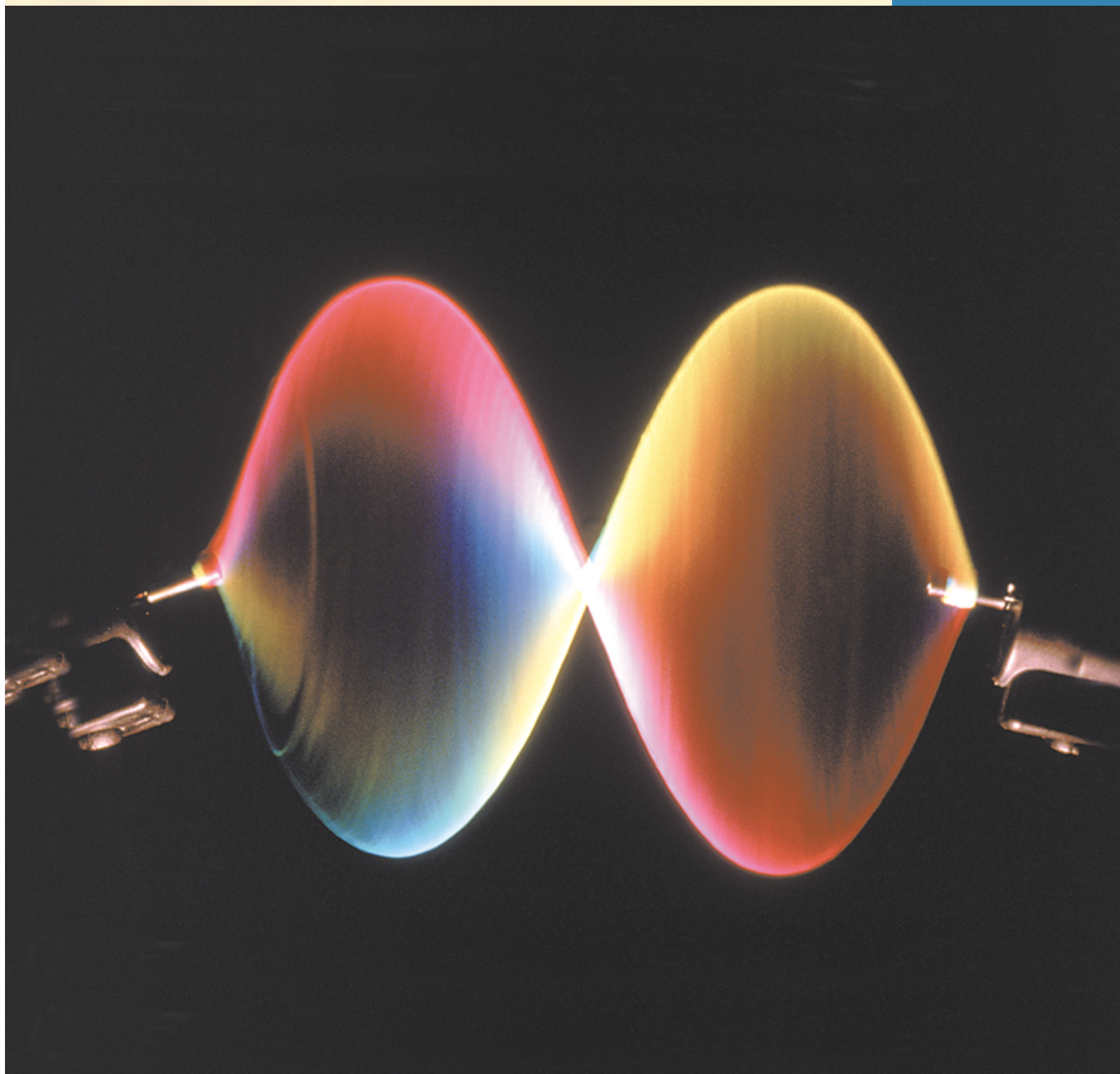
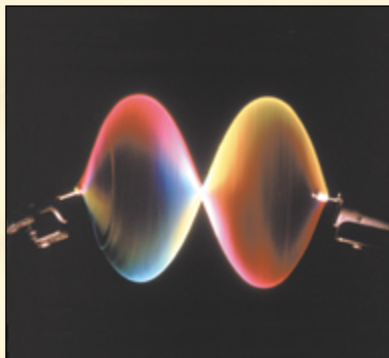


The Structure of Atoms

5





Descriptions of waves play an important role in our theories of light and of atomic structure.

OUTLINE

Subatomic Particles

- 5-1 Fundamental Particles
- 5-2 The Discovery of Electrons
- 5-3 Canal Rays and Protons
- 5-4 Rutherford and the Nuclear Atom
- 5-5 Atomic Number
- 5-6 Neutrons
- 5-7 Mass Number and Isotopes
- 5-8 Mass Spectrometry and Isotopic Abundance
- 5-9 The Atomic Weight Scale and Atomic Weights

The Electronic Structures of Atoms

- 5-10 Electromagnetic Radiation
- 5-11 The Photoelectric Effect
- 5-12 Atomic Spectra and the Bohr Atom
- 5-13 The Wave Nature of the Electron
- 5-14 The Quantum Mechanical Picture of the Atom
- 5-15 Quantum Numbers
- 5-16 Atomic Orbitals
- 5-17 Electron Configurations
- 5-18 The Periodic Table and Electron Configurations

OBJECTIVES

After you have studied this chapter, you should be able to

- *Describe the evidence for the existence and properties of electrons, protons, and neutrons*
- *Predict the arrangements of the particles in atoms*
- *Describe isotopes and their composition*
- *Calculate atomic weights from isotopic abundance*
- *Describe the wave properties of light and how wavelength, frequency, and speed are related*
- *Use the particle description of light, and explain how it is related to the wave description*
- *Relate atomic emission and absorption spectra to important advances in atomic theory*
- *Describe the main features of the quantum mechanical picture of the atom*
- *Describe the four quantum numbers, and give possible combinations of their values for specific atomic orbitals*
- *Describe the shapes of orbitals and recall the usual order of their relative energies*
- *Write the electron configurations of atoms*
- *Relate the electron configuration of an atom to its position in the periodic table*

The Dalton theory of the atom and related ideas were the basis for our study of *composition stoichiometry* (Chapter 2) and *reaction stoichiometry* (Chapter 3), but that level of atomic theory leaves many questions unanswered. *Why* do atoms combine to form compounds? *Why* do they combine only in simple numerical ratios? *Why* are particular numerical ratios of atoms observed in compounds? *Why* do different elements have different properties? *Why* are they gases, liquids, solids, metals, nonmetals, and so on? *Why* do some groups of elements have similar properties and form compounds with similar formulas? The answers to these and many other fascinating questions in chemistry are supplied by our modern understanding of the nature of atoms. But how can we study something as small as an atom?

Much of the development of modern atomic theory was based on two broad types of research carried out by dozens of scientists just before and after 1900. The first type dealt with the electrical nature of matter. These studies led scientists to recognize that atoms are composed of more fundamental particles and helped them to describe the approximate arrangements of these particles in atoms. The second broad area of research dealt with the interaction of matter with energy in the form of light. Such research included studies of the colors of the light that substances give off or absorb. These studies led to a much more detailed understanding of the arrangements of particles in atoms. It became clear that the arrangement of the particles determines the chemical and physical properties of each element. As we learn more about the structures of atoms, we are able to organize chemical facts in ways that help us to understand the behavior of matter.

We will first study the particles that make up atoms and the basic structure of atoms. Then we will take a look at the quantum mechanical theory of atoms and see how this theory describes the arrangement of the electrons in atoms. Current atomic theory is considerably less than complete. Even so, it is a powerful tool that helps us describe the forces holding atoms in chemical combination with one another.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.2, Structure of Atoms.



Accounts of some important developments in atomic theory appear on the World Wide Web; for example, The National Museum of Science and Industry can be found at <http://www.nmsi.ac.uk/on-line/Electron>

SUBATOMIC PARTICLES

5-1 FUNDAMENTAL PARTICLES

In our study of atomic structure, we look first at the **fundamental particles**. These are the basic building blocks of all atoms. Atoms, and hence *all* matter, consist principally of three fundamental particles: *electrons*, *protons*, and *neutrons*. Knowledge of the nature and functions of these particles is essential to understanding chemical interactions. The relative masses and charges of the three fundamental particles are shown in Table 5-1. The

Many other subatomic particles, such as quarks, positrons, neutrinos, pions, and muons, have also been discovered. It is not necessary to study their characteristics to learn the fundamentals of atomic structure that are important in chemical reactions.

TABLE 5-1 *Fundamental Particles of Matter*

Particle	Mass	Charge (relative scale)
electron (e^-)	0.00054858 amu	1-
proton (p or p^+)	1.0073 amu	1+
neutron (n or n^0)	1.0087 amu	none

mass of an electron is very small compared with the mass of either a proton or a neutron. The charge on a proton is equal in magnitude, but opposite in sign, to the charge on an electron. Let's examine these particles in more detail.

5-2 THE DISCOVERY OF ELECTRONS

The process is called chemical electrolysis. *Lysis* means “splitting apart.”

Study Figures 5-1 and 5-2 carefully as you read this section.

Some of the earliest evidence about atomic structure was supplied in the early 1800s by the English chemist Humphry Davy (1778–1829). He found that when he passed electric current through some substances, the substances decomposed. He therefore suggested that the elements of a chemical compound are held together by electrical forces. In 1832–1833, Michael Faraday (1791–1867), Davy's student, determined the quantitative relationship between the amount of electricity used in electrolysis and the amount of chemical reaction that occurs. Studies of Faraday's work by George Stoney (1826–1911) led him to suggest in 1874 that units of electric charge are associated with atoms. In 1891, he suggested that they be named *electrons*.

The most convincing evidence for the existence of electrons came from experiments using *cathode-ray tubes* (Figure 5-1). Two electrodes are sealed in a glass tube containing

