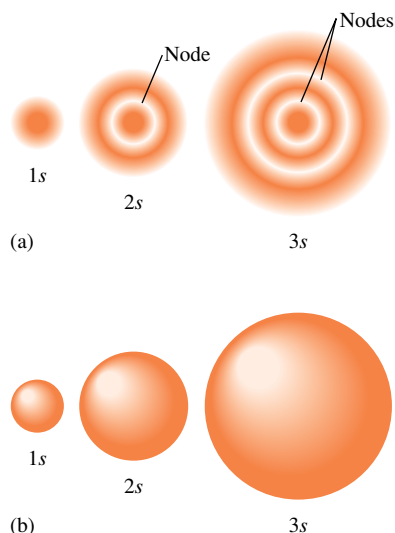


FIGURE 7.13

Two representations of the hydrogen $1s$, $2s$, and $3s$ orbitals. (a) The electron probability distribution. (b) The surface that contains 90% of the total electron probability (the size of the orbital, by definition).

The two types of representations for the $2p$ orbitals (there are no $1p$ orbitals) are shown in Fig. 7.14. Note that the p orbitals are not spherical like s orbitals but have two *lobes* separated by a node at the nucleus. The p orbitals are labeled according to the axis of the xyz coordinate system along which the lobes lie. For example, the $2p$ orbital with lobes centered along the x axis is called the $2p_x$ orbital.

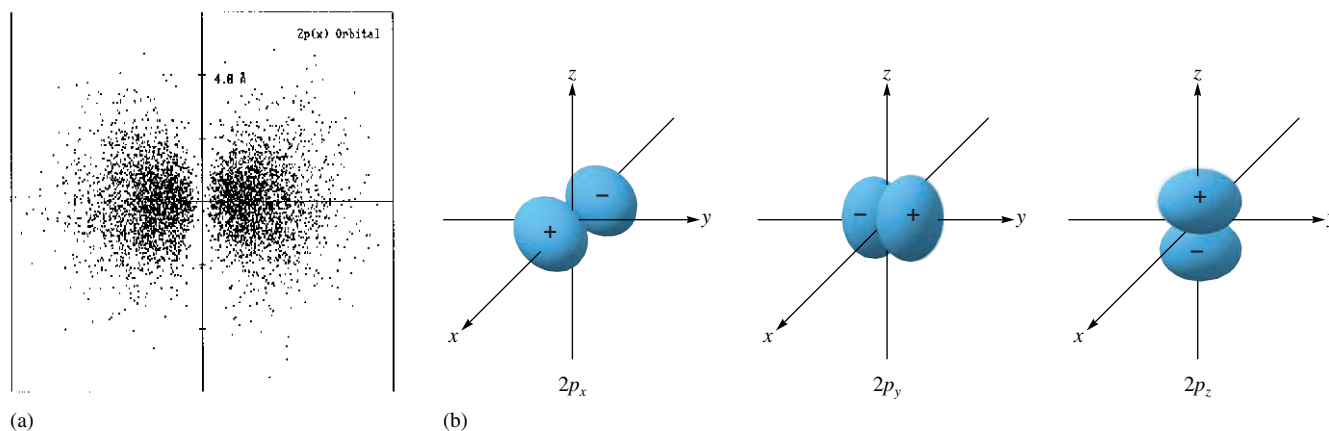
At this point it is useful to remember that mathematical functions have signs. For example, a simple sine wave (see Fig. 7.1) oscillates from positive to negative and repeats this pattern. Atomic orbital functions also have signs. The functions for s orbitals are positive everywhere in three-dimensional space. That is, when the s orbital function is evaluated at any point in space, it results in a positive number. In contrast, the p orbital functions have different signs in different regions of space. For example, the p_z orbital has a positive sign in all the regions of space in which z is positive and has a negative sign when z is negative. This behavior is indicated in Fig. 7.14(b) by the positive and negative signs inside their boundary surfaces. It is important to understand that these are mathematical signs, not charges. Just as a sine wave has alternating positive and negative phases, so too p orbitals have positive and negative phases. The phases of the p_x , p_y , and p_z orbitals are indicated in Fig. 7.14(b).

As you might expect from our discussion of the s orbitals, the $3p$ orbitals have a more complex probability distribution than that of the $2p$ orbitals (see Fig. 7.15), but they can still be represented by the same boundary surface shapes. The surfaces just grow larger as the value of n increases.

There are no d orbitals that correspond to principal quantum levels $n = 1$ and $n = 2$. The d orbitals ($\ell = 2$) first occur in level $n = 3$. The five $3d$ orbitals have the shapes shown in Fig. 7.16. The d orbitals have two different fundamental shapes. Four of the orbitals (d_{xz} , d_{yz} , d_{xy} , and $d_{x^2-y^2}$) have four lobes centered in the plane indicated in the orbital label. Note that d_{xy} and $d_{x^2-y^2}$ are both centered in the xy plane; however, the lobes of $d_{x^2-y^2}$ lie *along* the x and y axes, while the lobes of d_{xy} lie *between* the axes. The fifth orbital, d_{z^2} , has a unique shape with two lobes along the z axis and a belt centered in the xy plane. The d orbitals for levels $n > 3$ look like the $3d$ orbitals but have larger lobes.

The f orbitals first occur in level $n = 4$, and as might be expected, they have shapes even more complex than those of the d orbitals. Figure 7.17 shows representations of the $4f$ orbitals ($\ell = 3$) along with their designations. These orbitals are not involved in the bonding in any of the compounds we will consider in this text. Their shapes and labels are simply included for completeness.

So far we have talked about the shapes of the hydrogen atomic orbitals but not about their energies. For the hydrogen atom, the energy of a particular orbital is determined by its value of n . Thus *all* orbitals with the same value of n have the *same energy*—they are said to be **degenerate**. This is shown in Fig. 7.18, where the energies for the orbitals in the first three quantum levels for hydrogen are shown.

**FIGURE 7.14**

Representation of the $2p$ orbitals. (a) The electron probability distribution for a $2p$ orbital. (Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC 2402; reprinted with permission.) (b) The boundary surface representations of all three $2p$ orbitals. Note that the signs inside the surface indicate the phases (signs) of the orbital in that region of space.

Hydrogen's single electron can occupy any of its atomic orbitals. However, in the lowest energy state, the *ground state*, the electron resides in the $1s$ orbital. If energy is put into the atom, the electron can be transferred to a higher-energy orbital, producing an *excited state*.

A Summary of the Hydrogen Atom

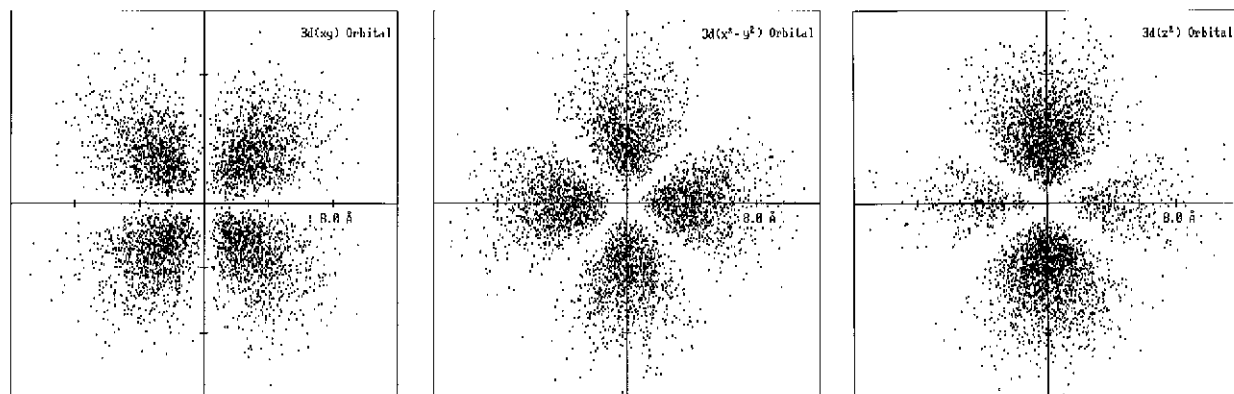
- In the quantum (wave) mechanical model, the electron is viewed as a standing wave. This representation leads to a series of wave functions (orbitals) that describe the possible energies and spatial distributions available to the electron.
- In agreement with the Heisenberg uncertainty principle, the model cannot specify the detailed electron motions. Instead, the square of the wave function represents the probability distribution of the electron in that orbital. This allows us to picture orbitals in terms of probability distributions, or electron density maps.
- The size of an orbital is arbitrarily defined as the surface that contains 90% of the total electron probability.
- The hydrogen atom has many types of orbitals. In the ground state, the single electron resides in the $1s$ orbital. The electron can be excited to higher-energy orbitals if energy is put into the atom.

**FIGURE 7.15**

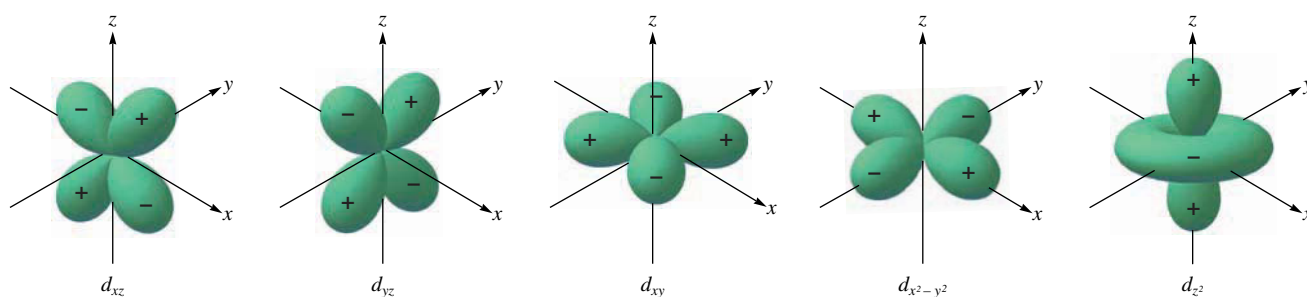
A cross section of the electron probability distribution for a $3p$ orbital.

7.8 Electron Spin and the Pauli Principle

The concept of **electron spin** was developed by Samuel Goudsmit and George Uhlenbeck while they were graduate students at the University of Leyden in the Netherlands. They found that a fourth quantum number (in addition to n , ℓ , and m_ℓ) was necessary to account for the details of the emission spectra of atoms. The spectral data indicate that the electron has a magnetic moment with two possible orientations when the atom is placed in an external magnetic field. Since they knew from classical physics that a spinning charge produces a magnetic moment, it seemed reasonable to assume that the electron could have two spin states, thus producing the two oppositely directed magnetic moments



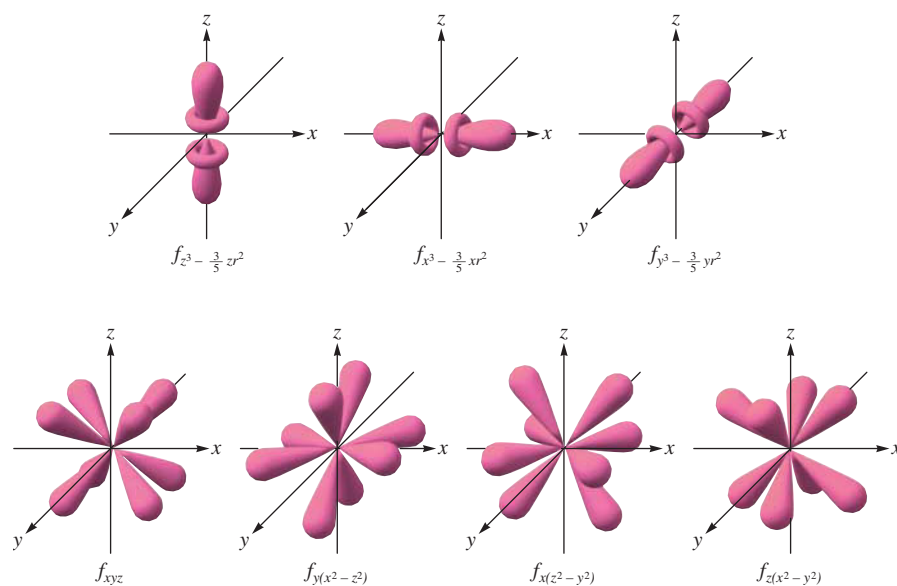
(a)



(b)

FIGURE 7.16

Representation of the $3d$ orbitals. (a) Electron density plots of selected $3d$ orbitals. (Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC 2402; reprinted with permission.) (b) The boundary surfaces of all five $3d$ orbitals, with the signs (phases) indicated.

**FIGURE 7.17**

Representation of the $4f$ orbitals in terms of their boundary surfaces.

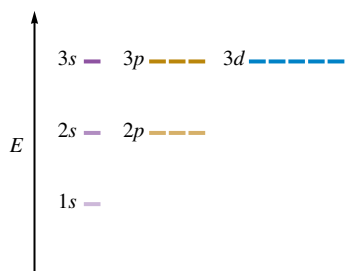


FIGURE 7.18
Orbital energy levels for the hydrogen atom.

$$m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

Each orbital can hold a maximum of two electrons.

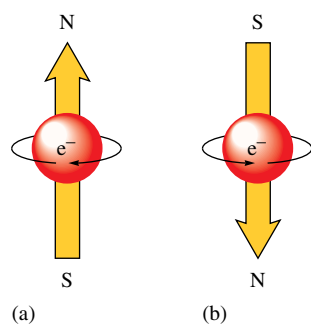


FIGURE 7.19
A picture of the spinning electron. Spinning in one direction, the electron produces the magnetic field oriented as shown in (a). Spinning in the opposite direction, it gives a magnetic field of the opposite orientation, as shown in (b).

(see Fig. 7.19). The new quantum number adopted to describe this phenomenon, called the **electron spin quantum number** (m_s), can have only one of two values, $+\frac{1}{2}$ and $-\frac{1}{2}$. We can interpret this to mean that the electron can spin in one of two opposite directions, although other interpretations also have been suggested.

For our purposes, the main significance of electron spin is connected with the postulate of Austrian physicist Wolfgang Pauli (1900–1958): *In a given atom no two electrons can have the same set of four quantum numbers (n , ℓ , m_ℓ , and m_s).* This is called the **Pauli exclusion principle**. Since electrons in the same orbital have the same values of n , ℓ , and m_ℓ , this postulate says that they must have different values of m_s . Then, since only two values of m_s are allowed, *an orbital can hold only two electrons, and they must have opposite spins*. This principle will have important consequences as we use the atomic model to account for the electron arrangements of the atoms in the periodic table.

7.9 Polyelectronic Atoms

The quantum mechanical model gives a description of the hydrogen atom that agrees very well with experimental data. However, the model would not be very useful if it did not account for the properties of all the other atoms as well.

To see how the model applies to **polyelectronic atoms**, that is, atoms with more than one electron, let's consider helium, which has two protons in its nucleus and two electrons:

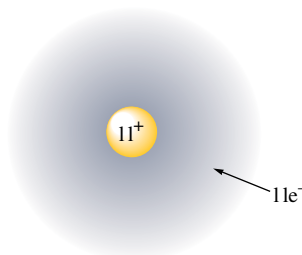


Three energy contributions must be considered in the description of the helium atom: (1) the kinetic energy of the electrons as they move around the nucleus, (2) the potential energy of attraction between the nucleus and the electrons, and (3) the potential energy of repulsion between the two electrons.

Although the helium atom can be readily described in terms of the quantum mechanical model, the Schrödinger equation that results cannot be solved exactly. The difficulty arises in dealing with the repulsions between the electrons. Since the electron pathways are unknown, the electron repulsions cannot be calculated exactly. This is called the *electron correlation problem*.

The electron correlation problem occurs with all polyelectronic atoms. To treat these systems using the quantum mechanical model, we must make approximations. Most commonly, the approximation used is to treat each electron as if it were moving in a *field of charge that is the net result of the nuclear attraction and the average repulsions of all the other electrons*.

For example, consider the sodium atom, which has 11 electrons:



Now let's single out the outermost electron and consider the forces this electron feels. The electron clearly is attracted to the highly charged nucleus. However, the electron also feels the repulsions caused by the other 10 electrons. The net effect is that the electron is not

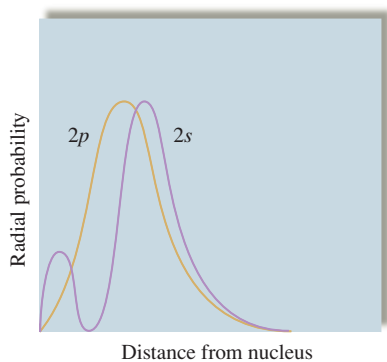
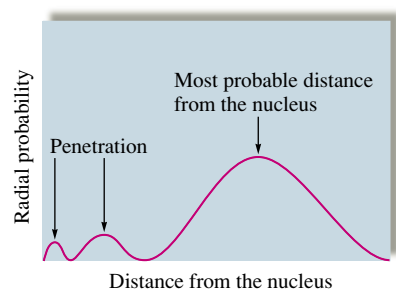
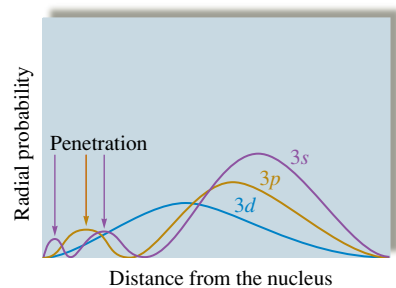


FIGURE 7.20
A comparison of the radial probability distributions of the 2s and 2p orbitals.



(a)



(b)

FIGURE 7.21
(a) The radial probability distribution for an electron in a 3s orbital. Although a 3s electron is mostly found far from the nucleus, there is a small but significant probability (shown by the arrows) of its being found close to the nucleus. The 3s electron penetrates the shield of inner electrons. (b) The radial probability distribution for the 3s, 3p, and 3d orbitals. The arrows indicate that the s orbital (red arrow) allows greater electron penetration than the p orbital (yellow arrow) does; the d orbital allows minimal electron penetration.

bound nearly as tightly to the nucleus as it would be if the other electrons were not present. We say that the electron is *screened* or *shielded* from the nuclear charge by the repulsions of the other electrons.

This picture of polyelectronic atoms leads to *hydrogenlike orbitals* for these atoms. They have the same general shapes as the orbitals for hydrogen, but their sizes and energies are different. The differences occur because of the interplay between nuclear attraction and the electron repulsions.

One especially important difference between polyelectronic atoms and the hydrogen atom is that for hydrogen all the orbitals in a given principal quantum level have the same energy (they are said to be *degenerate*). This is not the case for polyelectronic atoms, where we find that for a given principal quantum level the orbitals vary in energy as follows:

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

In other words, when electrons are placed in a particular quantum level, they “prefer” the orbitals in the order *s*, *p*, *d*, and then *f*. Why does this happen? Although the concept of orbital energies is a complicated matter, we can qualitatively understand why the 2s orbital has a lower energy than the 2p orbital in a polyelectronic atom by looking at the probability profiles of these orbitals (see Fig. 7.20). Notice that the 2p orbital has its maximum probability closer to the nucleus than the 2s. This might lead us to predict that the 2p would be preferable (lower energy) to the 2s orbital. However, notice the small hump of electron density that occurs in the 2s profile very near the nucleus. This means that although an electron in the 2s orbital spends most of its time a little farther from the nucleus than does an electron in the 2p orbital, it spends a small but very significant amount of time very near the nucleus. We say that the 2s electron *penetrates* to the nucleus more than one in the 2p orbital. This *penetration effect* causes an electron in a 2s orbital to be attracted to the nucleus more strongly than an electron in a 2p orbital. That is, the 2s orbital is lower in energy than the 2p orbitals in a polyelectronic atom.

The same thing happens in the other principal quantum levels as well. Figure 7.21 shows the radial probability profiles for the 3s, 3p, and 3d orbitals. Note again the hump in the 3s profile very near the nucleus. The innermost hump for the 3p is farther out, which causes the energy of the 3s orbital to be lower than that of the 3p. Notice that the 3d orbital has its maximum probability closer to the nucleus than either the 3s or 3p does, but its absence of probability near the nucleus causes it to be highest in energy of the three orbitals. The relative energies of the orbitals for $n = 3$ are

$$E_{3s} < E_{3p} < E_{3d}$$

In general, the more effectively an orbital allows its electron to penetrate the shielding electrons to be close to the nuclear charge, the lower is the energy of that orbital.

A summary diagram of the orders of the orbital energies for polyelectronic atoms is represented in Fig. 7.22. We will use these orbitals in Section 7.11 to show how the electrons are arranged in polyelectronic atoms.

7.10 The History of the Periodic Table

The modern periodic table contains a tremendous amount of useful information. In this section we will discuss the origin of this valuable tool; later we will see how the quantum mechanical model for the atom explains the periodicity of chemical properties. Certainly the greatest triumph of the quantum mechanical model is its ability to account for the arrangement of the elements in the periodic table.

The periodic table was originally constructed to represent the patterns observed in the chemical properties of the elements. As chemistry progressed during the eighteenth and nineteenth centuries, it became evident that the earth is composed of a great many

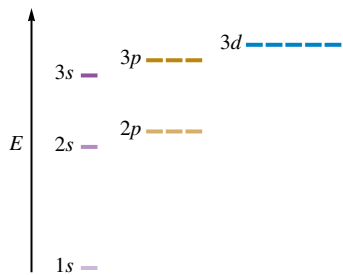


FIGURE 7.22
The orders of the energies of the orbitals in the first three levels of polyelectronic atoms.

elements with very different properties. Things are much more complicated than the simple model of earth, air, fire, and water suggested by the ancients. At first, the array of elements and properties was bewildering. Gradually, however, patterns were noticed.

The first chemist to recognize patterns was Johann Dobereiner (1780–1849), who found several groups of three elements that have similar properties, for example, chlorine, bromine, and iodine. However, as Dobereiner attempted to expand this model of *triads* (as he called them) to the rest of the known elements, it became clear that it was severely limited.

The next notable attempt was made by the English chemist John Newlands, who in 1864 suggested that elements should be arranged in *octaves*, based on the idea that certain properties seemed to repeat for every eighth element in a way similar to the musical scale, which repeats for every eighth tone. Even though this model managed to group several elements with similar properties, it was not generally successful.

The present form of the periodic table was conceived independently by two chemists: the German Julius Lothar Meyer (1830–1895) and Dmitri Ivanovich Mendeleev (1834–1907), a Russian (Fig. 7.23). Usually Mendeleev is given most of the credit, because it was he who emphasized how useful the table could be in predicting the existence and properties of still unknown elements. For example, in 1872 when Mendeleev first published his table (see Fig. 7.24), the elements gallium, scandium, and germanium were unknown. Mendeleev correctly predicted the existence and properties of these elements from gaps in his periodic table. The data for germanium (which Mendeleev called “*ekasilicon*”) are shown in Table 7.3. Note the excellent agreement between the actual values and Mendeleev’s predictions, which were based on the properties of other members in the group of elements similar to germanium.

Using his table, Mendeleev also was able to correct several values for atomic masses. For example, the original atomic mass of 76 for indium was based on the assumption that indium oxide had the formula InO . This atomic mass placed indium, which has metallic properties, among the nonmetals. Mendeleev assumed the atomic mass was probably incorrect and proposed that the formula of indium oxide was really In_2O_3 . Based on this correct formula, indium has an atomic mass of approximately 113, placing the element among the metals. Mendeleev also corrected the atomic masses of beryllium and uranium.

Because of its obvious usefulness, Mendeleev’s periodic table was almost universally adopted, and it remains one of the most valuable tools at the chemist’s disposal. For example, it is still used to predict the properties of elements recently discovered, as shown in Table 7.4.

A current version of the periodic table is shown inside the front cover of this book. The only fundamental difference between this table and that of Mendeleev is that it lists the elements in order by atomic number rather than by atomic mass. The reason for this will become clear later in this chapter as we explore the electron arrangements of the atom. Another recent format of the table is discussed in the following section.



FIGURE 7.23
Dmitri Ivanovich Mendeleev (1834–1907), born in Siberia as the youngest of 17 children, taught chemistry at the University of St. Petersburg. In 1860 Mendeleev heard the Italian chemist Cannizzaro lecture on a reliable method for determining the correct atomic masses of the elements. This important development paved the way for Mendeleev’s own brilliant contribution to chemistry—the periodic table. In 1861 Mendeleev returned to St. Petersburg, where he wrote a book on organic chemistry. Later Mendeleev also wrote a book on inorganic chemistry, and he was struck by the fact that the systematic approach characterizing organic chemistry was lacking in inorganic chemistry. In attempting to systematize inorganic chemistry, he eventually arranged the elements in the form of the periodic table.

Mendeleev was a versatile genius who was interested in many fields of science. He worked on many problems associated with Russia’s natural resources, such as coal, salt, and various metals. Being particularly interested in the petroleum industry, he visited the United States in 1876 to study the Pennsylvania oil fields. His interests also included meteorology and hot-air balloons. In 1887 he made an ascent in a balloon to study a total eclipse of the sun.

TABELLE II

| REIHEN | GRUPPE I. — R ² O | GRUPPE II. — RO | GRUPPE III. — R ² O ³ | GRUPPE IV. RH ⁴ RO ² | GRUPPE V. RH ³ R ² O ⁵ | GRUPPE VI. RH ² RO ³ | GRUPPE VII. RH R ² O 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 | — | — |

FIGURE 7.24

Mendeleev's early periodic table, published in 1872. Note the spaces left for missing elements with atomic masses 44, 68, 72, and 100.

(From *Annalen der Chemie und Pharmacie*, VIII, Supplementary Volume for 1872, page 511.)

TABLE 7.3 Comparison of the Properties of Germanium as Predicted by Mendeleev and as Actually Observed

| Properties of Germanium | Predicted in 1871 | Observed in 1886 |
|-------------------------|-----------------------|------------------------|
| Atomic weight | 72 | 72.3 |
| Density | 5.5 g/cm ³ | 5.47 g/cm ³ |
| Specific heat | 0.31 J/(°C · g) | 0.32 J/(°C · g) |
| Melting point | Very high | 960°C |
| Oxide formula | RO ₂ | GeO ₂ |
| Oxide density | 4.7 g/cm ³ | 4.70 g/cm ³ |
| Chloride formula | RCl ₄ | GeCl ₄ |
| bp of chloride | 100°C | 86°C |

TABLE 7.4 Predicted Properties of Elements 113 and 114

| Property | Element 113 | Element 114 |
|-----------------|-------------|-------------|
| Chemically like | Thallium | Lead |
| Atomic mass | 297 | 298 |
| Density | 16 g/mL | 14 g/mL |
| Melting point | 430°C | 70°C |
| Boiling point | 1100°C | 150°C |

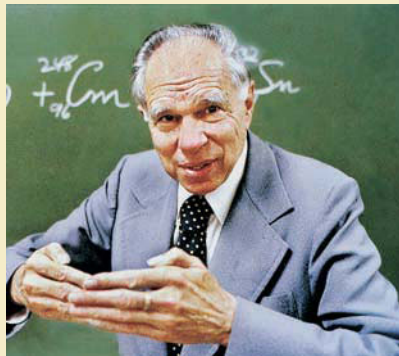


CHEMICAL IMPACT

The Growing Periodic Table

The periodic table of the elements has undergone significant changes since Mendeleev published his first version in 1869. In particular, in the past 60 years we have added 20 new elements beyond uranium. These so-called transuranium elements all have been synthesized using particle accelerators.

Edwin M. McMillan and Phillip H. Abelson succeeded in synthesizing the first transuranium element, neptunium (element 93), at the University of California, Berkeley, in 1940. In 1941, Glenn T. Seaborg synthesized and identified element 94 (plutonium), and over the next several years, researchers under his direction at UC Berkeley discovered nine other transuranium elements. In 1945 Seaborg suggested that the elements heavier than element 89 (actinium) were misplaced as transition metals and should be relocated on the periodic table in a series below the transition metals



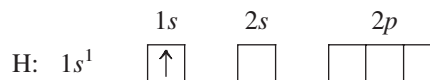
Dr. Glenn Seaborg.

(the actinide series). Seaborg was awarded a Nobel Prize in chemistry in 1951 for his contributions.

7.11 The Aufbau Principle and the Periodic Table

We can use the quantum mechanical model of the atom to show how the electron arrangements in the hydrogenlike atomic orbitals of the various atoms account for the organization of the periodic table. Our main assumption here is that all atoms have the same type of orbitals as have been described for the hydrogen atom. *As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these hydrogenlike orbitals.* This is called the **aufbau principle**.

Hydrogen has one electron, which occupies the $1s$ orbital in its ground state. The configuration for hydrogen is written as $1s^1$, which can be represented by the following *orbital diagram*:



The arrow represents an electron spinning in a particular direction.

The next element, *helium*, has two electrons. Since two electrons with opposite spins can occupy an orbital, according to the Pauli exclusion principle, the electrons for helium are in the $1s$ orbital with opposite spins, producing a $1s^2$ configuration:



Lithium has three electrons, two of which can go into the $1s$ orbital before the orbital is filled. Since the $1s$ orbital is the only orbital for $n = 1$, the third electron will occupy the lowest-energy orbital with $n = 2$, or the $2s$ orbital, giving a $1s^2 2s^1$ configuration:



Aufbau is German for “building up.”

H ($Z = 1$)

He ($Z = 2$)

Li ($Z = 3$)

Be ($Z = 4$)

B ($Z = 5$)

etc.

($Z =$ atomic number)

In recent years, three major research facilities have taken the lead in synthesizing new elements. Along with UC Berkeley, Nuclear Research in Dubna, Russia, and GSI in Darmstadt, Germany, were responsible for synthesizing elements 104–112 by the end of 1996.

As it turned out, naming the new elements has caused more controversy than anything else connected with their discovery. Traditionally, the discoverer of an element is allowed to name it. However, because there is some dispute among the researchers at Berkeley, Darmstadt, and Dubna about who really discovered the various elements, competing names were submitted. After years of controversy, the International Union of Pure and Applied Chemistry (IUPAC) finally settled on the names listed in the accompanying table.

The name for element 106 in honor of Glenn Seaborg caused special controversy because an element had never before been named for a living person (Dr. Seaborg died in 1999). However, because of Seaborg's commanding stature

in the scientific community, the name seaborgium was adopted.

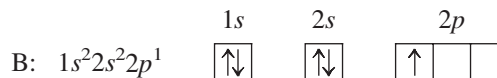
Names for the elements beyond 111 have not been decided, and these elements are represented on many periodic tables with three letters that symbolize their atomic numbers. More traditional names will no doubt be assigned in due time (hopefully with a minimum of controversy).

| Atomic Number | Name | Symbol |
|---------------|---------------|--------|
| 104 | Rutherfordium | Rf |
| 105 | Dubium | Db |
| 106 | Seaborgium | Sg |
| 107 | Bohrium | Bh |
| 108 | Hassium | Hs |
| 109 | Meitnerium | Mt |
| 110 | Darmstadtium | Ds |
| 111 | Roentgenium | Rg |

The next element, *beryllium*, has four electrons, which occupy the $1s$ and $2s$ orbitals:



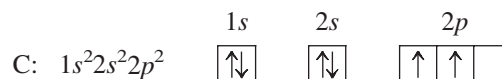
Boron has five electrons, four of which occupy the $1s$ and $2s$ orbitals. The fifth electron goes into the second type of orbital with $n = 2$, the $2p$ orbitals:



Since all the $2p$ orbitals have the same energy (are degenerate), it does not matter which $2p$ orbital the electron occupies.