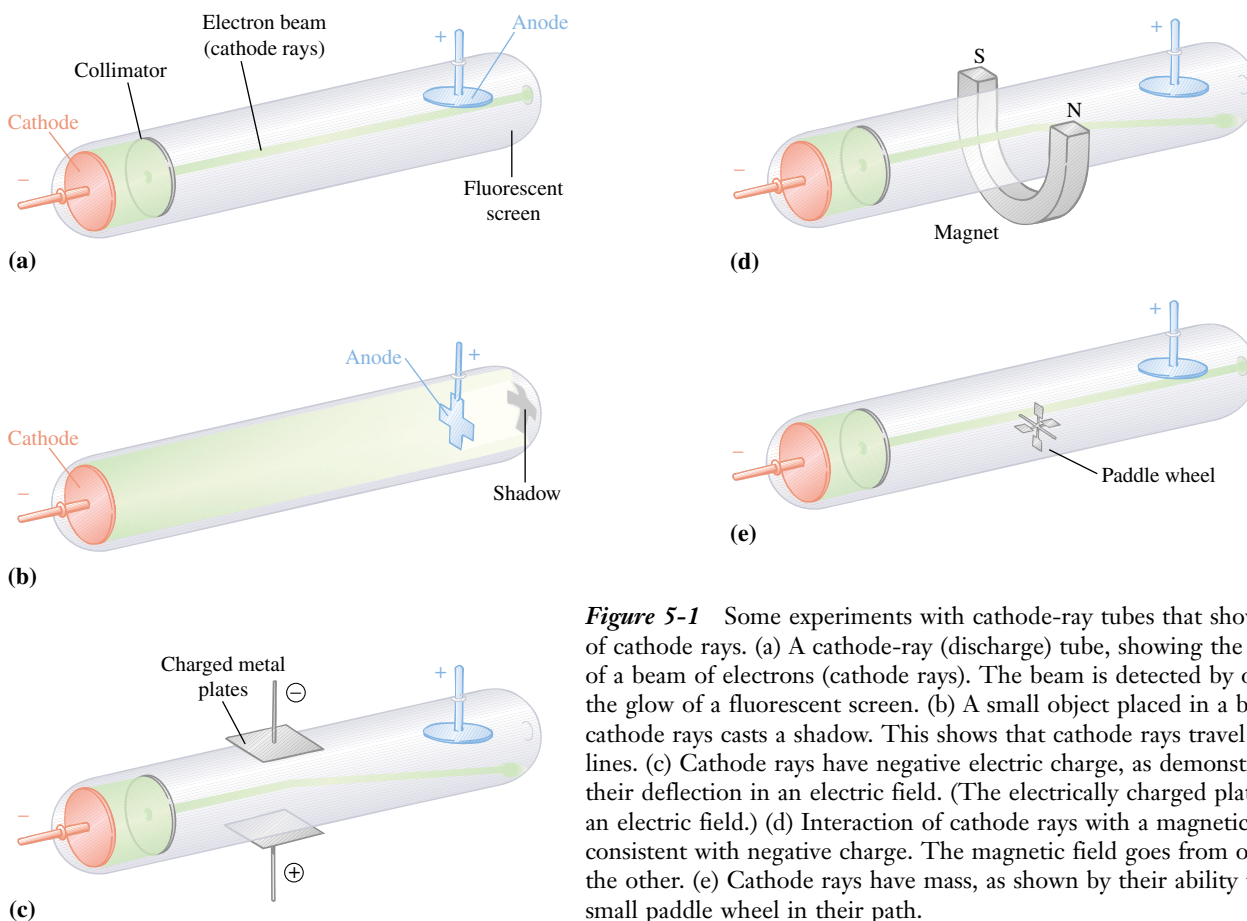


Figure 5-1 Some experiments with cathode-ray tubes that show the nature of cathode rays. (a) A cathode-ray (discharge) tube, showing the production of a beam of electrons (cathode rays). The beam is detected by observing the glow of a fluorescent screen. (b) A small object placed in a beam of cathode rays casts a shadow. This shows that cathode rays travel in straight lines. (c) Cathode rays have negative electric charge, as demonstrated by their deflection in an electric field. (The electrically charged plates produce an electric field.) (d) Interaction of cathode rays with a magnetic field is also consistent with negative charge. The magnetic field goes from one pole to the other. (e) Cathode rays have mass, as shown by their ability to turn a small paddle wheel in their path.

gas at a very low pressure. When a high voltage is applied, current flows and rays are given off by the cathode (negative electrode). These rays travel in straight lines toward the anode (positive electrode) and cause the walls opposite the cathode to glow. An object placed in the path of the cathode rays casts a shadow on a zinc sulfide screen placed near the anode. The shadow shows that the rays travel from the cathode toward the anode. The rays must therefore be negatively charged. Furthermore, they are deflected by electric and magnetic fields in the directions expected for negatively charged particles.

In 1897 J. J. Thomson (1856–1940) studied these negatively charged particles more carefully. He called them **electrons**, the name Stoney had suggested in 1891. By studying the degree of deflections of cathode rays in different electric and magnetic fields, Thomson determined the ratio of the charge (e) of the electron to its mass (m). The modern value for this ratio is

$$e/m = 1.75882 \times 10^8 \text{ coulomb (C)/gram}$$

This ratio is the same regardless of the type of gas in the tube, the composition of the electrodes, or the nature of the electric power source. The clear implication of Thomson's work was that electrons are fundamental particles present in all atoms. We now know that this is true and that all atoms contain integral numbers of electrons.

Once the charge-to-mass ratio for the electron had been determined, additional experiments were necessary to determine the value of either its mass or its charge, so that the other could be calculated. In 1909, Robert Millikan (1868–1953) solved this dilemma with the famous “oil-drop experiment,” in which he determined the charge of the electron. This experiment is described in Figure 5-2. All of the charges measured by Millikan turned

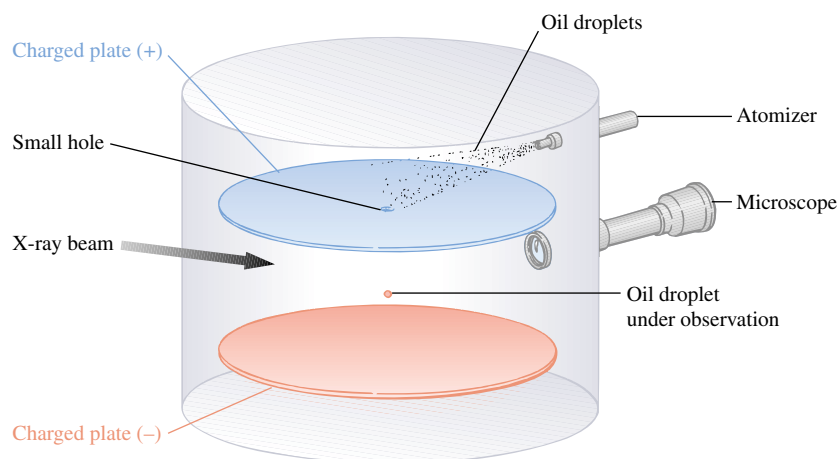


Figure 5-2 The Millikan oil-drop experiment. Tiny spherical oil droplets are produced by an atomizer. The mass of the spherical drop can be calculated from its volume (obtained from a measurement of the radius of the drop with a microscope) and the known density of the oil. A few droplets fall through the hole in the upper plate. Irradiation with X-rays gives some of these oil droplets a negative charge. When the voltage between the plates is increased, a negatively charged drop falls more slowly because it is attracted by the positively charged upper plate and repelled by the negatively charged lower plate. At one particular voltage, the electrical force (up) and the gravitational force (down) on the drop are exactly balanced, and the drop remains stationary. Knowing this voltage and the mass of the drop, we can calculate the charge on the drop.

The coulomb (C) is the standard unit of *quantity* of electric charge. It is defined as the quantity of electricity transported in one second by a current of one ampere. It corresponds to the amount of electricity that will deposit 0.00111798 g of silver in an apparatus set up for plating silver.

X-rays are a form of radiation of much shorter wavelength than visible light (see Section 5-10). They are sufficiently energetic to knock electrons out of the atoms in the air. In Millikan's experiment these free electrons became attached to some of the oil droplets.



Robert A. Millikan (*left*) was an American physicist who was a professor at the University of Chicago and later director of the physics laboratory at the California Institute of Technology. He won the 1923 Nobel Prize in physics.

The charge on one mole (Avogadro's number) of electrons is 96,485 coulombs.

The value of e/m obtained by Thomson and the values of e and m obtained by Millikan differ slightly from the modern values given in this text because early measurements were not as accurate as modern ones.

The proton was observed by Rutherford and James Chadwick in 1919 as a particle that is emitted by bombardment of certain atoms with α -particles.

out to be integral multiples of the same number. He assumed that this smallest charge was the charge on one electron. This value is 1.60218×10^{-19} coulomb (modern value).

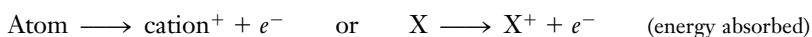
The charge-to-mass ratio, $e/m = 1.75882 \times 10^8$ C/g, can be used in inverse form to calculate the mass of the electron:

$$\begin{aligned} m &= \frac{1 \text{ g}}{1.75882 \times 10^8 \text{ C}} \times 1.60218 \times 10^{-19} \text{ C} \\ &= 9.10940 \times 10^{-28} \text{ g} \end{aligned}$$

This is only about 1/1836 the mass of a hydrogen atom, the lightest of all atoms. Millikan's simple oil-drop experiment stands as one of the cleverest, yet most fundamental, of all classic scientific experiments. It was the first experiment to suggest that atoms contain integral numbers of electrons; we now know this to be true.

5-3 CANAL RAYS AND PROTONS

In 1886, Eugen Goldstein (1850–1930) first observed that a cathode-ray tube also generates a stream of positively charged particles that moves toward the cathode. These were called **canal rays** because they were observed occasionally to pass through a channel, or "canal," drilled in the negative electrode (Figure 5-3). These *positive rays*, or *positive ions*, are created when the gaseous atoms in the tube lose electrons. Positive ions are formed by the process



Different elements give positive ions with different e/m ratios. The regularity of the e/m values for different ions led to the idea that there is a unit of positive charge and that it resides in the **proton**. The proton is a fundamental particle with a charge equal in magnitude but opposite in sign to the charge on the electron. Its mass is almost 1836 times that of the electron.

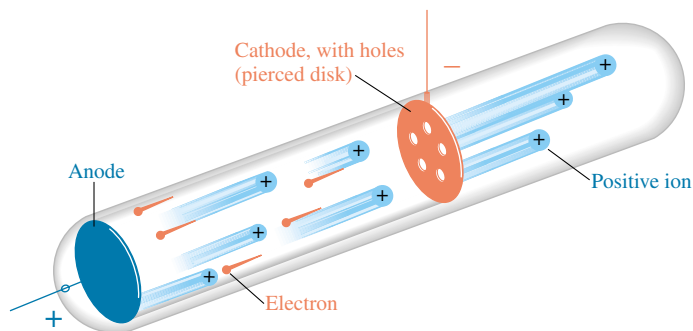


Figure 5-3 A cathode-ray tube with a different design and with a perforated cathode. Such a tube was used to produce canal rays and to demonstrate that they travel toward the cathode. Like cathode rays, these *positive rays* are deflected by electric or magnetic fields, but in the opposite direction from cathode rays. Canal ray particles have e/m ratios many times smaller than those of electrons, due to their much greater masses. When different elements are in the tube, positive ions with different e/m ratios are observed.

5-4 RUTHERFORD AND THE NUCLEAR ATOM

By the early 1900s, it was clear that each atom contains regions of both positive and negative charge. The question was, how are these charges distributed? The dominant view of that time was summarized in J. J. Thomson's model of the atom; the positive charge was assumed to be distributed evenly throughout the atom. The negative charges were pictured as being imbedded in the atom like plums in a pudding (the "plum pudding model").

Soon after Thomson developed his model, tremendous insight into atomic structure was provided by one of Thomson's former students, Ernest Rutherford (1871–1937), who was the outstanding experimental physicist of his time.

By 1909, Ernest Rutherford had established that alpha (α) particles are positively charged particles. They are emitted at high kinetic energies by some radioactive atoms, that is, atoms that disintegrate spontaneously. In 1910, Rutherford's research group carried out a series of experiments that had an enormous impact on the scientific world. They bombarded a very thin piece of gold foil with α -particles from a radioactive source. A fluorescent zinc sulfide screen was placed behind the foil to indicate the scattering of the α -particles by the gold foil (Figure 5-4). Scintillations (flashes) on the screen, caused by the individual α -particles, were counted to determine the relative numbers of α -particles deflected at various angles. Alpha particles were known to be extremely dense, much denser than gold.

If the Thomson model of the atom were correct, any α -particles passing through the foil would have been deflected by very small angles. Quite unexpectedly, nearly all of the α -particles passed through the foil with little or no deflection. A few, however, were

α -Particles are now known to be He^{2+} ions, that is, helium atoms without their two electrons. (See Chapter 26.)

Radioactivity is contrary to the Daltonian idea of the indivisibility of atoms.

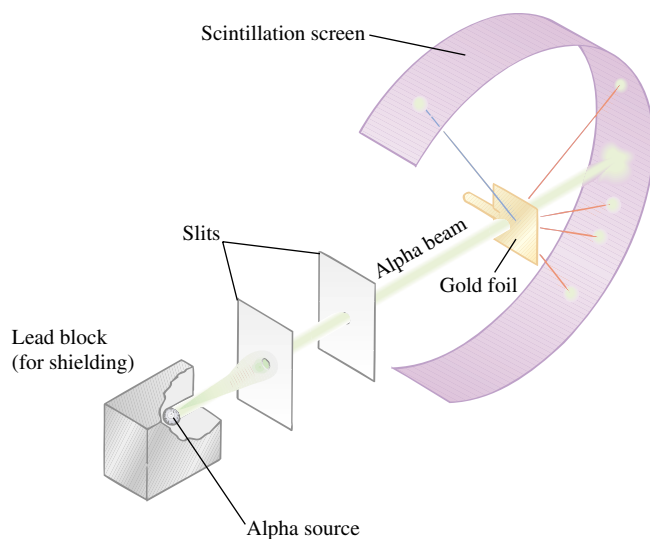


Figure 5-4 The Rutherford scattering experiment. A narrow beam of α -particles from a radioactive source was directed at a very thin sheet of gold foil. Most of the particles passed right through the gold foil (*brown*). Many were deflected through moderate angles (*shown in red*). These deflections were surprising, but the 0.001% of the total that were reflected at acute angles (*shown in blue*) were totally unexpected. Similar results were observed using foils of other metals.