Carbon is the next element and has six electrons. Two electrons occupy the $1s$ orbital, two occupy the $2s$ orbital, and two occupy $2p$ orbitals. Since there are three $2p$ orbitals with the same energy, the mutually repulsive electrons will occupy *separate* $2p$ orbitals. This behavior is summarized by **Hund's rule** (named for the German physicist F. H. Hund), which states that *the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate orbitals*. By convention, the unpaired electrons are represented as having parallel spins (with spin "up").

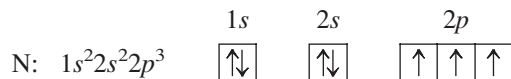
The configuration for carbon could be written $1s^2 2s^2 2p^1 2p^1$ to indicate that the electrons occupy separate $2p$ orbitals. However, the configuration is usually given as $1s^2 2s^2 2p^2$, and it is understood that the electrons are in different $2p$ orbitals. The orbital diagram for carbon is



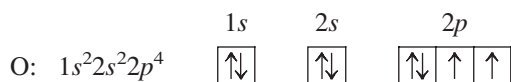
Note that the unpaired electrons in the $2p$ orbitals are shown with parallel spins.

For an atom with unfilled subshells, the lowest energy is achieved by electrons occupying separate orbitals with parallel spins, as far as allowed by the Pauli exclusion principle.

The configuration for *nitrogen*, which has seven electrons, is $1s^22s^22p^3$. The three electrons in the $2p$ orbitals occupy separate orbitals with parallel spins:

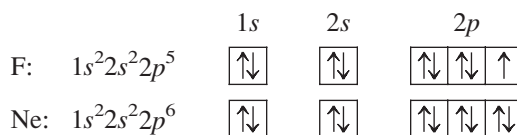


The configuration for *oxygen*, which has eight electrons, is $1s^22s^22p^4$. One of the $2p$ orbitals is now occupied by a pair of electrons with opposite spins, as required by the Pauli exclusion principle:



[Ne] is shorthand for $1s^22s^22p^6$.

The orbital diagrams and electron configurations for *fluorine* (nine electrons) and *neon* (ten electrons) are as follows:



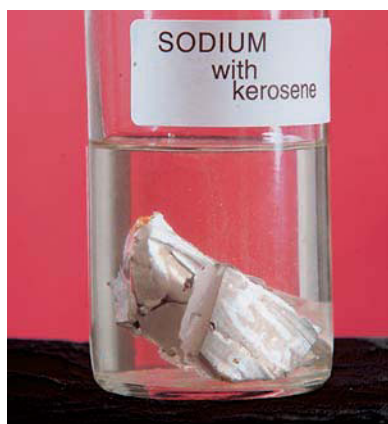
With neon, the orbitals with $n = 1$ and $n = 2$ are now completely filled.

For *sodium*, the first ten electrons occupy the $1s$, $2s$, and $2p$ orbitals, and the eleventh electron must occupy the first orbital with $n = 3$, the $3s$ orbital. The electron configuration for sodium is $1s^22s^22p^63s^1$. To avoid writing the inner-level electrons, this configuration is often abbreviated as $[\text{Ne}]3s^1$, where [Ne] represents the electron configuration of neon, $1s^22s^22p^6$.

The next element, *magnesium*, has the configuration $1s^22s^22p^63s^2$, or $[\text{Ne}]3s^2$. Then the next six elements, *aluminum* through *argon*, have configurations obtained by filling the $3p$ orbitals one electron at a time. Figure 7.25 summarizes the electron configurations of the first 18 elements by giving the number of electrons in the type of orbital occupied last.

At this point it is useful to introduce the concept of **valence electrons**, *the electrons in the outermost principal quantum level of an atom*. The valence electrons of the nitrogen atom, for example, are the $2s$ and $2p$ electrons. For the sodium atom, the valence electron is the electron in the $3s$ orbital, and so on. Valence electrons are the most important electrons to chemists because they are involved in bonding, as we will see in the next two chapters. The inner electrons are known as **core electrons**.

Note in Fig. 7.25 that a very important pattern is developing: *The elements in the same group (vertical column of the periodic table) have the same valence electron configuration*. Remember that Mendeleev originally placed the elements in groups based on similarities in chemical properties. Now we understand the reason behind these



Sodium metal is so reactive that it is stored under kerosene to protect it from the oxygen in the air.



A vial containing potassium metal. The sealed vial contains an inert gas to protect the potassium from reacting with oxygen.

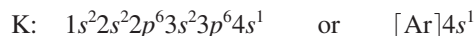
FIGURE 7.25

The electron configurations in the type of orbital occupied last for the first 18 elements.

| | | | | | | | | | |
|--------------|--------------|--|--|--------------|--------------|-------------|--------------|--------------|--------------|
| H $1s^1$ | | | | | | | He $1s^2$ | | |
| Li $2s^1$ | Be $2s^2$ | | | B $2p^1$ | C $2p^2$ | N $2p^3$ | O $2p^4$ | F $2p^5$ | Ne $2p^6$ |
| Na $3s^1$ | Mg $3s^2$ | | | Al $3p^1$ | Si $3p^2$ | P $3p^3$ | S $3p^4$ | Cl $3p^5$ | Ar $3p^6$ |

groupings. Elements with the same valence electron configuration show similar chemical behavior.

The element after argon is *potassium*. Since the $3p$ orbitals are fully occupied in argon, we might expect the next electron to go into a $3d$ orbital (recall that for $n = 3$ the orbitals are $3s$, $3p$, and $3d$). However, the chemistry of potassium is clearly very similar to that of lithium and sodium, indicating that the last electron in potassium occupies the $4s$ orbital instead of one of the $3d$ orbitals, a conclusion confirmed by many types of experiments. The electron configuration of potassium is



The next element is *calcium*:



The next element, *scandium*, begins a series of 10 elements (scandium through zinc) called the **transition metals**, whose configurations are obtained by adding electrons to the five $3d$ orbitals. The configuration of scandium is



That of *titanium* is



And that of *vanadium* is

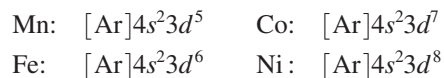


Chromium is the next element. The expected configuration is $[\text{Ar}]4s^2 3d^4$. However, the observed configuration is



The explanation for this configuration of chromium is beyond the scope of this book. In fact, chemists are still disagreeing over the exact cause of this anomaly. Note, however, that the observed configuration has both the $4s$ and $3d$ orbitals half-filled. This is a good way to remember the correct configuration.

The next four elements, *manganese* through *nickel*, have the expected configurations:



The configuration for *copper* is expected to be $[\text{Ar}]4s^2 3d^9$. However, the observed configuration is



In this case, a half-filled $4s$ orbital and a filled set of $3d$ orbitals characterize the actual configuration.

Zinc has the expected configuration:



The configurations of the transition metals are shown in Fig. 7.26. After that, the next six elements, *gallium* through *krypton*, have configurations that correspond to filling the $4p$ orbitals (see Fig. 7.26).

The entire periodic table is represented in Fig. 7.27 in terms of which orbitals are being filled. The valence electron configurations are given in Fig. 7.28. From these two figures, note the following additional points:

1. The $(n + 1)s$ orbitals always fill before the nd orbitals. For example, the $5s$ orbitals fill in rubidium and strontium before the $4d$ orbitals fill in the second row of transition



Calcium metal.



Chromium is often used to plate bumpers and hood ornaments, such as this statue of Mercury found on a 1929 Buick.

The $(n + 1)s$ orbital fills before the nd orbitals.

| | | | | | | | | | | | | | | | | | |
|----------------------|-----------------------|-----------------------|-----------------------|----------------------|---------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|--|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| K 4s ¹ | Ca 4s ² | Sc 3d ¹ | Ti 3d ² | V 3d ³ | Cr 4s ¹ 3d ⁵ | Mn 3d ⁵ | Fe 3d ⁶ | Co 3d ⁷ | Ni 3d ⁸ | Cu 4s ¹ 3d ¹⁰ | Zn 3d ¹⁰ | Ga 4p ¹ | Ge 4p ² | As 4p ³ | Se 4p ⁴ | Br 4p ⁵ | Kr 4p ⁶ |

FIGURE 7.26

Electron configurations for potassium through krypton. The transition metals (scandium through zinc) have the general configuration $[\text{Ar}]4s^23d^n$, except for chromium and copper.

metals (yttrium through cadmium). This early filling of the s orbitals can be explained by the penetration effect. For example, the $4s$ orbital allows for so much more penetration to the vicinity of the nucleus that it becomes lower in energy than the $3d$ orbital. Thus the $4s$ fills before the $3d$. The same things can be said about the $5s$ and $4d$, the $6s$ and $5d$, and the $7s$ and $6d$ orbitals.

Lanthanides are elements in which the $4f$ orbitals are being filled.

- After lanthanum, which has the configuration $[\text{Xe}]6s^25d^1$, a group of 14 elements called the **lanthanide series**, or the **lanthanides**, occurs. This series of elements corresponds to the filling of the seven $4f$ orbitals. Note that sometimes an electron occupies a $5d$ orbital instead of a $4f$ orbital. This occurs because the energies of the $4f$ and $5d$ orbitals are very similar.
- After actinium, which has the configuration $[\text{Rn}]7s^26d^1$, a group of 14 elements called the **actinide series**, or the **actinides**, occurs. This series corresponds to the filling of the seven $5f$ orbitals. Note that sometimes one or two electrons occupy the $6d$ orbitals instead of the $5f$ orbitals, because these orbitals have very similar energies.

Actinides are elements in which the $5f$ orbitals are being filled.

| | 1A | Group | | | | | | | | | | 8A | | | | | |
|---|----|-------|--|--|--|----|--|--|--|--|--|----|----|--|--|--|----|
| 1 | 1s | 2A | | | | | | | | | | | | | | | 1s |
| 2 | 2s | | | | | | | | | | | | 2p | | | | |
| 3 | 3s | | | | | | | | | | | | 3p | | | | |
| 4 | 4s | | | | | 3d | | | | | | | 4p | | | | |
| 5 | 5s | | | | | 4d | | | | | | | 5p | | | | |
| 6 | 6s | La | | | | 5d | | | | | | | 6p | | | | |
| 7 | 7s | Ac | | | | 6d | | | | | | | | | | | |
| | | | | | | | | | | | | | 4f | | | | |
| | | | | | | | | | | | | | 5f | | | | |

FIGURE 7.27

The orbitals being filled for elements in various parts of the periodic table. Note that in going along a horizontal row (a period), the $(n + 1)s$ orbital fills before the nd orbital. The group labels indicate the number of valence electrons (ns plus np electrons) for the elements in each group.

The group label tells the total number of valence electrons for that group.

- The group labels for Groups 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A indicate the *total number* of valence electrons for the atoms in these groups. For example, all the elements in Group 5A have the configuration ns^2np^3 . (The *d* electrons fill one period late and are usually not counted as valence electrons.) The meaning of the group labels for the transition metals is not as clear as for the Group A elements, and these will not be used in this text.
- The groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A are often called the **main-group**, or **representative, elements**. Every member of these groups has the same valence electron configuration.

The International Union of Pure and Applied Chemistry (IUPAC), a body of scientists organized to standardize scientific conventions, has recommended a new form for the periodic table, which the American Chemical Society has adopted (see the blue numbers in Fig. 7.28). In this new version the group number indicates the number of *s*, *p*, and *d* electrons added since the last noble gas. We will not use the new format in this book, but you

| Period number, highest occupied electron level | Representative Elements | | <i>d</i> -Transition Elements | | | | | | | | | | Representative Elements | | | | | Noble Gases | |
|--|----------------------------|-------------------------------|-------------------------------|-------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|------------------------|------------------------|------------------------|--|
| | 1A ns^1 | Group numbers 2A ns^2 | | | | | | | | | | | 3A ns^2np^1 | 4A ns^2np^2 | 5A ns^2np^3 | 6A ns^2np^4 | 7A ns^2np^5 | 18 8A ns^2np^6 | |
| 1 | 1 H $1s^1$ | 2 He $1s^2$ | | | | | | | | | | | | | | | | 2 He $1s^2$ | |
| 2 | 3 Li $2s^1$ | 4 Be $2s^2$ | | | | | | | | | | | 5 B $2s^2p^1$ | 6 C $2s^2p^2$ | 7 N $2s^2p^3$ | 8 O $2s^2p^4$ | 9 F $2s^2p^5$ | 10 Ne $2s^2p^6$ | |
| 3 | 11 Na $3s^1$ | 12 Mg $3s^2$ | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 Al $3s^23p^1$ | 14 Si $3s^23p^2$ | 15 P $3s^23p^3$ | 16 S $3s^23p^4$ | 17 Cl $3s^23p^5$ | 18 Ar $3s^23p^6$ | |
| 4 | 19 K $4s^1$ | 20 Ca $4s^2$ | 21 Sc $4s^23d^1$ | 22 Ti $4s^23d^2$ | 23 V $4s^23d^3$ | 24 Cr $4s^13d^5$ | 25 Mn $4s^23d^5$ | 26 Fe $4s^23d^6$ | 27 Co $4s^23d^7$ | 28 Ni $4s^23d^8$ | 29 Cu $4s^13d^{10}$ | 30 Zn $4s^23d^{10}$ | 31 Ga $4s^24p^1$ | 32 Ge $4s^24p^2$ | 33 As $4s^24p^3$ | 34 Se $4s^24p^4$ | 35 Br $4s^24p^5$ | 36 Kr $4s^24p^6$ | |
| 5 | 37 Rb $5s^1$ | 38 Sr $5s^2$ | 39 Y $5s^24d^1$ | 40 Zr $5s^24d^2$ | 41 Nb $5s^14d^4$ | 42 Mo $5s^14d^5$ | 43 Tc $5s^14d^6$ | 44 Ru $5s^14d^7$ | 45 Rh $5s^14d^8$ | 46 Pd $4d^{10}$ | 47 Ag $5s^14d^{10}$ | 48 Cd $5s^24d^{10}$ | 49 In $5s^25p^1$ | 50 Sn $5s^25p^2$ | 51 Sb $5s^25p^3$ | 52 Te $5s^25p^4$ | 53 I $5s^25p^5$ | 54 Xe $5s^25p^6$ | |
| 6 | 55 Cs $6s^1$ | 56 Ba $6s^2$ | 57 La* $6s^25d^1$ | 72 Hf $4f^{14}6s^25d^2$ | 73 Ta $6s^25d^3$ | 74 W $6s^25d^4$ | 75 Re $6s^25d^5$ | 76 Os $6s^25d^6$ | 77 Ir $6s^25d^7$ | 78 Pt $6s^15d^9$ | 79 Au $6s^15d^{10}$ | 80 Hg $6s^25d^{10}$ | 81 Tl $6s^26p^1$ | 82 Pb $6s^26p^2$ | 83 Bi $6s^26p^3$ | 84 Po $6s^26p^4$ | 85 At $6s^26p^5$ | 86 Rn $6s^26p^6$ | |
| 7 | 87 Fr $7s^1$ | 88 Ra $7s^2$ | 89 Ac** $7s^26d^1$ | 104 Rf $7s^26d^2$ | 105 Db $7s^26d^3$ | 106 Sg $7s^26d^4$ | 107 Bh $7s^26d^5$ | 108 Hs $7s^26d^6$ | 109 Mt $7s^26d^7$ | 110 Ds $7s^26d^8$ | 111 Rg $7s^16d^{10}$ | 112 Uub $7s^26d^{10}$ | 113 Uut $7s^26d^{10}7p^1$ | 114 Uuq $7s^26d^{10}7p^2$ | 115 Uup $7s^26d^{10}7p^3$ | | | | |
| | | | <i>f</i> -Transition Elements | | | | | | | | | | | | | | | | |
| *Lanthanides | 58 Ce $6s^24f^15d^1$ | 59 Pr $6s^24f^35d^0$ | 60 Nd $6s^24f^45d^0$ | 61 Pm $6s^24f^55d^0$ | 62 Sm $6s^24f^65d^0$ | 63 Eu $6s^24f^75d^0$ | 64 Gd $6s^24f^75d^1$ | 65 Tb $6s^24f^95d^0$ | 66 Dy $6s^24f^{10}5d^0$ | 67 Ho $6s^24f^{11}5d^0$ | 68 Er $6s^24f^{12}5d^0$ | 69 Tm $6s^24f^{13}5d^0$ | 70 Yb $6s^24f^{14}5d^0$ | 71 Lu $6s^24f^{14}5d^1$ | | | | | |
| **Actinides | 90 Th $7s^25f^06d^2$ | 91 Pa $7s^25f^26d^1$ | 92 U $7s^25f^36d^1$ | 93 Np $7s^25f^46d^1$ | 94 Pu $7s^25f^66d^0$ | 95 Am $7s^25f^76d^0$ | 96 Cm $7s^25f^76d^1$ | 97 Bk $7s^25f^96d^0$ | 98 Cf $7s^25f^{10}6d^0$ | 99 Es $7s^25f^{11}6d^0$ | 100 Fm $7s^25f^{12}6d^0$ | 101 Md $7s^25f^{13}6d^0$ | 102 No $7s^25f^{14}6d^0$ | 103 Lr $7s^25f^{14}6d^1$ | | | | | |

FIGURE 7.28 The periodic table with atomic symbols, atomic numbers, and partial electron configurations.

should be aware that the familiar periodic table may be soon replaced by this or a similar format.