Ernest Rutherford was one of the giants in the development of our understanding of atomic structure. While working with J. J. Thomson at Cambridge University, he discovered α and β radiation. He spent the years 1899–1907 at McGill University in Canada where he proved the nature of these two radiations, for which he received the Nobel Prize in chemistry in 1908. He returned to England in 1908, and it was there, at Manchester University, that he and his coworkers Hans Geiger and Ernst Marsden performed the famous gold foil experiments that led to the nuclear model of the atom. Not only did he perform much important research in physics and chemistry, but he also guided the work of ten future recipients of the Nobel Prize.

This representation is *not* to scale. If nuclei were as large as the black dots that represent them, each white region, which represents the size of an atom, would have a diameter of more than 30 feet!

deflected through large angles, and a very few α -particles even returned from the gold foil in the direction from which they had come! Rutherford was astounded. In his own words,

It was quite the most incredible event that has ever happened to me in my life. It was almost as if you fired a 15-inch shell into a piece of tissue paper and it came back and hit you.

Rutherford's mathematical analysis of his results showed that the scattering of positively charged α -particles was caused by repulsion from very dense regions of positive charge in the gold foil. He concluded that the mass of one of these regions is nearly equal to that of a gold atom, but that the diameter is no more than 1/10,000 that of an atom. Many experiments with foils of different metals yielded similar results. Realizing that these observations were inconsistent with previous theories about atomic structure, Rutherford discarded the old theory and proposed a better one. He suggested that each atom contains a *tiny, positively charged, massive center* that he called an **atomic nucleus**. Most α -particles pass through metal foils undeflected because atoms are *primarily* empty space populated only by the very light electrons. The few particles that are deflected are the ones that come close to the heavy, highly charged metal nuclei (Figure 5-5).

Rutherford was able to determine the magnitudes of the positive charges on the atomic nuclei. The picture of atomic structure that he developed is called the Rutherford model of the atom.

Atoms consist of very small, very dense positively charged nuclei surrounded by clouds of electrons at relatively great distances from the nuclei.

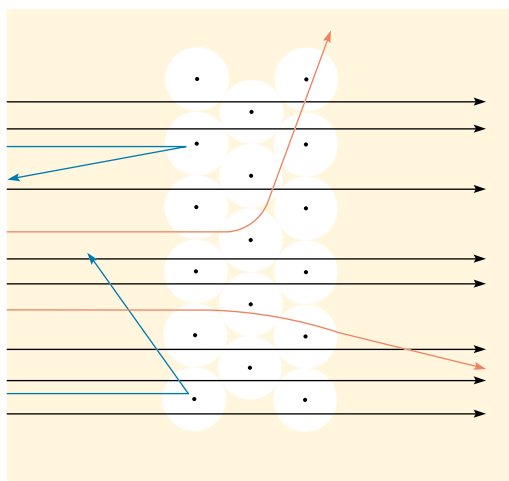


Figure 5-5 An interpretation of the Rutherford scattering experiment. The atom is pictured as consisting mostly of “open” space. At the center is a tiny and extremely dense nucleus that contains all of the atom’s positive charge and nearly all of its mass. The electrons are thinly distributed throughout the “open” space. Most of the positively charged α -particles (*black arrows*) pass through the open space undeflected, not coming near any gold nuclei. The few that pass fairly close to a nucleus (*red arrows*) are repelled by electrostatic forces and thereby deflected. The very few particles that are on a “collision course” with gold nuclei are repelled backward at acute angles (*blue arrows*). Calculations based on the results of the experiment indicated that the diameter of the open-space portion of the atom is from 10,000 to 100,000 times greater than the diameter of the nucleus.

5-5 ATOMIC NUMBER

Only a few years after Rutherford's scattering experiments, H. G. J. Moseley (1887–1915) studied X-rays given off by various elements. Max von Laue (1879–1960) had shown that X-rays could be diffracted by crystals into a spectrum in much the same way that visible light can be separated into its component colors. Moseley generated X-rays by aiming a beam of high-energy electrons at a solid target made of a single pure element (Figure 5-6).

The spectra of X-rays produced by targets of different elements were recorded photographically. Each photograph consisted of a series of lines representing X-rays at various wavelengths; each element produced its own distinct set of wavelengths. Comparison of results from different elements revealed that corresponding lines were displaced toward shorter wavelengths as atomic weights of the target materials increased, with a few exceptions. Moseley showed that the X-ray wavelengths could be better correlated with the atomic number. On the basis of his mathematical analysis of these X-ray data, he concluded that

each element differs from the preceding element by having one more positive charge in its nucleus.

For the first time it was possible to arrange all known elements in order of increasing nuclear charge. A plot illustrating this interpretation of Moseley's data appears in Figure 5-7.

We now know that every nucleus contains an integral number of protons exactly equal to the number of electrons in a neutral atom of the element. Every hydrogen atom contains

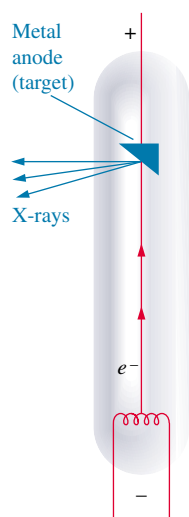


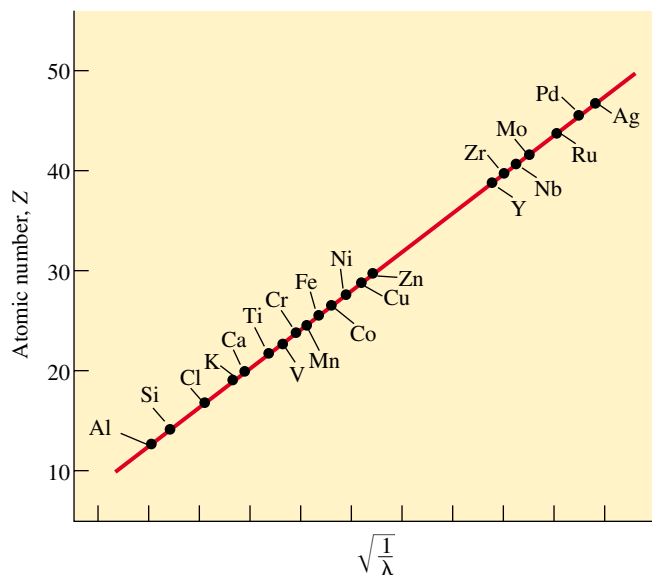
Figure 5-6 A simplified representation of the production of X-rays by bombardment of a solid target with a high-energy beam of electrons.

In a modern technique known as “X-ray fluorescence spectroscopy,” the wavelengths of X-rays given off by a sample target indicate which elements are present in the sample.



H. G. J. Moseley was one of the many remarkable scientists who worked with Ernest Rutherford. In 1913, Moseley found that the wavelengths of X-rays emitted by an element are related in a precise way to the atomic number of the element. This discovery led to the realization that atomic number, related to the electrical properties of the atom, was more fundamental to determining the properties of the elements than atomic weight. This put the ideas of the periodic table on a more fundamental footing. Moseley's scientific career was very short. He enlisted in the British army during World War I and died in battle in the Gallipoli campaign in 1915.

Figure 5-7 A plot of some of Moseley's X-ray data. The atomic number of an element is found to be directly proportional to the square root of the reciprocal of the wavelength of a particular X-ray spectral line. Wavelength (Section 5-10) is represented by λ .



one proton, every helium atom contains two protons, and every lithium atom contains three protons. The number of protons in the nucleus of an atom determines its identity; this number is known as the **atomic number** of that element.

5-6 NEUTRONS

The third fundamental particle, the neutron, eluded discovery until 1932. James Chadwick (1891–1974) correctly interpreted experiments on the bombardment of beryllium with high-energy α -particles. Later experiments showed that nearly all elements up to potassium, element 19, produce neutrons when they are bombarded with high-energy α -particles. The **neutron** is an uncharged particle with a mass slightly greater than that of the proton.

This does not mean that elements above number 19 do not have neutrons, only that neutrons are not generally knocked out of atoms of higher atomic number by α -particle bombardment.

Atoms consist of very small, very dense nuclei surrounded by clouds of electrons at relatively great distances from the nuclei. All nuclei contain protons; nuclei of all atoms except the common form of hydrogen also contain neutrons.

Nuclear diameters are about 10^{-5} nanometers (nm); atomic diameters are about 10^{-1} nm. To put this difference in perspective, suppose that you wish to build a model of an atom using a basketball (diameter about 9.5 inches) as the nucleus; on this scale, the atomic model would be nearly 6 miles across!

5-7 MASS NUMBER AND ISOTOPES

Most elements consist of atoms of different masses, called **isotopes**. The isotopes of a given element contain the same number of protons (and also the same number of electrons) because they are atoms of the same element. They differ in mass because they contain different numbers of neutrons in their nuclei.

Isotopes are atoms of the same element with different masses; they are atoms containing the same number of protons but different numbers of neutrons.

For example, there are three distinct kinds of hydrogen atoms, commonly called hydrogen, deuterium, tritium. (This is the only element for which we give each isotope a different name.) Each contains one proton in the atomic nucleus. The predominant form of hydrogen contains no neutrons, but each deuterium atom contains one neutron and each tritium atom contains two neutrons in its nucleus (Table 5-2). All three forms of hydrogen display very similar chemical properties.

The **mass number** of an atom is the sum of the number of protons and the number of neutrons in its nucleus; that is

$$\begin{aligned}\text{Mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{neutron number}\end{aligned}$$

A mass number is a count of the *number* of protons plus neutrons present, so it must be a whole number. Because the masses of the proton and the neutron are both about 1 amu, the mass number is *approximately* equal to the actual mass of the isotope (which is not a whole number).

The mass number for normal hydrogen atoms is 1; for deuterium, 2; and for tritium, 3. The composition of a nucleus is indicated by its **nuclide symbol**. This consists of the symbol for the element (E), with the atomic number (Z) written as a subscript at the lower left and the mass number (A) as a superscript at the upper left, ${}^A_Z E$. By this system, the three isotopes of hydrogen are designated as ${}^1_1\text{H}$, ${}^2_1\text{H}$, and ${}^3_1\text{H}$.

EXAMPLE 5-1 Determination of Atomic Makeup

Determine the number of protons, neutrons, and electrons in each of the following species. Are the members within each pair isotopes?

- (a) ${}^{35}_{17}\text{Cl}$ and ${}^{37}_{17}\text{Cl}$ (b) ${}^{63}_{29}\text{Cu}$ and ${}^{65}_{29}\text{Cu}$

Plan

Knowing that the number at the bottom left of the nuclide symbol is the atomic number or number of protons, we can verify the identity of the element in addition to knowing the number or protons per nuclide. From the mass number at the top left, we know the number of protons plus neutrons. The number of protons (atomic number) minus the number of electrons must equal the charge, if any, shown at the top right. From these data one can determine if two nuclides have the same number of protons and are therefore the same element. If they are the same element, they will be isotopes only if their mass numbers differ.

TABLE 5-2 The Three Isotopes of Hydrogen

Name	Symbol	Nuclide Symbol	Mass (amu)	Atomic Abundance in Nature	No. of Protons	No. of Neutrons	No. of Electrons (in neutral atoms)
hydrogen	H	${}^1_1\text{H}$	1.007825	99.985%	1	0	1
deuterium	D	${}^2_1\text{H}$	2.01400	0.015%	1	1	1
tritium*	T	${}^3_1\text{H}$	3.01605	0.000%	1	2	1

*No known natural sources; produced by decomposition of artificial isotopes.