The results considered in this section are very important. We have seen that the quantum mechanical model can be used to explain the arrangement of the elements in the periodic table. This model allows us to understand that the similar chemistry exhibited by the members of a given group arises from the fact that they all have the same valence electron configuration. Only the principal quantum number of the valence orbitals changes in going down a particular group.

It is important to be able to give the electron configuration for each of the main-group elements. This is most easily done by using the periodic table. If you understand how the table is organized, it is not necessary to memorize the order in which the orbitals fill. Review Figs. 7.27 and 7.28 to make sure that you understand the correspondence between the orbitals and the periods and groups.

Predicting the configurations of the transition metals ($3d$, $4d$, and $5d$ elements), the lanthanides ($4f$ elements), and the actinides ($5f$ elements) is somewhat more difficult because there are many exceptions of the type encountered in the first-row transition metals (the $3d$ elements). You should memorize the configurations of chromium and copper, the two exceptions in the first-row transition metals, since these elements are often encountered.

When an electron configuration is given in this text, the orbitals are listed in the order in which they fill.

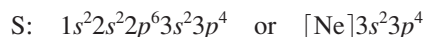
Cr: $[\text{Ar}]4s^13d^5$
Cu: $[\text{Ar}]4s^13d^{10}$

Sample Exercise 7.7 Electron Configurations

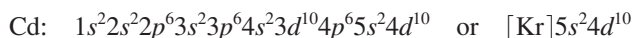
Give the electron configurations for sulfur (S), cadmium (Cd), hafnium (Hf), and radium (Ra) using the periodic table inside the front cover of this book.

Solution

Sulfur is element 16 and resides in Period 3, where the $3p$ orbitals are being filled (see Fig. 7.29). Since sulfur is the fourth among the “ $3p$ elements,” it must have four $3p$ electrons. Its configuration is



Cadmium is element 48 and is located in Period 5 at the end of the $4d$ transition metals, as shown in Fig. 7.29. It is the tenth element in the series and thus has 10 electrons in the $4d$ orbitals, in addition to the 2 electrons in the $5s$ orbital. The configuration is



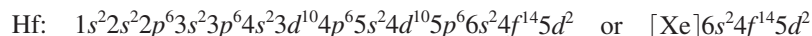
Hafnium is element 72 and is found in Period 6, as shown in Fig. 7.29. Note that it occurs just after the lanthanide series. Thus the $4f$ orbitals are already filled. Hafnium is

| | | Group | | | | | | | | | | | | | | | | | | |
|---|------|-------|----|----|----|--|--|--|--|--|------|--|--|----|----|----|------|------|----|--|
| | | 1A | 2A | | | | | | | | | | | 3A | 4A | 5A | 6A | 7A | 8A | |
| 1 | $1s$ | | | | | | | | | | | | | | | | | | | |
| 2 | $2s$ | | | | | | | | | | | | | | | | $2p$ | | | |
| 3 | $3s$ | | | | | | | | | | | | | | | | $3p$ | S | | |
| 4 | $4s$ | | | | | | | | | | $3d$ | | | | | | | $4p$ | | |
| 5 | $5s$ | | | | | | | | | | $4d$ | | | | | Cd | | $5p$ | | |
| 6 | $6s$ | | | La | Hf | | | | | | $5d$ | | | | | | | $6p$ | | |
| 7 | $7s$ | | | Ra | Ac | | | | | | $6d$ | | | | | | | | | |

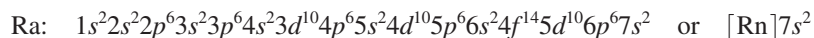
| | | | | | | | | | | | | | |
|--|--|--|--|--|--|--|--|------|--|--|--|--|--|
| | | | | | | | | $4f$ | | | | | |
| | | | | | | | | $5f$ | | | | | |

FIGURE 7.29
The positions of the elements considered in Sample Exercise 7.7.

the second member of the $5d$ transition series and has two $5d$ electrons. The configuration is



Radium is element 88 and is in Period 7 (and Group 2A), as shown in Fig. 7.29. Thus radium has two electrons in the $7s$ orbital, and the configuration is



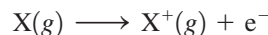
See Exercises 7.69 through 7.72.

7.12 Periodic Trends in Atomic Properties

We have developed a fairly complete picture of polyelectronic atoms. Although the model is rather crude because the nuclear attractions and electron repulsions are simply lumped together, it is very successful in accounting for the periodic table of elements. We will next use the model to account for the observed trends in several important atomic properties: ionization energy, electron affinity, and atomic size.

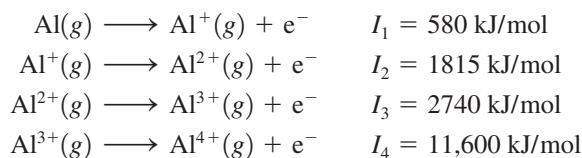
Ionization Energy

Ionization energy is the energy required to remove an electron from a gaseous atom or ion:



where the atom or ion is assumed to be in its ground state.

To introduce some of the characteristics of ionization energy, we will consider the energy required to remove several electrons in succession from aluminum in the gaseous state. The ionization energies are



Several important points can be illustrated from these results. In a stepwise ionization process, it is always the highest-energy electron (the one bound least tightly) that is removed first. The **first ionization energy** I_1 is the energy required to remove the highest-energy electron of an atom. The first electron removed from the aluminum atom comes from the $3p$ orbital (Al has the electron configuration $[\text{Ne}]3s^2 3p^1$). The second electron comes from the $3s$ orbital (since Al^+ has the configuration $[\text{Ne}]3s^2$). Note that the value of I_1 is considerably smaller than the value of I_2 , the **second ionization energy**.

This makes sense for several reasons. The primary factor is simply charge. Note that the first electron is removed from a neutral atom (Al), whereas the second electron is removed from a $1+$ ion (Al^+). The increase in positive charge binds the electrons more firmly, and the ionization energy increases. The same trend shows up in the third (I_3) and fourth (I_4) ionization energies, where the electron is removed from the Al^{2+} and Al^{3+} ions, respectively.

The increase in successive ionization energies for an atom also can be interpreted using our simple model for polyelectronic atoms. The increase in ionization energy from I_1 to I_2 makes sense because the first electron is removed from a $3p$ orbital that is higher in energy than the $3s$ orbital from which the second electron is removed. The largest jump in ionization energy by far occurs in going from the third ionization energy (I_3) to the fourth (I_4). This is so because I_4 corresponds to removing a core electron (Al^{3+} has the configuration $1s^2 2s^2 2p^6$), and core electrons are bound much more tightly than valence electrons.



Visualization: Periodic Table Trends

Ionization energy results in the formation of a **positive ion**.



Setting the aluminum cap on the Washington Monument in 1884. At that time, aluminum was regarded as a precious metal.

TABLE 7.5 Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

| Element | I_1 | I_2 | I_3 | I_4 | I_5 | I_6 | I_7 |
|---------|-------|-------|-------|-----------------|--------|--------|--------|
| Na | 495 | 4560 | | | | | |
| Mg | 735 | 1445 | 7730 | Core electrons* | | | |
| Al | 580 | 1815 | 2740 | 11,600 | | | |
| Si | 780 | 1575 | 3220 | 4350 | 16,100 | | |
| P | 1060 | 1890 | 2905 | 4950 | 6270 | 21,200 | |
| S | 1005 | 2260 | 3375 | 4565 | 6950 | 8490 | 27,000 |
| Cl | 1255 | 2295 | 3850 | 5160 | 6560 | 9360 | 11,000 |
| Ar | 1527 | 2665 | 3945 | 5770 | 7230 | 8780 | 12,000 |

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

↑ General decrease

→ General increase

TABLE 7.6 First Ionization Energies for the Alkali Metals and Noble Gases

| Atom | I_1 (kJ/mol) |
|-----------------|----------------|
| Group 1A | |
| Li | 520 |
| Na | 495 |
| K | 419 |
| Rb | 409 |
| Cs | 382 |
| Group 8A | |
| He | 2377 |
| Ne | 2088 |
| Ar | 1527 |
| Kr | 1356 |
| Xe | 1176 |
| Rn | 1042 |

Table 7.5 gives the values of ionization energies for all the Period 3 elements. Note the large jump in energy in each case in going from removal of valence electrons to removal of core electrons.

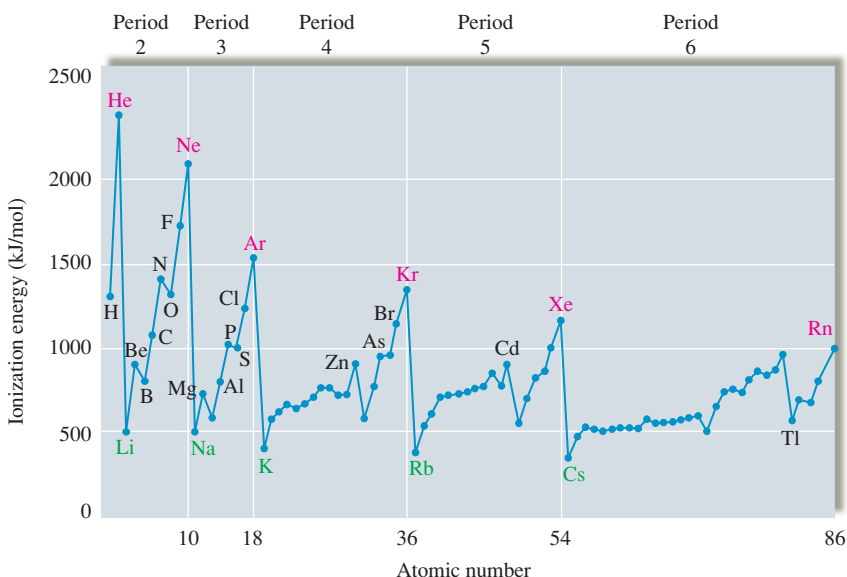
The values of the first ionization energies for the elements in the first six periods of the periodic table are graphed in Fig. 7.30. Note that in general as we go *across a period from left to right*, the first ionization energy increases. This is consistent with the idea that electrons added in the same principal quantum level do not completely shield the increasing nuclear charge caused by the added protons. Thus electrons in the same principal quantum level are generally more strongly bound as we move to the right on the periodic table, and there is a general increase in ionization energy values as electrons are added to a given principal quantum level.

On the other hand, *first ionization energy decreases in going down a group*. This can be seen most clearly by focusing on the Group 1A elements (the alkali metals) and the Group 8A elements (the noble gases), as shown in Table 7.6. The main reason for the decrease in ionization energy in going down a group is that the electrons being removed are, on average, farther from the nucleus. As n increases, the size of the orbital increases, and the electron is easier to remove.

First ionization energy increases across a period and decreases down a group.

FIGURE 7.30

The values of first ionization energy for the elements in the first six periods. In general, ionization energy decreases in going down a group. For example, note the decrease in values for Group 1A and Group 8A. In general, ionization energy increases in going left to right across a period. For example, note the sharp increase going across Period 2 from lithium through neon.



| | 1A | 2A | 3A | 4A | 5A | 6A | 7A | 8A |
|---|-----------|-----------|-----------|-----------|-----------|-----------|-------------|------------|
| 1 | H 1311 | | | | | | | He 2377 |
| 2 | Li 520 | Be 899 | | | | | | Ne 2088 |
| 3 | Na 495 | Mg 735 | B 800 | C 1086 | N 1402 | O 1314 | F 1681 | Ar 1527 |
| 4 | K 419 | Ca 590 | Al 580 | Si 780 | P 1060 | S 1005 | Cl 1255 | Kr 1356 |
| 5 | Rb 409 | Sr 549 | Ga 579 | Ge 761 | As 947 | Se 941 | Br 1143 | Xe 1176 |
| 6 | Cs 382 | Ba 503 | In 558 | Sn 708 | Sb 834 | Te 869 | I 1009 | Rn 1042 |
| | | | Tl 589 | Pb 715 | Bi 703 | Po 813 | At (926) | |

FIGURE 7.31

Trends in ionization energies (kJ/mol) for the representative elements.

In Fig. 7.30 we see that there are some discontinuities in ionization energy in going across a period. For example, for Period 2, discontinuities occur in going from beryllium to boron and from nitrogen to oxygen. These exceptions to the normal trend can be explained in terms of electron repulsions. The decrease in ionization energy in going from beryllium to boron reflects the fact that the electrons in the filled $2s$ orbital provide some shielding for electrons in the $2p$ orbital from the nuclear charge. The decrease in ionization energy in going from nitrogen to oxygen reflects the extra electron repulsions in the doubly occupied oxygen $2p$ orbital.

The ionization energies for the representative elements are summarized in Fig. 7.31.

Sample Exercise 7.8**Trends in Ionization Energies**

The first ionization energy for phosphorus is 1060 kJ/mol, and that for sulfur is 1005 kJ/mol. Why?

Solution

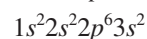
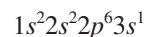
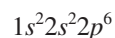
Phosphorus and sulfur are neighboring elements in Period 3 of the periodic table and have the following valence electron configurations: Phosphorus is $3s^23p^3$, and sulfur is $3s^23p^4$.

Ordinarily, the first ionization energy increases as we go across a period, so we might expect sulfur to have a greater ionization energy than phosphorus. However, in this case the fourth p electron in sulfur must be placed in an already occupied orbital. The electron–electron repulsions that result cause this electron to be more easily removed than might be expected.

See Exercises 7.93 and 7.94.

Sample Exercise 7.9**Ionization Energies**

Consider atoms with the following electron configurations:



Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices.