Solution

- (a) For ${}_{17}^{35}\text{Cl}$: Atomic number = 17. There are therefore 17 protons per nucleus.
 Mass number = 35. There are therefore 35 protons plus neutrons or, because we know that there are 17 protons, there are 18 neutrons.
 Because no charge is indicated, there must be equal numbers of protons and electrons, or 17 electrons.

For ${}_{17}^{37}\text{Cl}$: There are 17 protons, 20 neutrons, and 17 electrons per atom.

These are isotopes of the same element. Both have 17 protons, but they differ in their numbers of neutrons: one has 18 neutrons and the other has 20.

- (b) For ${}_{29}^{63}\text{Cu}$: Atomic number = 29. There are 29 protons per nucleus.
 Mass number = 63. There are 29 protons plus 34 neutrons.
 Because no charge is indicated, there must be equal numbers of protons and electrons, or 29 electrons.

For ${}_{29}^{65}\text{Cu}$: There are 29 protons, 36 neutrons, and 29 electrons per atom.

These are isotopes. Both have 29 protons, but they differ in their numbers of neutrons: one isotope has 34 neutrons and the other has 36.

You should now work Exercises 16 and 18.

5-8 MASS SPECTROMETRY AND ISOTOPIC ABUNDANCE

Mass spectrometers are instruments that measure the charge-to-mass ratio of charged particles (Figures 5-8). A gas sample at very low pressure is bombarded with high-energy electrons. This causes electrons to be ejected from some of the gas molecules, creating positive ions. The positive ions are then focused into a very narrow beam and accelerated by an electric field toward a magnetic field. The magnetic field deflects the ions from their straight-line path. The extent to which the beam of ions is deflected depends on four factors:

1. *Magnitude of the accelerating voltage (electric field strength).* Higher voltages result in beams of more rapidly moving particles that are deflected less than the beams of the more slowly moving particles produced by lower voltages.
2. *Magnetic field strength.* Stronger fields deflect a given beam more than weaker fields.
3. *Masses of the particles.* Because of their inertia, heavier particles are deflected less than lighter particles that carry the same charge.
4. *Charges on the particles.* Particles with higher charges interact more strongly with magnetic fields and are thus deflected more than particles of equal mass with smaller charges.

The mass spectrometer is used to measure masses of isotopes as well as isotopic abundances, that is, the relative amounts of the isotopes. Helium occurs in nature almost exclusively as ${}^4\text{He}$. Its atomic mass can be determined in an experiment such as that illustrated in Figure 5-8.

A beam of Ne^+ ions in the mass spectrometer is split into three segments. The mass spectrum of these ions (a graph of the relative numbers of ions of each mass) is shown in Figure 5-9. This indicates that neon occurs in nature as three isotopes: ${}^{20}_{10}\text{Ne}$, ${}^{21}_{10}\text{Ne}$, and

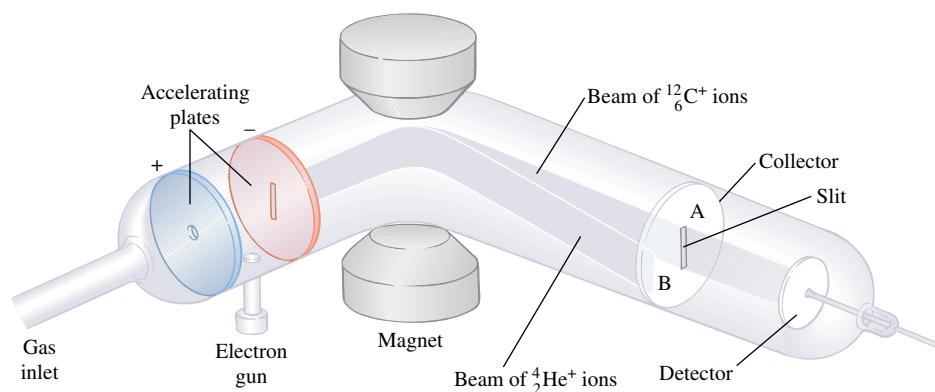


Figure 5-8 The mass spectrometer. In the mass spectrometer, gas molecules at low pressure are ionized and accelerated by an electric field. The ion beam is then passed through a magnetic field. In that field the beam is resolved into components, each containing particles of equal charge-to-mass ratio. Lighter particles are deflected more strongly than heavy ones with the same charge. In a beam containing $^{12}_6\text{C}^+$ and $^4_2\text{He}^+$ ions, the lighter $^4_2\text{He}^+$ ions would be deflected more than the heavier $^{12}_6\text{C}^+$ ions. The spectrometer shown is adjusted to detect the $^{12}_6\text{C}^+$ ions. By changing the magnitude of the magnetic or electric field, we can move the beam of $^4_2\text{He}^+$ ions striking the collector from B to A, where it would be detected. The relative masses of the ions are calculated from the changes required to refocus the beam.

$^{22}_{10}\text{Ne}$. In Figure 5-9 we see that the isotope $^{20}_{10}\text{Ne}$, mass 19.99244 amu, is the most abundant isotope (has the tallest peak). It accounts for 90.48% of the atoms. $^{22}_{10}\text{Ne}$, mass 21.99138, accounts for 9.25%, and $^{21}_{10}\text{Ne}$, mass 20.99384, for only 0.27% of the atoms.

Figure 5-10 shows a modern mass spectrometer. In nature, some elements, such as fluorine and phosphorus, exist in only one form, but most elements occur as isotopic mixtures. Some examples of natural isotopic abundances are given in Table 5-3. The percentages are based on the numbers of naturally occurring atoms of each isotope, *not* on their masses.

Isotopes are two or more forms of atoms of the same element with different masses; the atoms contain the same number of protons but different numbers of neutrons.

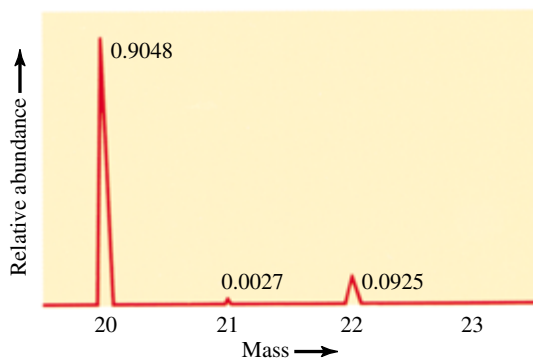
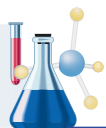


Figure 5-9 Mass spectrum of neon (1+ ions only). Neon consists of three isotopes, of which neon-20 is by far the most abundant (90.48%). The mass of that isotope, to five decimal places, is 19.99244 amu on the carbon-12 scale. The number by each peak corresponds to the fraction of all Ne^+ ions represented by the isotope with that mass.



The Development of Science

Stable Isotope Ratio Analysis

Many elements exist as two or more stable isotopes, although one isotope is usually present in far greater abundance. For example, there are two stable isotopes of carbon, ^{13}C and ^{12}C , of which ^{12}C is the more abundant, constituting 98.89% of all carbon. Similarly, there are two stable isotopes of nitrogen, ^{14}N and ^{15}N , of which ^{14}N makes up 99.63% of all nitrogen.

Differences in chemical and physical properties that arise from differences in atomic mass of an element are known as isotope effects. We know that the extranuclear structure of an element (the number of electrons and their arrangement) essentially determines its chemical behavior, whereas the nucleus has more influence on many of the physical properties of the element. Because all isotopes of a given element contain the same number and arrangement of electrons, it was assumed for a long time that isotopes would behave identically in chemical reactions. In reality, although isotopes behave very similarly in chemical reactions, the correspondence is not perfect. The mass differences between different isotopes of the same element cause them to have slightly different physical and chemical properties. For example, the presence of only one additional neutron in the nucleus of the heavier isotope can cause it to react a little more slowly than its lighter counterpart. Such an effect often results in a ratio of heavy isotope to light isotope in the product of a reaction that is different from the ratio found in the reactant.

Stable isotope ratio analysis (SIRA) is an analytical technique that takes advantage of the chemical and physical properties of isotopes. In SIRA the isotopic composition of a sample is measured using a mass spectrometer. This composition is then expressed as the relative ratios of two or more of the stable isotopes of a specific element. For instance, the ratio of ^{13}C to ^{12}C in a sample can be determined. This ratio is then compared with the isotope ratio of a defined standard. Because mass differences are most pronounced among the lightest elements, those elements experience the greatest isotope effects. Thus, the isotopes of the elements H, C, N, O, and S are used most frequently for SIRA. These elements have further significance because they are among the most abundant elements in biological systems.

The isotopic composition of a sample is usually expressed as a “del” value (δ), defined as

$$\delta X_{\text{sample}} (\text{‰}) = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \times 1000$$

where δX_{sample} is the isotope ratio relative to a standard, and R_{sample} and R_{standard} are the absolute isotope ratios of the sample and standard, respectively. Multiplying by 1000 allows the values to be expressed in parts per thousand (‰). If the del value is a positive number, the sample has a greater amount of the heavier isotope than does the standard. In such cases the sample is said to be “heavier” than the standard, or to have been “enriched” in the heavy isotope. Similarly, if the del value is negative, the sample has a higher proportion of the lighter isotope and thus is described as “lighter” than the standard.

The most frequently used element for SIRA is carbon. The first limited data on $^{13}\text{C}/^{12}\text{C}$ isotope ratios in natural materials were published in 1939. At that time, it was established that limestones, atmospheric CO_2 , marine plants, and terrestrial plants each possessed characteristic carbon isotope ratios. In the succeeding years, $^{13}\text{C}/^{12}\text{C}$ ratios were determined for a wide variety of things, including petroleum, coal, diamonds, marine organisms, and terrestrial organisms. Such data led to the important conclusion that a biological organism has an isotope ratio that depends on the main source of carbon to that organism—that is, its food source. For example, if an herbivore (an animal that feeds on plants) feeds exclusively on one type of plant, that animal’s carbon isotope ratio will be almost identical to that of the plant. If another animal were to feed exclusively on that herbivore, it would



also have a similar carbon isotope ratio. Suppose now that an animal, say a rabbit, has a diet comprising two plants, A and B. Plant A has a $\delta^{13}\text{C}$ value of -24‰ , and plant B has a $\delta^{13}\text{C}$ value of -10‰ . If the rabbit eats equal amounts of the two plants, the $\delta^{13}\text{C}$ value of the rabbit will be the average of the two values, or -17‰ . Values more positive than -17‰ would indicate a higher consumption of plant B than of plant A, whereas more negative values would reflect a preference for plant A.

Similar studies have been conducted with the stable isotopes of nitrogen. A major way in which nitrogen differs from carbon in isotopic studies relates to how $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values change as organic matter moves along the food chain—from inorganic nutrient to plant, then to herbivore, to carnivore, and on to higher carnivores. It has been pointed out that $\delta^{13}\text{C}$ remains nearly constant throughout successive levels of the food chain. In contrast, on average there is a $+3$ to $+5\text{‰}$ shift in the value of $\delta^{15}\text{N}$ at each successive level of the food chain. For instance, suppose a plant has a $\delta^{15}\text{N}$ value of 1‰ . If an herbivore, such as a rabbit, feeds exclusively on that one type of plant, it will have a $\delta^{15}\text{N}$ value of 4‰ . If another animal, such as a fox, feeds exclusively on that particular type of rabbit, it in turn will have a $\delta^{15}\text{N}$ value of 7‰ . An important implication of this phenomenon is that an organism's nitrogen isotope ratio can be used as an indicator of the level in the food chain at which that species of animal feeds.