Solution

The atom with the largest value of I_1 is the one with the configuration $1s^2 2s^2 2p^6$ (this is the neon atom), because this element is found at the right end of Period 2. Since the $2p$ electrons do not shield each other very effectively, I_1 will be relatively large. The other configurations given include $3s$ electrons. These electrons are effectively shielded by the core electrons and are farther from the nucleus than the $2p$ electrons in neon. Thus I_1 for these atoms will be smaller than for neon.

The atom with the smallest value of I_2 is the one with the configuration $1s^2 2s^2 2p^6 3s^2$ (the magnesium atom). For magnesium, both I_1 and I_2 involve valence electrons. For the atom with the configuration $1s^2 2s^2 2p^6 3s^1$ (sodium), the second electron lost (corresponding to I_2) is a core electron (from a $2p$ orbital).

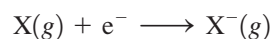
See Exercises 7.121 and 7.123.

Electron Affinity

Electron affinity is associated with the production of a **negative** ion.

The sign convention for electron affinity values follows the convention for energy changes used in Chapter 6.

Electron affinity is the energy change associated with the addition of an electron to a gaseous atom:



Because two different conventions have been used, there is a good deal of confusion in the chemical literature about the signs for electron affinity values. Electron affinity has been defined in many textbooks as the energy *released* when an electron is added to a gaseous atom. This convention requires that a positive sign be attached to an exothermic addition of an electron to an atom, which opposes normal thermodynamic conventions. Therefore, in this book we define electron affinity as a *change* in energy, which means that if the addition of the electron is exothermic, the corresponding value for electron affinity will carry a negative sign.

Figure 7.32 shows the electron affinity values for the atoms among the first 20 elements that form stable, isolated negative ions—that is, the atoms that undergo the addition of an electron as shown above. As expected, all these elements have negative (exothermic) electron affinities. Note that the *more negative* the energy, the greater the quantity of energy released. Although electron affinities generally become more negative from left to right across a period, there are several exceptions to this rule in each period. The dependence of electron affinity on atomic number can be explained by considering the changes in electron repulsions as a function of electron configurations. For example, the fact that the nitrogen atom does not form a stable, isolated $N^-(g)$ ion, whereas carbon forms $C^-(g)$, reflects the difference in the electron configurations of these atoms. An electron added to nitrogen ($1s^2 2s^2 2p^3$) to form the $N^-(g)$ ion ($1s^2 2s^2 2p^4$) would have to occupy a $2p$ orbital that already contains one electron. The extra repulsion between the electrons in this doubly occupied orbital causes $N^-(g)$ to be unstable. When an electron is added to carbon ($1s^2 2s^2 2p^2$) to form the $C^-(g)$ ion ($1s^2 2s^2 2p^3$), no such extra repulsions occur.

In contrast to the nitrogen atom, the oxygen atom can add one electron to form the stable $O^-(g)$ ion. Presumably oxygen's greater nuclear charge compared with that of nitrogen

FIGURE 7.32

The electron affinity values for atoms among the first 20 elements that form stable, isolated $X^-(g)$ ions. The lines shown connect adjacent elements. The absence of a line indicates missing elements (He, Be, N, Ne, Mg, and Ar) whose atoms do not add an electron exothermically and thus do not form stable, isolated $X^-(g)$ ions.

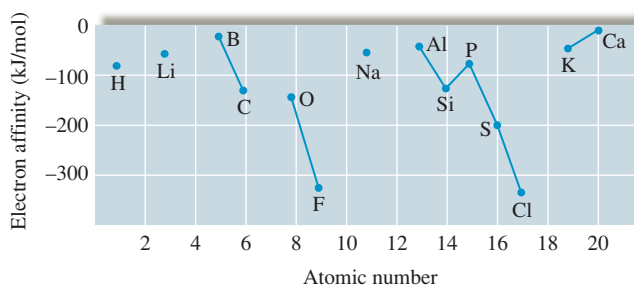
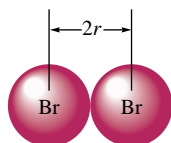


TABLE 7.7 Electron Affinities of the Halogens

| Atom | Electron Affinity (kJ/mol) |
|------|----------------------------|
| F | -327.8 |
| Cl | -348.7 |
| Br | -324.5 |
| I | -295.2 |

is sufficient to overcome the repulsion associated with putting a second electron into an already occupied $2p$ orbital. However, it should be noted that a second electron *cannot* be added to an oxygen atom [$O^-(g) + e^- \nrightarrow O^{2-}(g)$] to form an isolated oxide ion. This outcome seems strange in view of the many stable oxide compounds (MgO , Fe_2O_3 , and so on) that are known. As we will discuss in detail in Chapter 8, the O^{2-} ion is stabilized in ionic compounds by the large attractions that occur among the positive ions and the oxide ions.

When we go down a group, electron affinity should become more positive (less energy released), since the electron is added at increasing distances from the nucleus. Although this is generally the case, the changes in electron affinity in going down most groups are relatively small, and numerous exceptions occur. This behavior is demonstrated by the electron affinities of the Group 7A elements (the halogens) shown in Table 7.7. Note that the range of values is quite small compared with the changes that typically occur across a period. Also note that although chlorine, bromine, and iodine show the expected trend, the energy released when an electron is added to fluorine is smaller than might be expected. This smaller energy release has been attributed to the small size of the $2p$ orbitals. Because the electrons must be very close together in these orbitals, there are unusually large electron–electron repulsions. In the other halogens with their larger orbitals, the repulsions are not as severe.

**FIGURE 7.33**

The radius of an atom (r) is defined as half the distance between the nuclei in a molecule consisting of identical atoms.

Atomic Radius

Just as the size of an orbital cannot be specified exactly, neither can the size of an atom. We must make some arbitrary choices to obtain values for **atomic radii**. These values can be obtained by measuring the distances between atoms in chemical compounds. For example, in the bromine molecule, the distance between the two nuclei is known to be 228 pm. The bromine atomic radius is assumed to be half this distance, or 114 pm, as shown in Fig. 7.33. These radii are often called *covalent atomic radii* because of the way they are determined (from the distances between atoms in covalent bonds).

For nonmetallic atoms that do not form diatomic molecules, the atomic radii are estimated from their various covalent compounds. The radii for metal atoms (called *metallic radii*) are obtained from half the distance between metal atoms in solid metal crystals.

The values of the atomic radii for the representative elements are shown in Fig. 7.34. Note that these values are significantly smaller than might be expected from the 90% electron density volumes of isolated atoms, because when atoms form bonds, their electron “clouds” interpenetrate. However, these values form a self-consistent data set that can be used to discuss the trends in atomic radii.

Note from Fig. 7.34 that the atomic radii decrease in going from left to right across a period. This decrease can be explained in terms of the increasing effective nuclear charge (decreasing shielding) in going from left to right. This means that the valence electrons are drawn closer to the nucleus, decreasing the size of the atom.

Atomic radius increases down a group, because of the increases in the orbital sizes in successive principal quantum levels.



Visualization: Determining the Atomic Radius of a Nonmetal (Chlorine)



Visualization: Determining the Atomic Radius of a Nonmetal (Carbon)

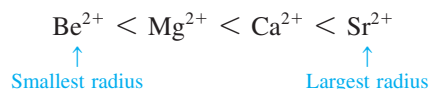
Sample Exercise 7.10

Trends in Radii

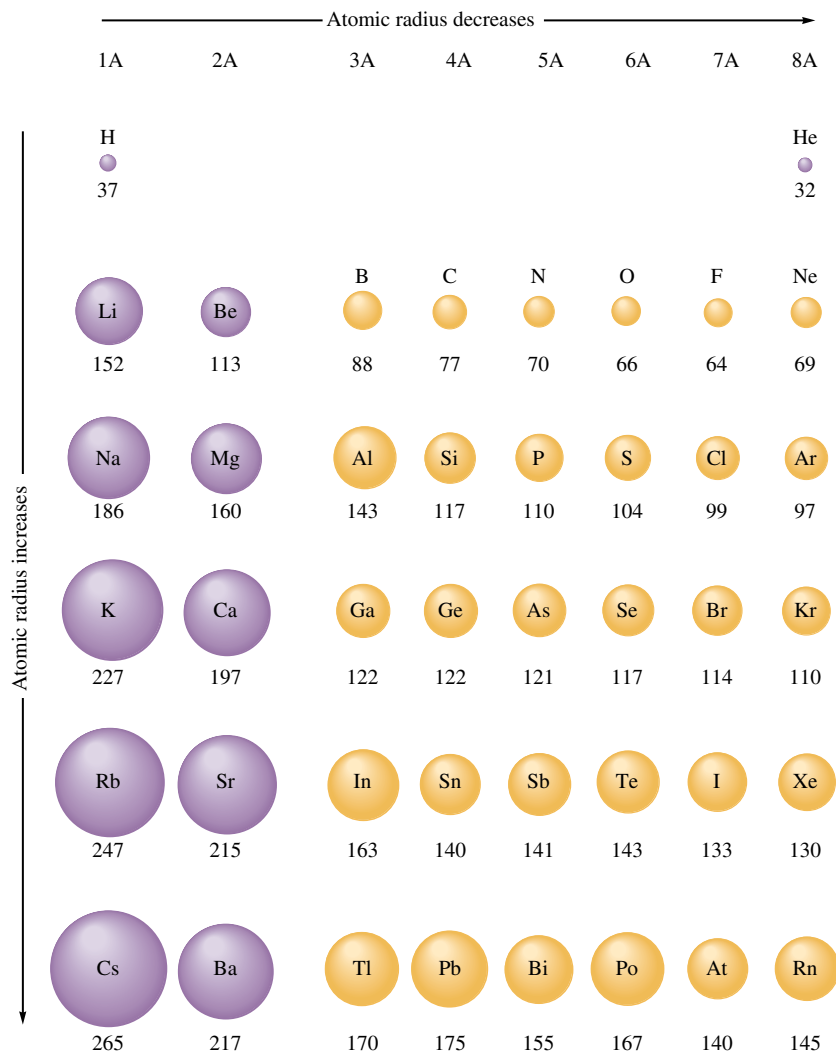
Predict the trend in radius for the following ions: Be^{2+} , Mg^{2+} , Ca^{2+} , and Sr^{2+} .

Solution

All these ions are formed by removing two electrons from an atom of a Group 2A element. In going from beryllium to strontium, we are going down the group, so the sizes increase:



See Exercises 7.85, 7.86, and 7.89.

**FIGURE 7.34**

Atomic radii (in picometers) for selected atoms. Note that atomic radius decreases going across a period and increases going down a group. The values for the noble gases are estimated, because data from bonded atoms are lacking.

7.13 The Properties of a Group: The Alkali Metals

We have seen that the periodic table originated as a way to portray the systematic properties of the elements. Mendeleev was primarily responsible for first showing its usefulness in correlating and predicting the elemental properties. In this section we will summarize much of the information available from the table. We also will illustrate the usefulness of the table by discussing the properties of a representative group, the alkali metals.

Information Contained in the Periodic Table

1. The essence of the periodic table is that the groups of representative elements exhibit similar chemical properties that change in a regular way. The quantum mechanical model of the atom has allowed us to understand the basis for the similarity of properties in a group—that each group member has the same valence electron configuration. *It is the number and type of valence electrons that primarily determine an atom's chemistry.*
2. One of the most valuable types of information available from the periodic table is the electron configuration of any representative element. If you understand the organization

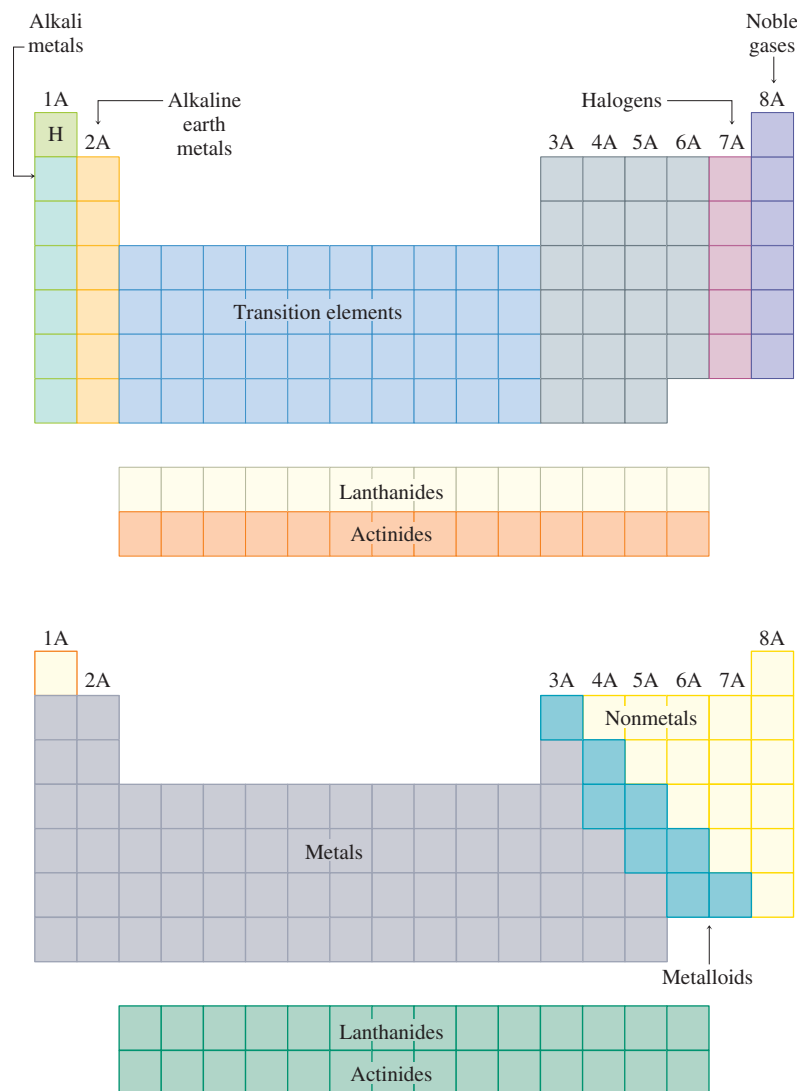


FIGURE 7.35
Special names for groups in the periodic table.

of the table, you will not need to memorize electron configurations for these elements. Although the predicted electron configurations for transition metals are sometimes incorrect, this is not a serious problem. You should, however, memorize the configurations of two exceptions, chromium and copper, since these $3d$ transition elements are found in many important compounds.

- As we mentioned in Chapter 2, certain groups in the periodic table have special names. These are summarized in Fig. 7.35. Groups are often referred to by these names, so you should learn them.
- The most basic division of the elements in the periodic table is into metals and nonmetals. The most important chemical property of a metal atom is the tendency to give up one or more electrons to form a positive ion; metals tend to have low ionization energies. The metallic elements are found on the left side of the table, as shown in Fig. 7.35. The most chemically reactive metals are found on the lower left-hand portion of the table, where the ionization energies are smallest. The most distinctive chemical property of a nonmetal atom is the ability to gain one or more electrons to form an anion when reacting with a metal. Thus nonmetals are elements

Metals and nonmetals were first discussed in Chapter 2.

with large ionization energies and the most negative electron affinities. The nonmetals are found on the right side of the table, with the most reactive ones in the upper right-hand corner, except for the noble gas elements, which are quite unreactive. The division into metals and nonmetals shown in Fig. 7.35 is only approximate. Many elements along the division line exhibit both metallic and nonmetallic properties under certain circumstances. These elements are often called **metalloids**, or sometimes **semimetals**.

The Alkali Metals

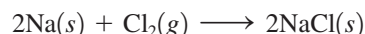
The metals of Group 1A, the alkali metals, illustrate very well the relationships among the properties of the elements in a group. Lithium, sodium, potassium, rubidium, cesium, and francium are the most chemically reactive of the metals. We will not discuss francium here because it occurs in nature in only very small quantities. Although hydrogen is found in Group 1A of the periodic table, it behaves as a nonmetal, in contrast to the other members of that group. The fundamental reason for hydrogen's nonmetallic character is its very small size (see Fig. 7.34). The electron in the small $1s$ orbital is bound tightly to the nucleus.