An interesting application of SIRA is the determination of the adulteration of food. As already mentioned, the iso-

tope ratios of different plants and animals have been determined. For instance, corn has a $\delta^{13}\text{C}$ value of about -12‰ and most flowering plants have $\delta^{13}\text{C}$ values of about -26‰ . The difference in these $\delta^{13}\text{C}$ values arises because these plants carry out photosynthesis by slightly different chemical reactions. In the first reaction of photosynthesis, corn produces a molecule that contains four carbons, whereas flowering plants produce a molecule that has only three carbons. High-fructose corn syrup (HFCS) is thus derived from a " C_4 " plant, whereas the nectar that bees gather comes from " C_3 " plants. The slight differences in the photosynthetic pathways of C_3 and C_4 plants create the major differences in their $\delta^{13}\text{C}$ values. Brokers who buy and sell huge quantities of "sweet" products are able to monitor HFCS adulteration of honey, maple syrup, apple juice, and so on by taking advantage of the SIRA technique. If the $\delta^{13}\text{C}$ value of one of these products is not appropriate, then the product obviously has had other substances added to it, i.e., has been adulterated. The U.S. Department of Agriculture conducts routine isotope analyses to ensure the purity of those products submitted for subsidy programs. Similarly, the honey industry monitors itself with the SIRA technique.

Another interesting use of SIRA is in the determination of the diets of prehistoric human populations. It is known that marine plants have higher $\delta^{15}\text{N}$ values than terrestrial plants. This difference in $\delta^{15}\text{N}$ is carried up food chains, causing marine animals to have higher $\delta^{15}\text{N}$ values than terrestrial animals. The $\delta^{15}\text{N}$ values of humans feeding on marine food sources are therefore higher than those of people feeding on terrestrial food. This phenomenon has been used to estimate the marine and terrestrial components of the diets of historic and prehistoric human groups through the simple determination of the $\delta^{15}\text{N}$ value of bone collagen collected from excavated skeletons.

Stable isotope ratio analysis is a powerful tool; many of its potential uses are only slowly being recognized by researchers. In the meantime, the use of stable isotope methods in research is becoming increasingly common, and through these methods scientists are attaining new levels of understanding of chemical, biological, and geological processes.

Beth A. Trust



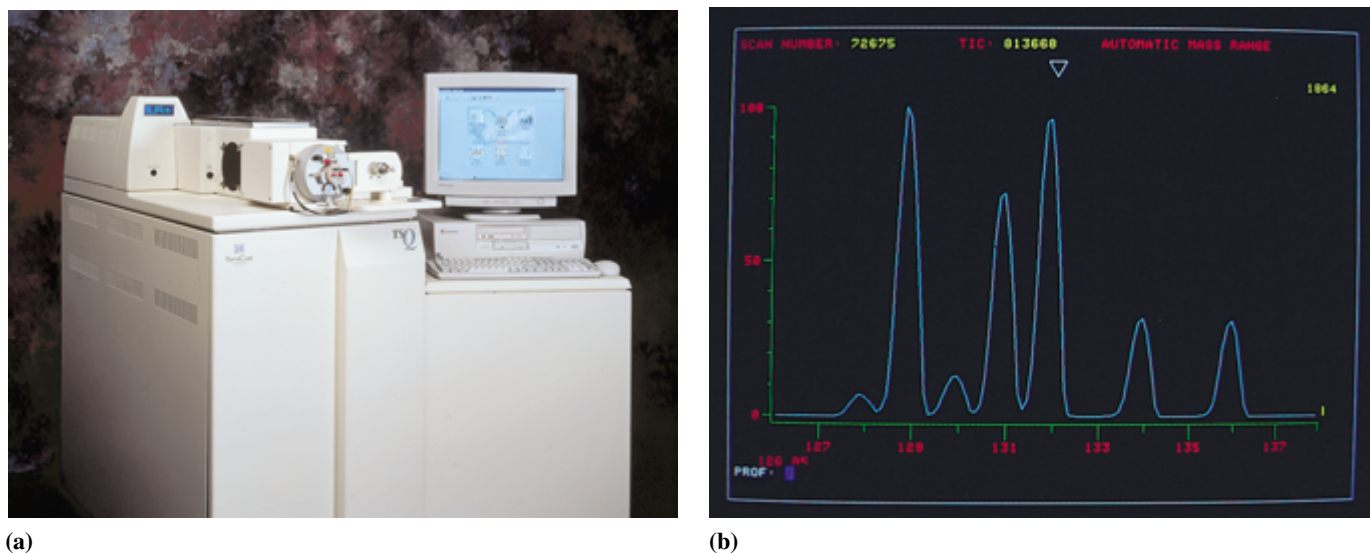


Figure 5-10 (a) A modern mass spectrometer. (b) The mass spectrum of Xe^+ ions. The isotope $^{126}_{54}\text{Xe}$ is at too low an abundance (0.090%) to appear in this experiment.

The distribution of isotopic masses, although nearly constant, does vary somewhat depending on the source of the element. For example, the abundance of ^{13}C in atmospheric CO_2 is slightly different from that in seashells. The chemical history of a compound can be inferred from small differences in isotope ratios.

TABLE 5-3 *Some Naturally Occurring Isotopic Abundances*

Element	Atomic Weight (amu)	Isotope	% Natural Abundance	Mass (amu)
boron	10.811	$^{10}_5\text{B}$	19.91	10.01294
		$^{11}_5\text{B}$	80.09	11.00931
oxygen	15.9994	$^{16}_8\text{O}$	99.762	15.99492
		$^{17}_8\text{O}$	0.038	16.99913
		$^{18}_8\text{O}$	0.200	17.99916
chlorine	35.4527	$^{35}_{17}\text{Cl}$	75.770	34.96885
		$^{37}_{17}\text{Cl}$	24.230	36.96590
uranium	238.0289	$^{234}_{92}\text{U}$	0.0055	234.0409
		$^{235}_{92}\text{U}$	0.720	235.0439
		$^{238}_{92}\text{U}$	99.2745	238.0508

The 20 elements that have only one naturally occurring isotope are ^4_2Be , $^{19}_9\text{F}$, $^{23}_{11}\text{Na}$, $^{27}_{13}\text{Al}$, $^{31}_{15}\text{P}$, $^{45}_{21}\text{Sc}$, $^{55}_{25}\text{Mn}$, $^{59}_{27}\text{Co}$, $^{75}_{33}\text{As}$, $^{89}_{39}\text{Y}$, $^{93}_{41}\text{Nb}$, $^{103}_{45}\text{Rh}$, $^{127}_{53}\text{I}$, $^{133}_{55}\text{Cs}$, $^{141}_{59}\text{Pr}$, $^{159}_{65}\text{Tb}$, $^{165}_{67}\text{Ho}$, $^{169}_{69}\text{Tm}$, $^{197}_{79}\text{Au}$, and $^{209}_{83}\text{Bi}$. There are however other, artificially produced isotopes of these elements.

5-9 THE ATOMIC WEIGHT SCALE AND ATOMIC WEIGHTS

We said in Section 2-5 that the **atomic weight scale** is based on the mass of the carbon-12 isotope. As a result of action taken by the International Union of Pure and Applied Chemistry in 1962,

one **amu** is exactly 1/12 of the mass of a carbon-12 atom.

Described another way, the mass of one atom of $^{12}_6\text{C}$ is *exactly* 12 amu.

This is approximately the mass of one atom of ^1H , the lightest isotope of the element with lowest mass.

In Section 2-6 we said that one mole of atoms, contains 6.022×10^{23} atoms. The mass of one mole of atoms of any element, in grams, is numerically equal to the atomic weight of the element. Because the mass of one carbon-12 atom is exactly 12 amu, the mass of one mole of carbon-12 atoms is exactly 12 grams.

To show the relationship between atomic mass units and grams, let us calculate the mass, in amu, of 1.000 gram of $^{12}_6\text{C}$ atoms.

$$\begin{aligned} \underline{?} \text{ amu} &= 1.000 \text{ g } ^{12}_6\text{C atoms} \times \frac{1 \text{ mol } ^{12}_6\text{C}}{12 \text{ g } ^{12}_6\text{C atoms}} \times \frac{6.022 \times 10^{23} \text{ } ^{12}_6\text{C atoms}}{1 \text{ mol } ^{12}_6\text{C atoms}} \times \frac{12 \text{ amu}}{^{12}_6\text{C atom}} \\ &= 6.022 \times 10^{23} \text{ amu (in 1 gram)} \end{aligned}$$

Thus,

$$1 \text{ g} = 6.022 \times 10^{23} \text{ amu} \quad \text{or} \quad 1 \text{ amu} = 1.660 \times 10^{-24} \text{ g}$$

We saw in Chapter 2 that Avogadro's number is the number of particles of a substance in one mole of that substance. We now see that Avogadro's number also represents the number of amu in one gram. You may wish to verify that the same result is obtained regardless of the element or isotope chosen.

At this point, we emphasize the following:

1. The *atomic number*, Z , is an integer equal to the number of protons in the nucleus of an atom of the element. It is also equal to the number of electrons in a neutral atom. It is the same for all atoms of an element.
2. The *mass number*, A , is an integer equal to the *sum* of the number of protons and the number of neutrons in the nucleus of an atom of a *particular isotope* of an element. It is different for different isotopes of the same element.
3. Many elements occur in nature as mixtures of isotopes. The *atomic weight* of such an element is the weighted average of the masses of its isotopes. Atomic weights are fractional numbers, not integers.

The atomic weight that we determine experimentally (for an element that consists of more than one isotope) is such a weighted average. The following example shows how an atomic weight can be calculated from measured isotopic abundances.

EXAMPLE 5-2 Calculation of Atomic Weight

Three isotopes of magnesium occur in nature. Their abundances and masses, determined by mass spectrometry, are listed in the following table. Use this information to calculate the atomic weight of magnesium.

Isotope	% Abundance	Mass (amu)
${}^{24}_{12}\text{Mg}$	78.99	23.98504
${}^{25}_{12}\text{Mg}$	10.00	24.98584
${}^{26}_{12}\text{Mg}$	11.01	25.98259

Plan

We multiply the fraction of each isotope by its mass and add these numbers to obtain the atomic weight of magnesium.

Solution

$$\begin{aligned} \text{Atomic weight} &= 0.7899(23.98504 \text{ amu}) + 0.1000(24.98584 \text{ amu}) + 0.1101(25.98259 \text{ amu}) \\ &= 18.946 \text{ amu} \quad + 2.4986 \text{ amu} \quad + 2.8607 \text{ amu} \\ &= 24.30 \text{ amu} \quad (\text{to four significant figures}) \end{aligned}$$

The two heavier isotopes make small contributions to the atomic weight of magnesium because most magnesium atoms are the lightest isotope.

You should now work Exercises 26 and 28.

**Problem-Solving Tip: “Weighted” Averages**

Consider the following analogy to the calculation of atomic weights. Suppose you want to calculate the average weight of your classmates. Imagine that one half of them weigh 100 pounds each, and the other half weigh 200 pounds each. The average weight would be

$$\text{Average weight} = \frac{1}{2}(100 \text{ lb}) + \frac{1}{2}(200 \text{ lb}) = 150 \text{ lb}$$

Imagine, however, that three quarters of the class members weigh 100 pounds each, and the other quarter weigh 200 pounds each. Now, the average weight would be

$$\text{Average weight} = \frac{3}{4}(100 \text{ lb}) + \frac{1}{4}(200 \text{ lb}) = 125 \text{ lb}$$

We can express the fractions in this calculation in decimal form:

$$\text{Average weight} = 0.750(100 \text{ lb}) + 0.250(200 \text{ lb}) = 125 \text{ lb}$$

In such a calculation, the value (in this case, the weight) of each thing (people, atoms) is multiplied by the fraction of things that have that value. In Example 5-2 we expressed each percentage as a decimal fraction, such as

$$78.99\% = \frac{78.99 \text{ parts}}{100 \text{ parts total}} = 0.7899$$

Example 5-3 shows how the process can be reversed. Isotopic abundances can be calculated from isotopic masses and from the atomic weight of an element that occurs in nature as a mixture of only two isotopes.

EXAMPLE 5-3 *Calculation of Isotopic Abundance*

The atomic weight of gallium is 69.72 amu. The masses of the naturally occurring isotopes are 68.9257 amu for $^{69}_{31}\text{Ga}$ and 70.9249 amu for $^{71}_{31}\text{Ga}$. Calculate the percent abundance of each isotope.

Plan

We represent the fraction of each isotope algebraically. Atomic weight is the weighted average of the masses of the constituent isotopes. So the fraction of each isotope is multiplied by its mass, and the sum of the results is equal to the atomic weight.

Solution

Let x = fraction of $^{69}_{31}\text{Ga}$. Then $(1 - x)$ = fraction of $^{71}_{31}\text{Ga}$.

$$\begin{aligned} x(68.9257 \text{ amu}) + (1 - x)(70.9249 \text{ amu}) &= 69.72 \text{ amu} \\ 68.9257x + 70.9249 - 70.9249x &= 69.72 \\ -1.9992x &= -1.20 \\ x &= 0.600 \end{aligned}$$

$$x = 0.600 = \text{fraction of } ^{69}_{31}\text{Ga} \quad \therefore \quad 60.0\% \text{ } ^{69}_{31}\text{Ga}$$

$$(1 - x) = 0.400 = \text{fraction of } ^{71}_{31}\text{Ga} \quad \therefore \quad 40.0\% \text{ } ^{71}_{31}\text{Ga}$$

When a quantity is represented by fractions, the sum of the fractions must always be unity. In this case, $x + (1 - x) = 1$.

You should now work Exercise 30.

THE ELECTRONIC STRUCTURES OF ATOMS

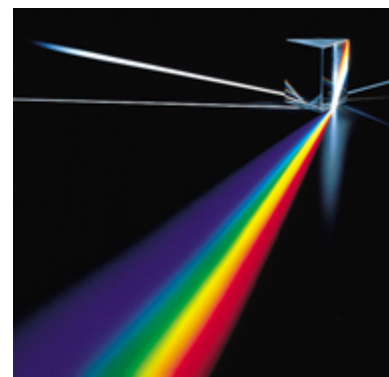
The Rutherford model of the atom is consistent with the evidence presented so far, but it has some serious limitations. It does not answer such important questions as: *Why* do different elements have such different chemical and physical properties? *Why* does chemical bonding occur at all? *Why* does each element form compounds with characteristic formulas? *How* can atoms of different elements give off or absorb light only of characteristic colors (as was known long before 1900)?

To improve our understanding, we must first learn more about the arrangements of electrons in atoms. The theory of these arrangements is based largely on the study of the light given off and absorbed by atoms. Then we will develop a detailed picture of the *electron configurations* of different elements. A knowledge of these arrangements will help us to understand the periodic table and chemical bonding.

5-10 ELECTROMAGNETIC RADIATION

Our ideas about the arrangements of electrons in atoms have evolved slowly. Much of the information has been derived from **atomic emission spectra**. These are the lines, or bands, produced on photographic film by radiation that has passed through a refracting glass prism after being emitted from electrically or thermally excited atoms. To help us understand the nature of atomic spectra, we first describe electromagnetic radiation.

All types of electromagnetic radiation, or radiant energy, can be described in the terminology of waves. To help characterize any wave, we specify its *wavelength* (or its *frequency*).



White light is dispersed by a prism into a *continuous* spectrum.


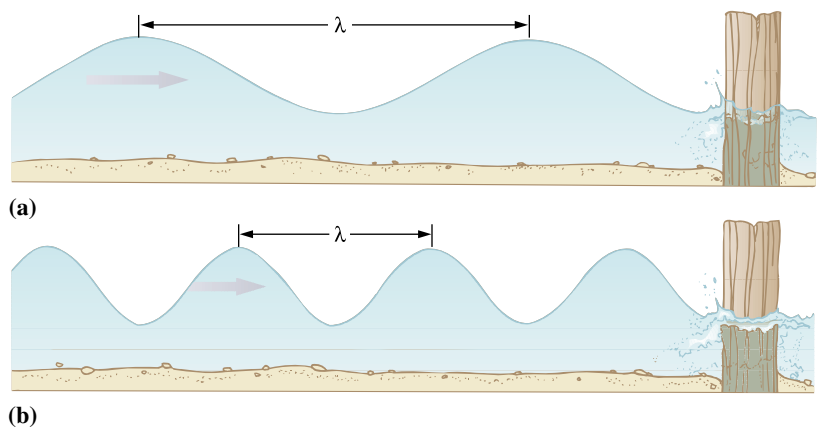
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.3, Electromagnetic Radiation.

Figure 5-11 Illustrations of the wavelength and frequency of water waves. The distance between any two identical points, such as crests, is the wavelength, λ . We could measure the frequency, ν , of the wave by observing how often the level rises and falls at a fixed point in its path—for instance, at the post—or how often crests hit the post. (a) and (b) represent two waves that are traveling at the same speed. In (a) the wave has long wavelength and low frequency; in (b) the wave has shorter wavelength and higher frequency.



One cycle per second is also called one *hertz* (Hz), after Heinrich Hertz (1857–1894). In 1887, Hertz discovered electromagnetic radiation outside the visible range and measured its speed and wavelengths.

Let us use a familiar kind of wave, that on the surface of water (Figure 5-11), to illustrate these terms. The significant feature of wave motion is its repetitive nature. The **wavelength**, λ , is the distance between any two adjacent identical points of the wave, for instance, two adjacent crests. The **frequency** is the number of wave crests passing a given point per unit time; it is represented by the symbol ν (Greek letter “nu”) and is usually expressed in cycles per second or, more commonly, simply as $1/s$ or s^{-1} with “cycles” understood. For a wave that is “traveling” at some speed, the wavelength and the frequency are related to each other by

$$\lambda \nu = \text{speed of propagation of the wave} \quad \text{or} \quad \lambda \nu = c$$

Thus, wavelength and frequency are inversely proportional to each other; for the same wave speed, shorter wavelengths correspond to higher frequencies.

For water waves, it is the surface of the water that changes repetitively; for a vibrating violin string, it is the displacement of any point on the string. Electromagnetic radiation is a form of energy that consists of electric and magnetic fields that vary repetitively. The electromagnetic radiation most obvious to us is visible light. It has wavelengths ranging from about 4.0×10^{-7} m (violet) to about 7.5×10^{-7} m (red). Expressed in frequencies, this range is about 7.5×10^{14} Hz (violet) to about 4.0×10^{14} Hz (red).

Isaac Newton (1642–1727) first recorded the separation of sunlight into its component colors by allowing it to pass through a prism. Because sunlight (white light) contains all wavelengths of visible light, it gives the *continuous spectrum* observed in a rainbow (Figure 5-12a). Visible light represents only a tiny segment of the electromagnetic radiation spectrum (Figure 5-12b). In addition to all wavelengths of visible light, sunlight also contains shorter wavelength (ultraviolet) radiation as well as longer wavelength (infrared) radiation. Neither of these can be detected by the human eye. Both may be detected and recorded photographically or by detectors designed for that purpose. Many other familiar kinds of radiation are simply electromagnetic radiation of longer or shorter wavelengths.

In a vacuum, the speed of electromagnetic radiation, c , is the same for all wavelengths, 2.99792458×10^8 m/s. The relationship between the wavelength and frequency of electromagnetic radiation, with c rounded to three significant figures, is

$$\lambda \nu = c = 3.00 \times 10^8 \text{ m/s}$$



The diffraction of white light by the closely spaced grooves of a compact disk spreads the light into its component colors. Diffraction is described as the constructive and destructive interference of light waves.

Sir Isaac Newton, one of the giants of science. You probably know of him from his theory of gravitation. In addition, he made enormous contributions to the understanding of many other aspects of physics, including the nature and behavior of light, optics, and the laws of motion. He is credited with the discoveries of differential calculus and of expansions into infinite series.

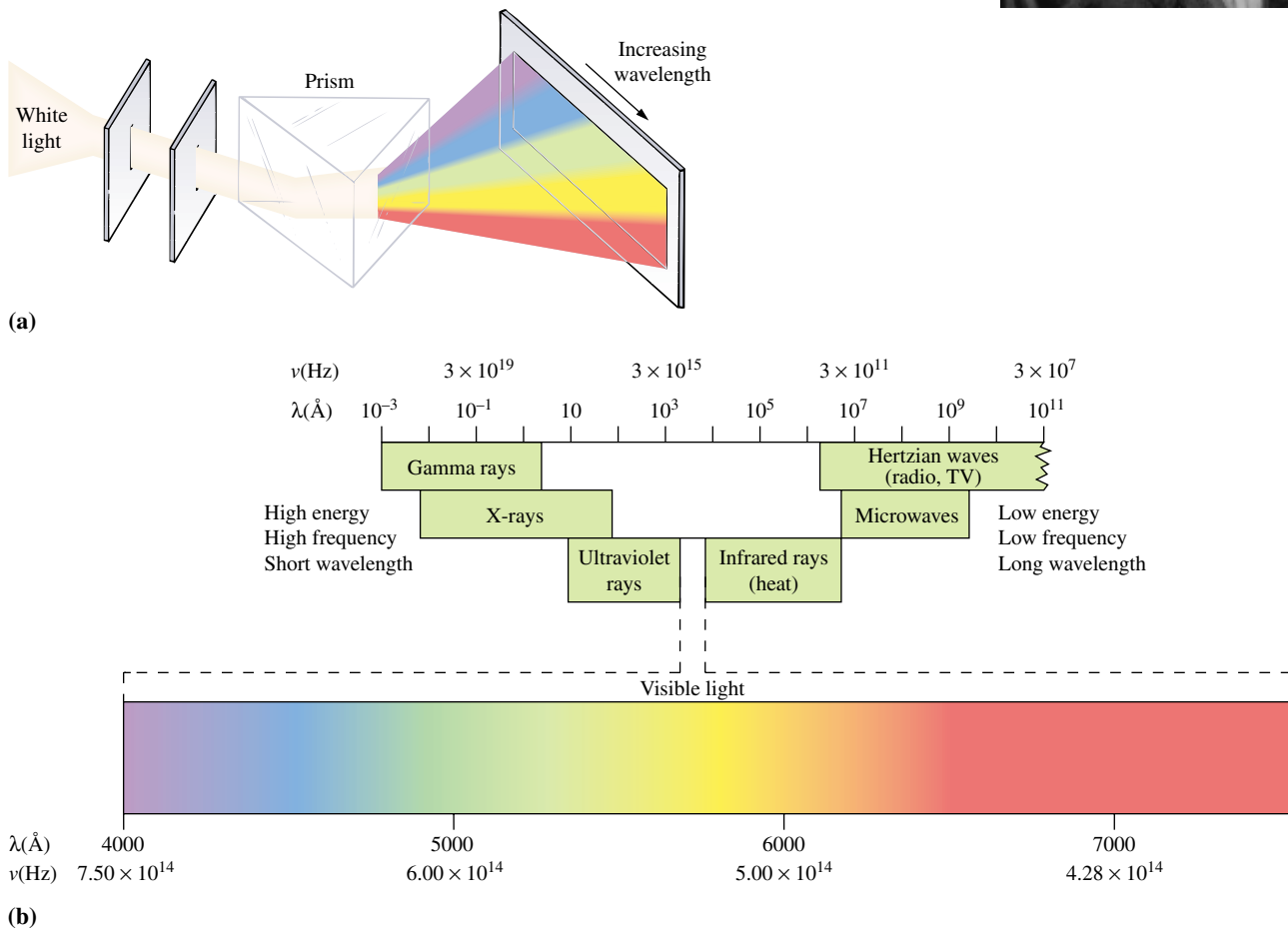


Figure 5-12 (a) Dispersion of visible light by a prism. Light from a source of white light is passed through a slit and then through a prism. It is spread into a continuous spectrum of all wavelengths of visible light. (b) Visible light is only a very small portion of the electromagnetic spectrum. Some radiant energy has longer or shorter wavelengths than our eyes can detect. The upper part shows the approximate ranges of the electromagnetic spectrum on a logarithmic scale. The lower part shows the visible region on an expanded scale. Note that wavelength increases as frequency decreases.