Some important properties of the first five alkali metals are shown in Table 7.8. The data in Table 7.8 show that in going down the group, the first ionization energy decreases and the atomic radius increases. This agrees with the general trends discussed in Section 7.12.

The overall increase in density in going down Group 1A is typical of all groups. This occurs because atomic mass generally increases more rapidly than atomic size. Thus there is more mass per unit volume for each succeeding element.

The smooth decrease in melting point and boiling point in going down Group 1A is not typical; in most other groups more complicated behavior occurs. Note that the melting point of cesium is only 29°C . Cesium can be melted readily using only the heat from your hand. This is very unusual—metals typically have rather high melting points. For example, tungsten melts at 3410°C . The only other metals with low melting points are mercury (mp -38°C) and gallium (mp 30°C).

The chemical property most characteristic of a metal is the ability to lose its valence electrons. The Group 1A elements are very reactive. They have low ionization energies and react with nonmetals to form ionic solids. A typical example involves the reaction of sodium with chlorine to form sodium chloride:



where sodium chloride contains Na^+ and Cl^- ions. This is an oxidation–reduction reaction in which chlorine oxidizes sodium. In the reactions between metals and nonmetals,

Hydrogen will be discussed further in Chapter 19.

Other groups will be discussed in Chapters 19 and 20.

Oxidation–reduction reactions were discussed in Chapter 4.

TABLE 7.8 Properties of Five Alkali Metals

| Element | Valence Electron Configuration | Density at 25°C (g/cm^3) | mp ($^\circ\text{C}$) | bp ($^\circ\text{C}$) | First Ionization Energy (kJ/mol) | Atomic (covalent) Radius (pm) | Ionic (M^+) Radius (pm) |
|---------|--------------------------------|--|-------------------------|-------------------------|--|--|---|
| Li | $2s^1$ | 0.53 | 180 | 1330 | 520 | 152 | 60 |
| Na | $3s^1$ | 0.97 | 98 | 892 | 495 | 186 | 95 |
| K | $4s^1$ | 0.86 | 64 | 760 | 419 | 227 | 133 |
| Rb | $5s^1$ | 1.53 | 39 | 668 | 409 | 247 | 148 |
| Cs | $6s^1$ | 1.87 | 29 | 690 | 382 | 265 | 169 |



CHEMICAL IMPACT

Potassium—Too Much of a Good Thing Can Kill You

Potassium is widely recognized as an essential element. In fact, our daily requirement for potassium is more than twice that for sodium. Because most foods contain potassium, serious deficiency of this element in humans is rare. However, potassium deficiency can be caused by kidney malfunction or by the use of certain diuretics. Potassium deficiency leads to muscle weakness, irregular heartbeat, and depression.

Potassium is found in the fluids of the body as the K^+ ion, and its presence is essential to the operation of our nervous system. The passage of impulses along the nerves requires the flow of K^+ (and Na^+) through channels in the membranes of the nerve cells. Failure of this ion flow prevents nerve transmissions and results in death. For example, the black mamba snake kills its victims by injecting a venom that blocks the potassium channels in the nerve cells.

Although a steady intake of potassium is essential to preserve life, ironically, too much potassium can be lethal. In fact, the deadly ingredient in the drug mixture used for executing criminals is potassium chloride. Injection of a large amount of a potassium chloride solution produces an excess of K^+ ion in



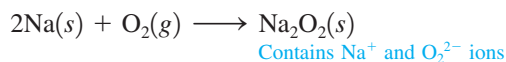
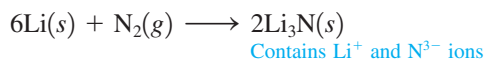
The black mamba snake's venom kills by blocking the potassium channels in the nerve cells of victims.

the fluids surrounding the cells and prevents the essential flow of K^+ out the cells to allow nerve impulses to occur. This causes the heart to stop beating. Unlike other forms of execution, death by lethal injection of potassium chloride does not harm the organs of the body. Thus condemned criminals who are executed in this manner could potentially donate their organs for transplants. However, this idea is very controversial.



Potassium reacts violently with water.

it is typical for the nonmetal to behave as the oxidizing agent and the metal to behave as the reducing agent, as shown by the following reactions:



For reactions of the types just shown, the relative reducing powers of the alkali metals can be predicted from the first ionization energies listed in Table 7.8. Since it is much easier to remove an electron from a cesium atom than from a lithium atom, cesium should be the better reducing agent. The expected trend in reducing ability is

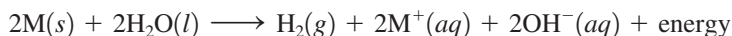


This order is observed experimentally for direct reactions between the solid alkali metals and nonmetals. However, this is not the order for reducing ability found when the alkali

TABLE 7.9 Hydration Energies for Li⁺, Na⁺, and K⁺ Ions

| Ion | Hydration Energy (kJ/mol) |
|-----------------|---------------------------|
| Li ⁺ | -510 |
| Na ⁺ | -402 |
| K ⁺ | -314 |

metals react in aqueous solution. For example, the reduction of water by an alkali metal is very vigorous and exothermic:



The order of reducing abilities observed for this reaction for the first three group members is



In the gas phase potassium loses an electron more easily than sodium, and sodium more easily than lithium. Thus it is surprising that lithium is the best reducing agent toward water.

This reversal occurs because the formation of the M⁺ ions in aqueous solution is strongly influenced by the hydration of these ions by the polar water molecules. The *hydration energy* of an ion represents the change in energy that occurs when water molecules attach to the M⁺ ion. The hydration energies for the Li⁺, Na⁺, and K⁺ ions (shown in Table 7.9) indicate that the process is exothermic in each case. However, nearly twice as much energy is released by the hydration of the Li⁺ ion as for the K⁺ ion. This difference is caused by size effects; the Li⁺ ion is much smaller than the K⁺ ion, and thus its *charge density* (charge per unit volume) is also much greater. This means that the polar water molecules are more strongly attracted to the small Li⁺ ion. Because the Li⁺ ion is so strongly hydrated, its formation from the lithium atom occurs more readily than the formation of the K⁺ ion from the potassium atom. Although a potassium atom in the gas phase loses its valence electron more readily than a lithium atom in the gas phase, the opposite is true in aqueous solution. This anomaly is an example of the importance of the polarity of the water molecule in aqueous reactions.

There is one more surprise involving the highly exothermic reactions of the alkali metals with water. Experiments show that in water lithium is the best reducing agent, so we might expect that lithium should react the most violently with water. However, this is not true. Sodium and potassium react much more vigorously. Why is this so? The answer lies in the relatively high melting point of lithium. When sodium and potassium react with water, the heat evolved causes them to melt, giving a larger area of contact with water. Lithium, on the other hand, does not melt under these conditions and reacts more slowly. This illustrates the important principle (which we will discuss in detail in Chapter 12) that the energy change for a reaction and the rate at which it occurs are not necessarily related.

In this section we have seen that the trends in atomic properties summarized by the periodic table can be a great help in understanding the chemical behavior of the elements. This fact will be emphasized over and over as we proceed in our study of chemistry.

Key Terms

Section 7.1

electromagnetic radiation
wavelength
frequency

Section 7.2

Planck's constant
photon
photoelectric effect
 $E = mc^2$
dual nature of light
diffraction
diffraction pattern

Section 7.3

continuous spectrum
line spectrum

For Review

Electromagnetic radiation

- Characterized by its wavelength (λ), frequency (ν), and speed ($c = 2.9979 \times 10^8$ m/s)

$$\lambda \nu = c$$

- Can be viewed as a stream of "particles" called photons, each with energy $h\nu$, where h is Planck's constant (6.626×10^{-34} J · s)

Photoelectric effect

- When light strikes a metal surface, electrons are emitted
- Analysis of the kinetic energy and numbers of the emitted electrons led Einstein to suggest that electromagnetic radiation can be viewed as a stream of photons

Hydrogen spectrum

- The emission spectrum of hydrogen shows discrete wavelengths
- Indicates that hydrogen has discrete energy levels

Section 7.4

quantum model
ground state

Section 7.5

standing wave
wave function
orbital
quantum (wave) mechanical model
Heisenberg uncertainty principle
probability distribution
radial probability distribution

Section 7.6

quantum numbers
principal quantum number (n)
angular momentum quantum number (ℓ)
magnetic quantum number (m_ℓ)
subshell

Section 7.7

nodal surface
node
degenerate orbital

Section 7.8

electron spin
electron spin quantum number
Pauli exclusion principle

Section 7.9

polyelectronic atoms

Section 7.11

aufbau principle
Hund's rule
valence electrons
core electrons
transition metals
lanthanide series
actinide series
main-group elements (representative elements)

Section 7.12

first ionization energy
second ionization energy
electron affinity
atomic radii

Section 7.13

metalloids (semimetals)

Bohr model of the hydrogen atom

- Using the data from the hydrogen spectrum and assuming angular momentum to be quantized, Bohr devised a model in which the electron traveled in circular orbits
- Although an important pioneering effort, this model proved to be entirely incorrect

Wave (quantum) mechanical model

- An electron is described as a standing wave
- The square of the wave function (often called an orbital) gives a probability distribution for the electron position
- The exact position of the electron is never known, which is consistent with the Heisenberg uncertainty principle: it is impossible to know accurately both the position and the momentum of a particle simultaneously
- Probability maps are used to define orbital shapes
- Orbitals are characterized by the quantum numbers n , ℓ , and m_ℓ

Electron spin

- Described by the spin quantum number m_s , which can have values of $\pm\frac{1}{2}$
- Pauli exclusion principle: no two electrons in a given atom can have the same set of quantum numbers n , ℓ , m_ℓ , and m_s
- Only two electrons with opposite spins can occupy a given orbital

Periodic table

- By populating the orbitals from the wave mechanical model (the aufbau principle), the form of the periodic table can be explained
- According to the wave mechanical model, atoms in a given group have the same valence (outer) electron configuration
- The trends in properties such as ionization energies and atomic radii can be explained in terms of the concepts of nuclear attraction, electron repulsions, shielding, and penetration

REVIEW QUESTIONS

1. Four types of electromagnetic radiation (EMR) are ultraviolet, microwaves, gamma rays, and visible. All of these types of EMR can be characterized by wavelength, frequency, photon energy, and speed of travel. Define these terms and rank the four types of electromagnetic radiation in order of increasing wavelength, frequency, photon energy, and speed.
2. Characterize the Bohr model of the atom. In the Bohr model, what do we mean when we say something is quantized? How does the Bohr model of the hydrogen atom explain the hydrogen emission spectrum? Why is the Bohr model fundamentally incorrect?
3. What experimental evidence supports the quantum theory of light? Explain the wave-particle duality of all matter. For what size particles must one consider both the wave and the particle properties?
4. List the most important ideas of the quantum mechanical model of the atom. Include in your discussion the terms or names *wave function*, *orbital*, *Heisenberg uncertainty principle*, *de Broglie*, *Schrödinger*, and *probability distribution*.
5. What are quantum numbers? What information do we get from the quantum numbers n , ℓ , and m_ℓ ? We define a spin quantum number (m_s), but do we know that an electron literally spins?
6. How do $2p$ orbitals differ from each other? How do $2p$ and $3p$ orbitals differ from each other? What is a nodal surface in an atomic orbital? What is wrong with $1p$, $1d$, $2d$, $1f$, $2f$, and $3f$ orbitals? Explain what we mean when we say that a $4s$ electron is more penetrating than a $3d$ electron.

- Four blocks of elements in a periodic table refer to various atomic orbitals being filled. What are the four blocks and the corresponding orbitals? How do you get the energy ordering of the atomic orbitals from the periodic table? What is the aufbau principle? Hund's rule? The Pauli exclusion principle? There are two common exceptions to the ground-state electron configuration for elements 1–36 as predicted by the periodic table. What are they?
- What is the difference between core electrons and valence electrons? Why do we emphasize the valence electrons in an atom when discussing atomic properties? What is the relationship between valence electrons and elements in the same group of the periodic table?
- Using the element phosphorus as an example, write the equation for a process in which the energy change will correspond to the ionization energy and to the electron affinity.

Explain why the first ionization energy tends to increase as one proceeds from left to right across a period. Why is the first ionization energy of aluminum lower than that of magnesium, and the first ionization energy of sulfur lower than that of phosphorus?

Why do the successive ionization energies of an atom always increase? Note the successive ionization energies for silicon given in Table 7.5. Would you expect to see any large jumps between successive ionization energies of silicon as you removed all the electrons, one by one, beyond those shown in the table?

- The radius trend and the ionization energy trend are exact opposites. Does this make sense? Define electron affinity. Electron affinity values are both exothermic (negative) and endothermic (positive). However, ionization energy values are always endothermic (positive). Explain.

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- What does it mean for something to have wavelike properties? Particulate properties? Electromagnetic radiation can be discussed in terms of both particles and waves. Explain the experimental verification for each of these views.
- Defend and criticize Bohr's model. Why was it reasonable that such a model was proposed, and what evidence was there that it "works"? Why do we no longer "believe" in it?
- The first four ionization energies for the elements *X* and *Y* are shown below. The units are not kJ/mol.

| | <i>X</i> | <i>Y</i> |
|--------|----------|----------|
| First | 170 | 200 |
| Second | 350 | 400 |
| Third | 1800 | 3500 |
| Fourth | 2500 | 5000 |

Identify the elements *X* and *Y*. There may be more than one correct answer, so explain completely.

- Compare the first ionization energy of helium to its second ionization energy, remembering that both electrons come from the $1s$ orbital. Explain the difference without using actual numbers from the text.
- Which has the larger second ionization energy, lithium or beryllium? Why?
- Explain why a graph of ionization energy versus atomic number (across a row) is not linear. Where are the exceptions? Why are there exceptions?
- Without referring to your text, predict the trend of second ionization energies for the elements sodium through argon. Compare your answer with Table 7.5. Explain any differences.
- Account for the fact that the line that separates the metals from the nonmetals on the periodic table is diagonal downward to the right instead of horizontal or vertical.
- Explain *electron* from a quantum mechanical perspective, including a discussion of atomic radii, probabilities, and orbitals.
- Choose the best response for the following. The ionization energy for the chlorine atom is equal in magnitude to the electron affinity for
 - the Cl atom.
 - the Cl^- ion.
 - the Cl^+ ion.
 - the F atom.
 - none of these.

Explain each choice. Justify your choice, and for the choices you did not select, explain what is incorrect about them.

- Consider the following statement: "The ionization energy for the potassium atom is negative, because when K loses an electron to become K^+ , it achieves a noble gas electron configuration." Indicate everything that is correct in this statement. Indicate everything that is incorrect. Correct the incorrect information and explain.
- In going across a row of the periodic table, electrons are added and ionization energy generally increases. In going down a column of the periodic table, electrons are also being added but ionization energy decreases. Explain.
- How does probability fit into the description of the atom?
- What is meant by an *orbital*?
- Does the minimization of electron–electron repulsions correlate with Hund's rule?
- In the hydrogen atom, what is the physical significance of the state for which $n = \infty$ and $E = 0$?
- The work function is the energy required to remove an electron from an atom on the surface of a metal. How does this definition differ from that for ionization energy?
- Many more anhydrous lithium salts are hygroscopic (readily absorb water) than are those of the other alkali metals. Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide*.