EXAMPLE 5-4 *Wavelength of Light*

Light near the middle of the ultraviolet region of the electromagnetic radiation spectrum has a frequency of $2.73 \times 10^{16} \text{ s}^{-1}$. Yellow light near the middle of the visible region of the spectrum has a frequency of $5.26 \times 10^{14} \text{ s}^{-1}$. Calculate the wavelength that corresponds to each of these two frequencies of light.

Plan

Wavelength and frequency are inversely proportional to each other, $\lambda\nu = c$. We solve this relationship for λ and calculate the wavelengths.

Solution

$$\text{(ultraviolet light)} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2.73 \times 10^{16} \text{ s}^{-1}} = 1.10 \times 10^{-8} \text{ m} \quad (1.10 \times 10^2 \text{ \AA})$$

$$\text{(yellow light)} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{5.26 \times 10^{14} \text{ s}^{-1}} = 5.70 \times 10^{-7} \text{ m} \quad (5.70 \times 10^3 \text{ \AA})$$

You should now work Exercise 38.

We have described light in terms of wave behavior. Under certain conditions, it is also possible to describe light as composed of *particles*, or **photons**. According to the ideas presented by Max Planck (1858–1947) in 1900, each photon of light has a particular amount (a **quantum**) of energy. The amount of energy possessed by a photon depends on the frequency of the light. The energy of a photon of light is given by Planck's equation

$$E = h\nu \quad \text{or} \quad E = \frac{hc}{\lambda}$$

where h is Planck's constant, $6.6260755 \times 10^{-34} \text{ J} \cdot \text{s}$, and ν is the frequency of the light. Thus, energy is directly proportional to frequency. Planck's equation is used in Example 5-5 to show that a photon of ultraviolet light has more energy than a photon of yellow light.

EXAMPLE 5-5 *Energy of Light*

In Example 5-4 we calculated the wavelengths of ultraviolet light of frequency $2.73 \times 10^{16} \text{ s}^{-1}$ and of yellow light of frequency $5.26 \times 10^{14} \text{ s}^{-1}$. Calculate the energy, in joules, of an individual photon of each. Compare these photons by calculating the ratio of their energies.

Plan

We use each frequency to calculate the photon energy from the relationship $E = h\nu$. Then we calculate the required ratio.

Solution

$$\text{(ultraviolet light)} \quad E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.73 \times 10^{16} \text{ s}^{-1}) = 1.81 \times 10^{-17} \text{ J}$$

$$\text{(yellow light)} \quad E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(5.26 \times 10^{14} \text{ s}^{-1}) = 3.49 \times 10^{-19} \text{ J}$$

(You can check these answers by calculating the energies directly from the wavelengths, using the equation $E = hc/\lambda$.)

Now, we compare the energies of these two photons.

$$\frac{E_{\text{uv}}}{E_{\text{yellow}}} = \frac{1.81 \times 10^{-17} \text{ J}}{3.49 \times 10^{-19} \text{ J}} = 51.9$$

A photon of light near the middle of the ultraviolet region is more than 51 times more energetic than a photon of light near the middle of the visible region.

You should now work Exercise 39.

5-11 THE PHOTOELECTRIC EFFECT

One experiment that had not been satisfactorily explained with the wave theory of light was the **photoelectric effect**. The apparatus for the photoelectric effect is shown in Figure 5-13. The negative electrode in the evacuated tube is made of a pure metal such as cesium. When light of a sufficiently high energy strikes the metal, electrons are knocked off its surface. They then travel to the positive electrode and form a current flowing through the circuit. The important observations follow.

1. Electrons can be ejected only if the light is of sufficiently short wavelength (has sufficiently high energy), no matter how long or how brightly the light shines. This wavelength limit is different for different metals.
2. The current (the number of electrons emitted per second) increases with increasing *brightness* (intensity) of the light. The current, however, does not depend on the color of the light, as long as the wavelength is short enough (has high enough energy).

Classical theory said that even “low-” energy light should cause current to flow if the metal is irradiated long enough. Electrons should accumulate energy and be released when they have enough energy to escape from the metal atoms. According to the old theory, if the light is made more energetic, then the current should increase even though the light intensity remains the same. Such is *not* the case.

The answer to the puzzle was provided by Albert Einstein (1879–1955). In 1905, he extended Planck’s idea that light behaves as though it were composed of *photons*, each with a particular amount (a quantum) of energy. According to Einstein, each photon can transfer its energy to a single electron during a collision. When we say that the intensity of light is increased, we mean that the number of photons striking a given area per second is increased. The picture is now one of a particle of light striking an electron near the surface of the metal and giving up its energy to the electron. If that energy is equal to or greater than the amount needed to liberate the electron, it can escape to join the photoelectric current. For this explanation, Einstein received the 1921 Nobel Prize in physics.



The photoelectric effect is used in the photocells of automatic cameras. The photoelectric sensors that open some supermarket and elevator doors also utilize this effect.

This is one reason why ultraviolet (UV) light damages your skin much more rapidly than visible light. Another reason is that many of the organic compounds in the skin absorb UV light more readily than visible light. The absorbed ultraviolet light breaks bonds in many biologically important molecules.

The intensity of light is the brightness of the light. In wave terms, it is related to the amplitude of the light waves.

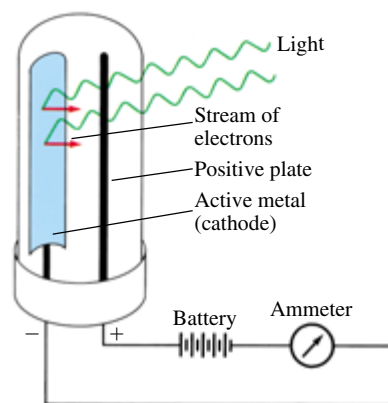


Figure 5-13 The photoelectric effect. When electromagnetic radiation of sufficient minimum energy strikes the surface of a metal (negative electrode) inside an evacuated tube, electrons are stripped off the metal to create an electric current. The current increases with increasing radiation intensity.

5-12 ATOMIC SPECTRA AND THE BOHR ATOM

Incandescent (“red hot” or “white hot”) solids, liquids, and high-pressure gases give continuous spectra. When an electric current is passed through a gas in a vacuum tube at very low pressures, however, the light that the gas emits can be dispersed by a prism into distinct lines (Figure 5-14a). Such an **emission spectrum** is described as a *bright line spectrum*. The lines can be recorded photographically, and the wavelength of light that produced each line can be calculated from the position of that line on the photograph.

Similarly, we can shine a beam of white light (containing a continuous distribution of wavelengths) through a gas and analyze the beam that emerges. We find that only certain wavelengths have been absorbed (Figure 5-14b). The wavelengths that are absorbed in this **absorption spectrum** are also given off in the emission experiment. Each spectral line corresponds to a specific wavelength of light and thus to a specific amount of energy that is either absorbed or emitted. An atom of each element displays its own characteristic set of lines in its emission or absorption spectrum (Figure 5-15). These spectra can serve as “fingerprints” that allow us to identify different elements present in a sample, even in trace amounts.

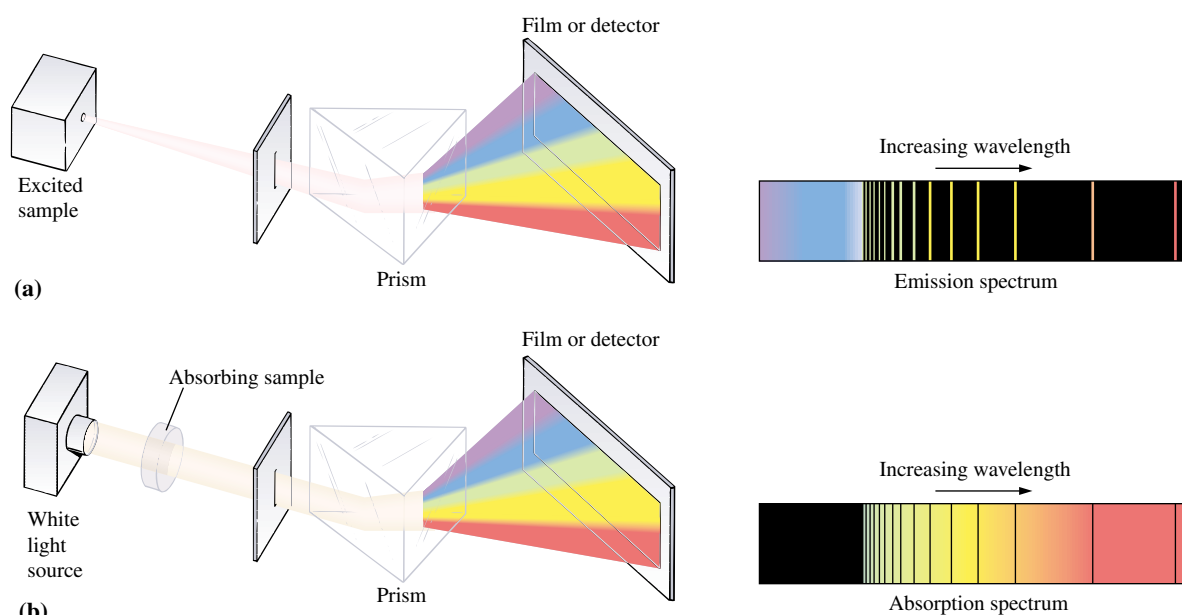


Figure 5-14 (a) *Atomic emission*. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus, an emission spectrum, which is a photographic recording of the separated wavelengths, is called a line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. (b) *Atomic absorption*. When white light is passed through unexcited hydrogen and then through a slit and a prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in part (a). The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

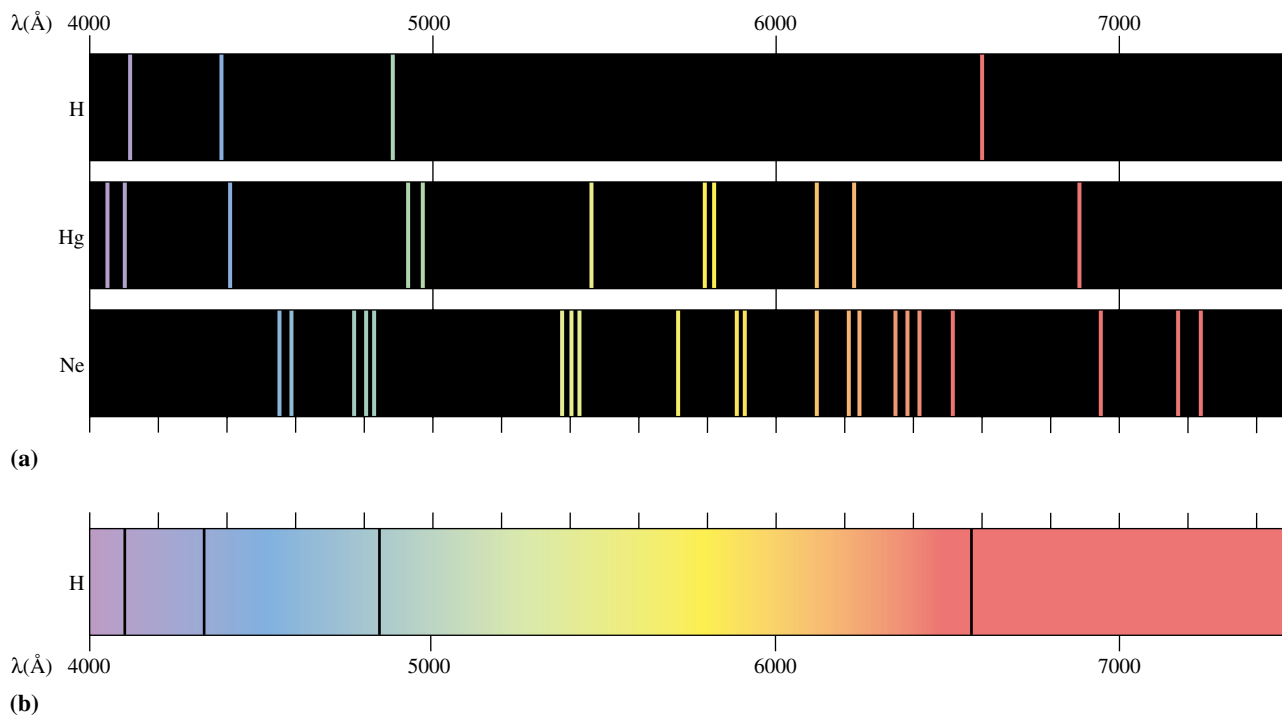


Figure 5-15 Atomic spectra in the visible region for some elements. Figure 5-14a shows how such spectra are produced. (a) Emission spectra for some elements. (b) Absorption spectrum for hydrogen. Compare the positions of these lines with those in the emission spectrum for H in (a).