Questions

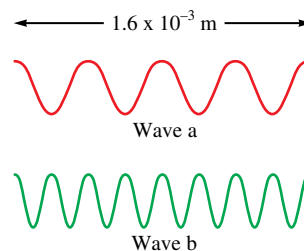
- What type of relationship (direct or inverse) exists between wavelength, frequency, and photon energy? What does a photon energy unit of a Joule equal?
- Explain the photoelectric effect.
- How does the wavelength of a fast-pitched baseball compare to the wavelength of an electron traveling at 1/10 the speed of light? What is the significance of this comparison? See Sample Exercise 7.3.
- The Bohr model only works for one electron species. Why do we discuss it in this text (what's good about it)?
- Describe the significance of the radial probability distribution shown in Fig. 7.12(b).
- The periodic table consists of four blocks of elements which correspond to *s*, *p*, *d*, and *f* orbitals being filled. After *f* orbitals come *g* and *h* orbitals. In theory, if a *g* block and an *h* block of elements existed, how long would the rows of *g* and *h* elements be in this theoretical periodic table?
- Many times the claim is made that subshells half-filled with electrons are particularly stable. Can you suggest a possible physical basis for this claim?
- Diagonal relationships in the periodic table exist as well as the vertical relationships. For example, Be and Al are similar in some of their properties, as are B and Si. Rationalize why these diagonal relationships hold for properties such as size, ionization energy, and electron affinity.
- Elements with very large ionization energies also tend to have highly exothermic electron affinities. Explain. Which group of elements would you expect to be an exception to this statement?
- The changes in electron affinity as one goes down a group in the periodic table are not nearly as large as the variations in ionization energies. Why?
- Why is it much harder to explain the line spectra of polyelectronic atoms and ions than it is to explain the line spectra of hydrogen and hydrogenlike ions?
- Scientists use emission spectra to confirm the presence of an element in materials of unknown composition. Why is this possible?

Exercises

In this section similar exercises are paired.

Light and Matter

- Photosynthesis uses 660-nm light to convert CO_2 and H_2O into glucose and O_2 . Calculate the frequency of this light.
- An FM radio station broadcasts at 99.5 MHz. Calculate the wavelength of the corresponding radio waves.
- Microwave radiation has a wavelength on the order of 1.0 cm. Calculate the frequency and the energy of a single photon of this radiation. Calculate the energy of an Avogadro's number of photons (called an *einstein*) of this radiation.
- A photon of ultraviolet (UV) light possesses enough energy to mutate a strand of human DNA. What is the energy of a single UV photon and a mole of UV photons having a wavelength of 25 nm?
- Consider the following waves representing electromagnetic radiation:



Which wave has the longer wavelength? Calculate the wavelength. Which wave has the higher frequency and larger photon energy? Calculate these values. Which wave has the faster velocity? What type of electromagnetic radiation are illustrated?

- One type of electromagnetic radiation has a frequency of 107.1 MHz, another type has a wavelength of $2.12 \times 10^{-10} \text{ m}$, and another type of electromagnetic radiation has photons with energy equal to $3.97 \times 10^{-19} \text{ J/photon}$. Identify each type of electromagnetic radiation and place them in order of increasing photon energy and increasing frequency.
- Carbon absorbs energy at a wavelength of 150. nm. The total amount of energy emitted by a carbon sample is $1.98 \times 10^5 \text{ J}$. Calculate the number of carbon atoms present in the sample, assuming that each atom emits one photon.

38. A carbon–oxygen double bond in a certain organic molecule absorbs radiation that has a frequency of $6.0 \times 10^{13} \text{ s}^{-1}$.
- What is the wavelength of this radiation?
 - To what region of the spectrum does this radiation belong?
 - What is the energy of this radiation per photon? Per mole of photons?
 - A carbon–oxygen bond in a different molecule absorbs radiation with frequency equal to $5.4 \times 10^{13} \text{ s}^{-1}$. Is this radiation more or less energetic?
39. The work function of an element is the energy required to remove an electron from the surface of the solid element. The work function for lithium is 279.7 kJ/mol (that is, it takes 279.7 kJ of energy to remove one mole of electrons from one mole of Li atoms on the surface of Li metal). What is the maximum wavelength of light that can remove an electron from an atom on the surface of lithium metal?
40. It takes 208.4 kJ of energy to remove 1 mole of electrons from an atom on the surface of rubidium metal. How much energy does it take to remove a single electron from an atom on the surface of solid rubidium? What is the maximum wavelength of light capable of doing this?
41. Calculate the de Broglie wavelength for each of the following.
- an electron with a velocity 10.% of the speed of light
 - a tennis ball (55 g) served at 35 m/s ($\sim 80 \text{ mi/h}$)
42. Neutron diffraction is used in determining the structures of molecules.
- Calculate the de Broglie wavelength of a neutron moving at 1.00% of the speed of light.
 - Calculate the velocity of a neutron with a wavelength of 75 pm (1 pm = 10^{-12} m).
43. A particle has a velocity that is 90.% of the speed of light. If the wavelength of the particle is $1.5 \times 10^{-15} \text{ m}$, calculate the mass of the particle.
44. Calculate the velocities of electrons with de Broglie wavelengths of $1.0 \times 10^2 \text{ nm}$ and 1.0 nm , respectively.

Hydrogen Atom: The Bohr Model

- Calculate the wavelength of light emitted when each of the following transitions occur in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?
 - $n = 3 \rightarrow n = 2$
 - $n = 4 \rightarrow n = 2$
 - $n = 2 \rightarrow n = 1$
- Calculate the wavelength of light emitted when each of the following transitions occur in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?
 - $n = 4 \rightarrow n = 3$
 - $n = 5 \rightarrow n = 4$
 - $n = 5 \rightarrow n = 3$
- Using vertical lines, indicate the transitions from Exercise 45 on an energy-level diagram for the hydrogen atom (see Fig. 7.8).
- Using vertical lines, indicate the transitions from Exercise 46 on an energy-level diagram for the hydrogen atom (see Fig. 7.8).
- Does a photon of visible light ($\lambda \approx 400 \text{ to } 700 \text{ nm}$) have sufficient energy to excite an electron in a hydrogen atom from the $n = 1$ to the $n = 5$ energy state? from the $n = 2$ to the $n = 6$ energy state?
- An electron is excited from the $n = 1$ ground state to the $n = 3$ state in a hydrogen atom. Which of the following statements are true? Correct the false statements to make them true.
 - It takes more energy to ionize (completely remove) the electron from $n = 3$ than from the ground state.
 - The electron is farther from the nucleus on average in the $n = 3$ state than in the $n = 1$ state.
 - The wavelength of light emitted if the electron drops from $n = 3$ to $n = 2$ will be shorter than the wavelength of light emitted if the electron falls from $n = 3$ to $n = 1$.
 - The wavelength of light emitted when the electron returns to the ground state from $n = 3$ will be the same as the wavelength of light absorbed to go from $n = 1$ to $n = 3$.
 - For $n = 3$, the electron is in the first excited state.
- Calculate the maximum wavelength of light capable of removing an electron for a hydrogen atom from the energy state characterized by $n = 1$. by $n = 2$.
- Consider an electron for a hydrogen atom in an excited state. The maximum wavelength of electromagnetic radiation that can completely remove (ionize) the electron from the H atom is 1460 nm. What is the initial excited state for the electron ($n = ?$)?
- An excited hydrogen atom with an electron in the $n = 5$ state emits light having a frequency of $6.90 \times 10^{14} \text{ s}^{-1}$. Determine the principal quantum level for the final state in this electronic transition.
- An excited hydrogen atom emits light with a wavelength of 397.2 nm to reach the energy level for which $n = 2$. In which principal quantum level did the electron begin?

Quantum Mechanics, Quantum Numbers, and Orbitals

- Using the Heisenberg uncertainty principle, calculate Δx for each of the following.
 - an electron with $\Delta v = 0.100 \text{ m/s}$
 - a baseball (mass = 145 g) with $\Delta v = 0.100 \text{ m/s}$
 - How does the answer in part a compare with the size of a hydrogen atom?
 - How does the answer in part b correspond to the size of a baseball?
- The Heisenberg uncertainty principle can be expressed in the form

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

where E represents energy and t represents time. Show that the units for this form are the same as the units for the form used in this chapter:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

- What are the possible values for the quantum numbers n , ℓ , and m_ℓ ?

58. Which of the following orbital designations are incorrect: $1s$, $1p$, $7d$, $9s$, $3f$, $4f$, $2d$?

59. Which of the following sets of quantum numbers are not allowed in the hydrogen atom? For the sets of quantum numbers that are incorrect, state what is wrong in each set.

- $n = 3, \ell = 2, m_\ell = 2$
- $n = 4, \ell = 3, m_\ell = 4$
- $n = 0, \ell = 0, m_\ell = 0$
- $n = 2, \ell = -1, m_\ell = 1$

60. Which of the following sets of quantum numbers are not allowed? For each incorrect set, state why it is incorrect.

- $n = 3, \ell = 3, m_\ell = 0, m_s = -\frac{1}{2}$
- $n = 4, \ell = 3, m_\ell = 2, m_s = -\frac{1}{2}$
- $n = 4, \ell = 1, m_\ell = 1, m_s = +\frac{1}{2}$
- $n = 2, \ell = 1, m_\ell = -1, m_s = -1$
- $n = 5, \ell = -4, m_\ell = 2, m_s = +\frac{1}{2}$
- $n = 3, \ell = 1, m_\ell = 2, m_s = -\frac{1}{2}$

61. What is the physical significance of the value of ψ^2 at a particular point in an atomic orbital?

62. In defining the sizes of orbitals, why must we use an arbitrary value, such as 90% of the probability of finding an electron in that region?

Polyelectronic Atoms

63. How many orbitals in an atom can have the designation $5p$, $3d_{z^2}$, $4d$, $n = 5$, $n = 4$?

64. How many electrons in an atom can have the designation $1p$, $6d_{x^2-y^2}$, $4f$, $7p_y$, $2s$, $n = 3$?

65. Give the maximum number of electrons in an atom that can have these quantum numbers:

- $n = 4$
- $n = 5, m_\ell = +1$
- $n = 5, m_s = +\frac{1}{2}$
- $n = 3, \ell = 2$
- $n = 2, \ell = 1$

66. Give the maximum number of electrons in an atom that can have these quantum numbers:

- $n = 0, \ell = 0, m_\ell = 0$
- $n = 2, \ell = 1, m_\ell = -1, m_s = -\frac{1}{2}$
- $n = 3, m_s = +\frac{1}{2}$
- $n = 2, \ell = 2$
- $n = 1, \ell = 0, m_\ell = 0$

67. Draw atomic orbital diagrams representing the ground-state electron configuration for each of the following elements.

- Na
- Co
- Kr

How many unpaired electrons are present in each element?

68. For elements 1–36, there are two exceptions to the filling order as predicted from the periodic table. Draw the atomic orbital diagrams for the two exceptions and indicate how many unpaired electrons are present.

69. The elements Si, Ga, As, Ge, Al, Cd, S, and Se are all used in the manufacture of various semiconductor devices. Write the expected electron configuration for these atoms.

70. The elements Cu, O, La, Y, Ba, Tl, and Bi are all found in high-temperature ceramic superconductors. Write the expected electron configuration for these atoms.

71. Write the expected electron configurations for each of the following atoms: Sc, Fe, P, Cs, Eu, Pt, Xe, Br.

72. Write the expected electron configurations for each of the following atoms: Cl, Sb, Sr, W, Pb, Cf.

73. Write the expected ground-state electron configuration for the following.

- the element with one unpaired $5p$ electron that forms a covalent with compound fluorine
- the (as yet undiscovered) alkaline earth metal after radium
- the noble gas with electrons occupying $4f$ orbitals
- the first-row transition metal with the most unpaired electrons

74. Using only the periodic table inside the front cover of the text, write the expected ground-state electron configurations for

- the third element in Group 5A.
- element number 116.
- an element with three unpaired $5d$ electrons.
- the halogen with electrons in the $6p$ atomic orbitals.

75. In the ground state of mercury, Hg,

- how many electrons occupy atomic orbitals with $n = 3$?
- how many electrons occupy d atomic orbitals?
- how many electrons occupy p_z atomic orbitals?
- how many electrons have spin “up” ($m_s = +\frac{1}{2}$)?

76. In the ground state of element 115, Uup,

- how many electrons have $n = 5$ as one of their quantum numbers?
- how many electrons have $\ell = 3$ as one of their quantum numbers?
- how many electrons have $m_\ell = 1$ as one of their quantum numbers?
- how many electrons have $m_s = -\frac{1}{2}$ as one of their quantum numbers?

77. Give a possible set of values of the four quantum numbers for all the electrons in a boron atom and a nitrogen atom if each is in the ground state.

78. Give a possible set of values of the four quantum numbers for the $4s$ and $3d$ electrons in titanium.

79. A certain oxygen atom has the electron configuration $1s^2 2s^2 2p_x^2 2p_y^2$. How many unpaired electrons are present? Is this an excited state of oxygen? In going from this state to the ground state would energy be released or absorbed?

80. Which of the following electron configurations correspond to an excited state? Identify the atoms and write the ground-state electron configuration where appropriate.

- $1s^2 2s^2 3p^1$
- $1s^2 2s^2 2p^6$
- $1s^2 2s^2 2p^4 3s^1$
- $[\text{Ar}] 4s^2 3d^5 4p^1$

How many unpaired electrons are present in each of these species?

81. Which of elements 1–36 have two unpaired electrons in the ground state?
82. Which of elements 1–36 have one unpaired electron in the ground state?
83. One bit of evidence that the quantum mechanical model is “correct” lies in the magnetic properties of matter. Atoms with unpaired electrons are attracted by magnetic fields and thus are said to exhibit *paramagnetism*. The degree to which this effect is observed is directly related to the number of unpaired electrons present in the atom. Consider the ground-state electron configurations for Li, N, Ni, Te, Ba, and Hg. Which of these atoms would be expected to be paramagnetic, and how many unpaired electrons are present in each paramagnetic atom?
84. How many unpaired electrons are present in each of the following in the ground state: O, O⁺, O[−], Os, Zr, S, F, Ar?

The Periodic Table and Periodic Properties

85. Arrange the following groups of atoms in order of increasing size.
- Te, S, Se
 - K, Br, Ni
 - Ba, Si, F
86. Arrange the following groups of atoms in order of increasing size.
- Rb, Na, Be
 - Sr, Se, Ne
 - Fe, P, O
87. Arrange the atoms in Exercise 85 in order of increasing first ionization energy.
88. Arrange the atoms in Exercise 86 in order of increasing first ionization energy.
89. In each of the following sets, which atom or ion has the smallest radius?
- H, He
 - Cl, In, Se
 - element 120, element 119, element 117
 - Nb, Zn, Si
 - Na[−], Na, Na⁺
90. In each of the following sets, which atom or ion has the smallest ionization energy?
- Ca, Sr, Ba
 - K, Mn, Ga
 - N, O, F
 - S^{2−}, S, S²⁺
 - Cs, Ge, Ar
91. Element 106 has been named seaborgium, Sg, in honor of Glenn Seaborg, discoverer of the first transuranium element.
- Write the expected electron configuration for element 106.
 - What other element would be most like element 106 in its properties?
 - Write the formula for a possible oxide and a possible oxyanion of element 106.
92. Predict some of the properties of element 117 (the symbol is Uus, following conventions proposed by the International Union of Pure and Applied Chemistry, or IUPAC).
- What will be its electron configuration?
 - What element will it most resemble chemically?
 - What will be the formula of the neutral binary compounds it forms with sodium, magnesium, carbon, and oxygen?
 - What oxyanions would you expect Uus to form?
93. The first ionization energies of As and Se are 0.947 and 0.941 MJ/mol, respectively. Rationalize these values in terms of electron configurations.
94. Rank the elements Be, B, C, N, and O in order of increasing first ionization energy. Explain your reasoning.
95. For each of the following pairs of elements
- (C and N) (Ar and Br)
- pick the atom with
- more favorable (exothermic) electron affinity.
 - higher ionization energy.
 - larger size.
96. For each of the following pairs of elements
- (Mg and K) (F and Cl)
- pick the atom with
- more favorable (exothermic) electron affinity.
 - higher ionization energy.
 - larger size.
97. The electron affinities of the elements from aluminum to chlorine are −44, −120, −74, −200.4, and −384.7 kJ/mol, respectively. Rationalize the trend in these values.
98. The electron affinity for sulfur is more exothermic than that for oxygen. How do you account for this?
99. Order each of the following sets from the least exothermic electron affinity to the most exothermic electron affinity.
- F, Cl, Br, I
 - N, O, F
100. Which has the more negative electron affinity, the oxygen atom or the O[−] ion? Explain your answer.
101. Write equations corresponding to the following.
- The fourth ionization energy of Se
 - The electron affinity of S[−]
 - The electron affinity of Fe³⁺
 - The ionization energy of Mg
102. Using data from the text, determine the following values (justify your answer):
- the electron affinity of Mg²⁺
 - the ionization energy of Cl[−]
 - the electron affinity of Cl⁺
 - the ionization energy of Mg[−] (Electron affinity of Mg = 230 kJ/mol)

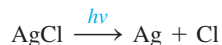
Alkali Metals

103. An ionic compound of potassium and oxygen has the empirical formula KO. Would you expect this compound to be potassium(II) oxide or potassium peroxide? Explain.
104. Give the name and formula of each of the binary compounds formed from the following elements.
- Li and N
 - Na and Br
 - K and S

105. Cesium was discovered in natural mineral waters in 1860 by R. W. Bunsen and G. R. Kirchhoff using the spectroscope they invented in 1859. The name came from the Latin *caesius* (“sky blue”) because of the prominent blue line observed for this element at 455.5 nm. Calculate the frequency and energy of a photon of this light.
106. The bright yellow light emitted by a sodium vapor lamp consists of two emission lines at 589.0 and 589.6 nm. What are the frequency and the energy of a photon of light at each of these wavelengths? What are the energies in kJ/mol?
107. Does the information on alkali metals in Table 7.8 of the text confirm the general periodic trends in ionization energy and atomic radius? Explain.
108. Predict the atomic number of the next alkali metal after francium and give its ground-state electron configuration.
109. Complete and balance the equations for the following reactions.
- $\text{Li}(s) + \text{N}_2(g) \rightarrow$
 - $\text{Rb}(s) + \text{S}(s) \rightarrow$
110. Complete and balance the equations for the following reactions.
- $\text{Cs}(s) + \text{H}_2\text{O}(l) \rightarrow$
 - $\text{Na}(s) + \text{Cl}_2(g) \rightarrow$

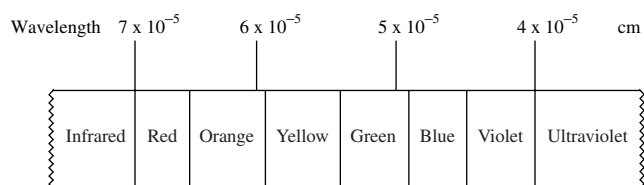
Additional Exercises

111. Photogray lenses incorporate small amounts of silver chloride in the glass of the lens. When light hits the AgCl particles, the following reaction occurs:



The silver metal that is formed causes the lenses to darken. The enthalpy change for this reaction is 3.10×10^2 kJ/mol. Assuming all this energy must be supplied by light, what is the maximum wavelength of light that can cause this reaction?

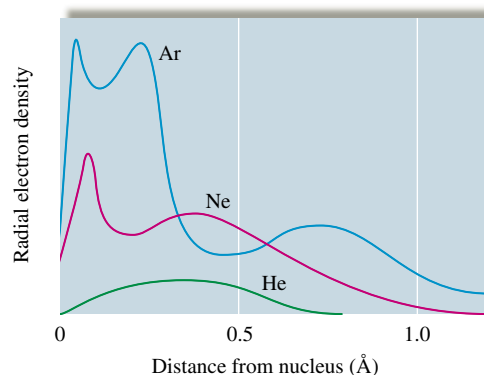
112. A certain microwave oven delivers 750. watts (joule/s) of power to a coffee cup containing 50.0 g of water at 25.0°C. If the wavelength of microwaves in the oven is 9.75 cm, how long does it take, and how many photons must be absorbed, to make the water boil? The specific heat capacity of water is $4.18 \text{ J}^\circ\text{C} \cdot \text{g}$ and assume only the water absorbs the energy of the microwaves.
113. Mars is roughly 60 million km from earth. How long does it take for a radio signal originating from earth to reach Mars?
114. Consider the following approximate visible light spectrum:



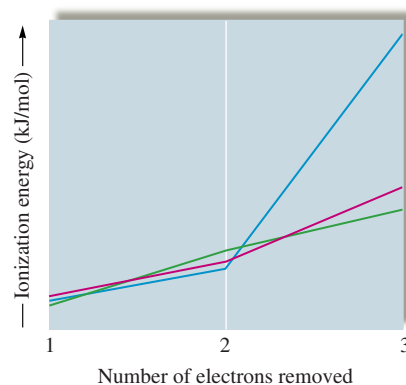
Barium emits light in the visible region of the spectrum. If each photon of light emitted from barium has an energy of 3.59×10^{-19} J, what color of visible light is emitted?

115. One of the visible lines in the hydrogen emission spectrum corresponds to the $n = 6$ to $n = 2$ electronic transition. What color light is this transition? See Exercise 114.

116. Using Fig. 7.28, list the elements (ignore the lanthanides and actinides) that have ground-state electron configurations that differ from those we would expect from their positions in the periodic table.
117. Are the following statements true for the hydrogen atom only, true for all atoms, or not true for any atoms?
- The principal quantum number completely determines the energy of a given electron.
 - The angular momentum quantum number, ℓ , determines the shapes of the atomic orbitals.
 - The magnetic quantum number, m_ℓ , determines the direction that the atomic orbitals point in space.
118. Although no currently known elements contain electrons in g orbitals in the ground state, it is possible that these elements will be found or that electrons in excited states of known elements could be in g orbitals. For g orbitals, the value of ℓ is 4. What is the lowest value of n for which g orbitals could exist? What are the possible values of m_ℓ ? How many electrons could a set of g orbitals hold?
119. Consider the representations of the p and d atomic orbitals in Figs. 7.14 and 7.16. What do the + and - signs indicate?
120. Total radial probability distributions for the helium, neon, and argon atoms are shown in the following graph. How can one interpret the shapes of these curves in terms of electron configurations, quantum numbers, and nuclear charges?



121. The following graph plots the first, second, and third ionization energies for Mg, Al, and Si.



Without referencing the text, which plot corresponds to which element? In one of the plots, there is a huge jump in energy

between I_2 and I_3 , unlike in the other two plots. Explain this phenomenon.

122. An ion having a 4+ charge and a mass of 49.9 amu has 2 electrons with principal quantum number $n = 1$, 8 electrons with $n = 2$, and 10 electrons with $n = 3$. Supply as many of the properties for the ion as possible from the information given. *Hint:* In forming ions for this species, the 4s electrons are lost before the 3d electrons.

- the atomic number
- total number of s electrons
- total number of p electrons
- total number of d electrons
- the number of neutrons in the nucleus
- the ground-state electron configuration of the neutral atom

123. The successive ionization energies for an unknown element are
 $I_1 = 896$ kJ/mol
 $I_2 = 1752$ kJ/mol
 $I_3 = 14,807$ kJ/mol
 $I_4 = 17,948$ kJ/mol

To which family in the periodic table does the unknown element most likely belong?

124. An unknown element is a nonmetal and has a valence electron configuration of ns^2np^4 .

- How many valence electrons does this element have?
- What are some possible identities for this element?
- What is the formula of the compound this element would form with potassium?
- Would this element have a larger or smaller radius than barium?
- Would this element have a greater or smaller ionization energy than fluorine?

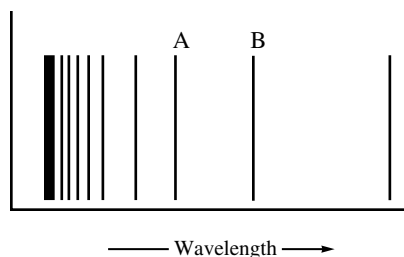
125. Using data from this chapter, calculate the change in energy expected for each of the following processes.

- $\text{Na}(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)$
- $\text{Mg}(g) + \text{F}(g) \rightarrow \text{Mg}^+(g) + \text{F}^-(g)$
- $\text{Mg}^+(g) + \text{F}(g) \rightarrow \text{Mg}^{2+}(g) + \text{F}^-(g)$
- $\text{Mg}(g) + 2\text{F}(g) \rightarrow \text{Mg}^{2+}(g) + 2\text{F}^-(g)$

Challenge Problems

126. One of the emission spectral lines for Be^{3+} has a wavelength of 253.4 nm for an electronic transition that begins in the state with $n = 5$. What is the principal quantum number of the lower-energy state corresponding to this emission? (*Hint:* The Bohr model can be applied to one-electron ions. Don't forget the Z factor: $Z = \text{nuclear charge} = \text{atomic number}$.)

127. The figure below represents part of the emission spectrum for a one-electron ion in the gas phase. All the lines result from electronic transitions from excited states to the $n = 3$ state. (See Exercise 126.)



- What electronic transitions correspond to lines A and B?
- If the wavelength of line B is 142.5 nm, calculate the wavelength of line A.

128. When the excited electron in a hydrogen atom falls from $n = 5$ to $n = 2$, a photon of blue light is emitted. If an excited electron in He^+ falls from $n = 4$, to which energy level must it fall so that a similar blue light (as with the hydrogen) is emitted? Prove it. (See Exercise 126.)

129. The wave function for the $2p_z$ orbital in the hydrogen atom is

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos \theta$$

where a_0 is the value for the radius of the first Bohr orbit in meters (5.29×10^{-11}), $\sigma = Z(r/a_0)$, r is the value for the distance from the nucleus in meters, and θ is an angle. Calculate the value of $\psi_{2p_z}^2$ at $r = a_0$ for $\theta = 0$ (z axis) and for $\theta = 90^\circ$ (xy plane).

130. Answer the following questions assuming that m_s could have three values rather than two and that the rules for n , ℓ , and m_ℓ are the normal ones.

- How many electrons would an orbital be able to hold?
- How many elements would the first and second periods in the periodic table contain?
- How many elements would be contained in the first transition metal series?
- How many electrons would the set of 4f orbitals be able to hold?

131. Assume that we are in another universe with different physical laws. Electrons in this universe are described by four quantum numbers with meanings similar to those we use. We will call these quantum numbers p , q , r , and s . The rules for these quantum numbers are as follows:

$$p = 1, 2, 3, 4, 5, \dots$$

q takes on positive odd integer and $q \leq p$.

r takes on all even integer values from $-q$ to $+q$. (Zero is considered an even number.)

$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

- Sketch what the first four periods of the periodic table will look like in this universe.
- What are the atomic numbers of the first four elements you would expect to be least reactive?
- Give an example, using elements in the first four rows, of ionic compounds with the formulas XY, XY₂, X₂Y, XY₃, and X₂Y₃.
- How many electrons can have $p = 4$, $q = 3$?
- How many electrons can have $p = 3$, $q = 0$, $r = 0$?
- How many electrons can have $p = 6$?

132. Without looking at data in the text, sketch a qualitative graph of the third ionization energy versus atomic number for the elements Na through Ar, and explain your graph.

133. The following numbers are the ratios of second ionization energy to first ionization energy:

| | |
|-----|-----|
| Na: | 9.2 |
| Mg: | 2.0 |
| Al: | 3.1 |
| Si: | 2.0 |

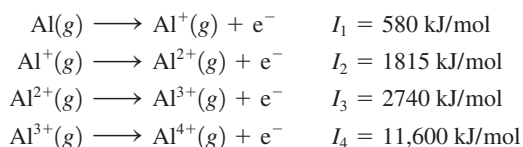
P: 1.8
S: 2.3
Cl: 1.8
Ar: 1.8

Explain these relative numbers.

134. We expect the atomic radius to increase going down a group in the periodic table. Can you suggest why the atomic radius of hafnium breaks this rule? (See data below.)

| Atomic Radii, in pm | | | |
|---------------------|-------|----|-------|
| Sc | 157 | Ti | 147.7 |
| Y | 169.3 | Zr | 159.3 |
| La | 191.5 | Hf | 147.6 |

135. Consider the following ionization energies for aluminum:



- Account for the trend in the values of the ionization energies.
 - Explain the large increase between I_3 and I_4 .
 - Which one of the four ions has the greatest electron affinity? Explain.
 - List the four aluminum ions given in order of increasing size, and explain your ordering. (*Hint*: Remember that most of the size of an atom or ion is due to its electrons.)
136. While Mendeleev predicted the existence of several undiscovered elements, he did not predict the existence of the noble gases, the lanthanides, or the actinides. Propose reasons why Mendeleev was not able to predict the existence of the noble gases.
137. An atom of a particular element is traveling at 1.00% of the speed of light. The de Broglie wavelength is found to be 3.31×10^{-3} pm. Which element is this? Prove it.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

138. As the weapons officer aboard the *Starship Chemistry*, it is your duty to configure a photon torpedo to remove an electron from the outer hull of an enemy vessel. You know that the work function (the binding energy of the electron) of the hull of the enemy ship is 7.52×10^{-19} J.
- What wavelength does your photon torpedo need to be to eject an electron?
 - You find an extra photon torpedo with a wavelength of 259 nm and fire it at the enemy vessel. Does this photon torpedo do any damage to the ship (does it eject an electron)?
 - If the hull of the enemy vessel is made of the element with an electron configuration of $[\text{Ar}]4s^13d^{10}$, what metal is this?

139. Francium, Fr, is a radioactive element found in some uranium minerals and is formed as a result of the decay of actinium.
- What are the electron configurations of francium and its predicted most common ion?
 - It has been estimated that at any one time, there is only one (1.0) ounce of francium on earth. Assuming this is true, what number of francium atoms exist on earth?
 - The longest-lived isotope of francium is ^{223}Fr . What is the total mass in grams of the neutrons in one atom of this isotope?
140. Answer the following questions based on the given electron configurations and identify the elements.
- Arrange these atoms in order of increasing size: $[\text{Kr}]5s^24d^{10}5p^6$; $[\text{Kr}]5s^24d^{10}5p^1$; $[\text{Kr}]5s^24d^{10}5p^3$.
 - Arrange these atoms in order of decreasing first ionization energy: $[\text{Ne}]3s^23p^5$; $[\text{Ar}]4s^23d^{10}4p^3$; $[\text{Ar}]4s^23d^{10}4p^5$.

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

141. From the information below, identify element X.
- The wavelength of the radio waves sent by an FM station broadcasting at 97.1 MHz is 30.0 million (3.00×10^7) times greater than the wavelength corresponding to the energy difference between a particular excited state of the hydrogen atom and the ground state.
 - Let V represent the principal quantum number for the valence shell of element X. If an electron in the hydrogen atom falls from shell V to the inner shell corresponding to the excited state mentioned above in part a, the wavelength of light emitted is the same as the wavelength of an electron moving at a speed of 570. m/s.
 - The number of unpaired electrons for element X in the ground state is the same as the maximum number of electrons in an atom that can have the quantum number designations $n = 2$, $m_\ell = -1$, and $m_s = -\frac{1}{2}$.
 - Let A equal the charge of the stable ion that would form when the undiscovered element 120 forms ionic compounds. This value of A also represents the angular momentum quantum number for the subshell containing the unpaired electron(s) for element X.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

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