EXAMPLE 5-6 Energy of Light

A green line of wavelength 4.86×10^{-7} m is observed in the emission spectrum of hydrogen. Calculate the energy of one photon of this green light.

Plan

We know the wavelength of the light, and we calculate its frequency so that we can then calculate the energy of each photon.

Solution

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(4.86 \times 10^{-7} \text{ m})} = 4.09 \times 10^{-19} \text{ J/photon}$$

To gain a better appreciation of the amount of energy involved, let's calculate the total energy, in kilojoules, emitted by one mole of atoms. (Each atom emits one photon.)

$$\frac{\text{kJ}}{\text{mol}} = 4.09 \times 10^{-19} \frac{\text{J}}{\text{atom}} \times \frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}} \times \frac{6.02 \times 10^{23} \text{ atoms}}{\text{mol}} = 2.46 \times 10^2 \text{ kJ/mol}$$

This calculation shows that when each atom in one mole of hydrogen atoms emits light of wavelength 4.86×10^{-7} m, the mole of atoms loses **246 kJ** of energy as green light. (This would be enough energy to operate a 100-watt light bulb for more than 40 minutes.)

You should now work Exercises 40 and 42.



The lightning flashes produced in electrical storms and the light produced by neon gas in neon signs are two familiar examples of visible light produced by electronic transitions.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.7, Bohr's Model of the Hydrogen Atom.

When an electric current is passed through hydrogen gas at very low pressures, several series of lines in the spectrum of hydrogen are produced. These lines were studied intensely by many scientists. In the late nineteenth century, Johann Balmer (1825–1898) and Johannes Rydberg (1854–1919) showed that the wavelengths of the various lines in the hydrogen spectrum can be related by a mathematical equation:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Here R is $1.097 \times 10^7 \text{ m}^{-1}$ and is known as the Rydberg constant. The n 's are positive integers, and n_1 is smaller than n_2 . The Balmer-Rydberg equation was derived from numerous observations, not theory. It is thus an empirical equation.

In 1913, Niels Bohr (1885–1962), a Danish physicist, provided an explanation for Balmer and Rydberg's observations. He wrote equations that described the electron of a hydrogen atom as revolving around its nucleus in circular orbits. He included the assumption that the electronic energy is *quantized*; that is, only certain values of electronic energy are possible. This led him to suggest that electrons can only be in certain discrete orbits, and that they absorb or emit energy in discrete amounts as they move from one orbit to another. Each orbit thus corresponds to a definite *energy level* for the electron. When an electron is promoted from a lower energy level to a higher one, it absorbs a definite (or quantized) amount of energy. When the electron falls back to the original energy level,

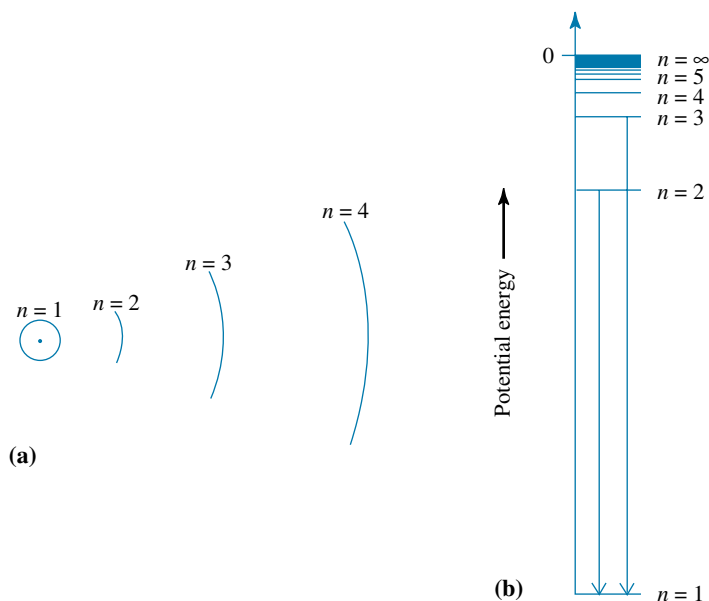
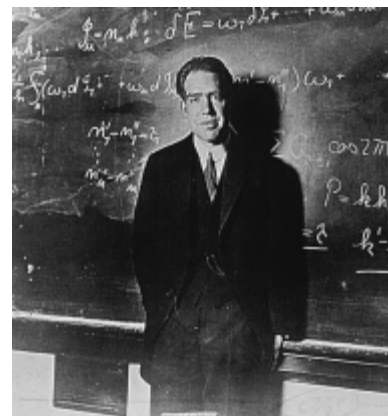


Figure 5-16 (a) The radii of the first four Bohr orbits for a hydrogen atom. The dot at the center represents the nuclear position. The radius of each orbit is proportional to n^2 , so these four are in the ratio 1:4:9:16. (b) Relative values for the energies associated with the various energy levels in a hydrogen atom. The energies become closer together as n increases. They are so close together for large values of n that they form a continuum. By convention, potential energy is defined as zero when the electron is at an infinite distance from the atom. Any more stable arrangement would have a lower energy. Potential energies of electrons in atoms are therefore always negative. Some possible electronic transitions corresponding to lines in the hydrogen emission spectrum are indicated by arrows. Transitions in the opposite directions account for lines in the absorption spectrum.

The Danish physicist Niels Bohr was one of the most influential scientists of the twentieth century. Like many other now-famous physicists of his time, he worked for a time in England with J. J. Thomson and later with Ernest Rutherford. During this period, he began to develop the ideas that led to the publication of his explanation of atomic spectra and his theory of atomic structure, for which he received the Nobel Prize in 1922. After escaping from German-occupied Denmark to Sweden in 1943, he helped to arrange the escape of hundreds of Danish Jews from the Hitler regime. He later went to the United States, where, until 1945, he worked with other scientists at Los Alamos, New Mexico, on the development of the atomic bomb. From then until his death in 1962, he worked for the development and use of atomic energy for peaceful purposes.



it emits exactly the same amount of energy it absorbed in moving from the lower to the higher energy level. Figure 5-16 illustrates these transactions schematically. The values of n_1 and n_2 in the Balmer-Rydberg equation identify the lower and higher levels, respectively, of these electronic transitions.

The Bohr Theory and the Balmer-Rydberg Equation

From mathematical equations describing the orbits for the hydrogen atom, together with the assumption of quantization of energy, Bohr was able to determine two significant aspects of each allowed orbit:

1. *Where* the electron can be with respect to the nucleus—that is, the radius, r , of the circular orbit. This is given by

$$r = n^2 a_0$$

where n is a positive integer (1, 2, 3, . . .) that tells which orbit is being described and a_0 is the *Bohr radius*. Bohr was able to calculate the value of a_0 from a combination of Planck's constant, the charge of the electron, and the mass of the electron as

$$a_0 = 5.292 \times 10^{-11} \text{ m} = 0.5292 \text{ \AA}$$

2. *How stable* the electron would be in that orbit—that is, its potential energy, E . This is given by

$$E = -\frac{1}{n^2} \left(\frac{h^2}{8\pi^2 m a_0^2} \right) = -\frac{2.180 \times 10^{-18} \text{ J}}{n^2}$$

where h = Planck's constant, m = the mass of the electron, and the other symbols have the same meaning as before. E is always negative when the electron is in the atom; $E = 0$ when the electron is completely removed from the atom ($n = \text{infinity}$).

Results of evaluating these equations for some of the possible values of n (1, 2, 3, . . .) are shown in Figure 5-17. The larger the value of n , the farther from the nucleus is the orbit being described, and the radius of this orbit increases as the *square of n* increases. As n increases, n^2 increases, $1/n^2$ decreases, and thus the electronic energy increases (becomes less negative and smaller in magnitude). For orbits farther from the nucleus, the electronic potential energy is higher (less negative—the electron is in a *higher* energy level or in a less



Note: r is proportional to n^2 .

Note: E is proportional to $-\frac{1}{n^2}$.

We define the potential energy of a set of charged particles to be zero when the particles are infinitely far apart.

(Enrichment, continued)

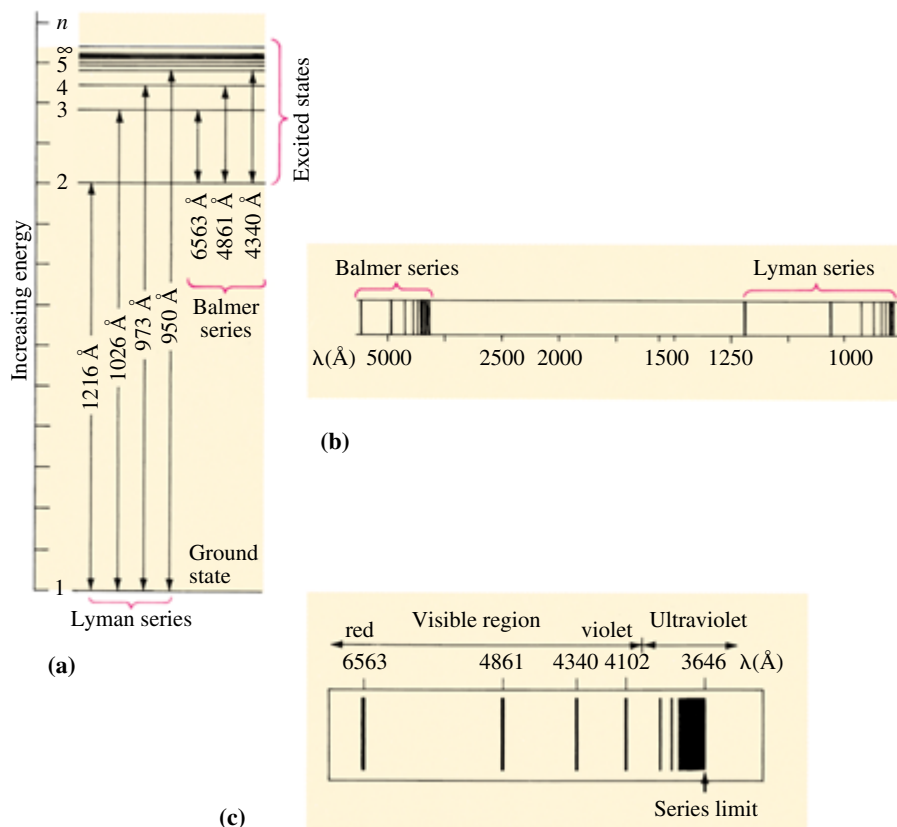


Figure 5-17 (a) The energy levels that the electron can occupy in a hydrogen atom and a few of the transitions that cause the emission spectrum of hydrogen. The numbers on the vertical lines show the wavelengths of light emitted when the electron falls to a lower energy level. (Light of the same wavelength is absorbed when the electron is promoted to the higher energy level.) The difference in energy between two given levels is exactly the same for all hydrogen atoms, so it corresponds to a specific wavelength and to a specific line in the emission spectrum of hydrogen. In a given sample, some hydrogen atoms could have their electrons excited to the $n = 2$ level. Some of these electrons could then fall to the $n = 1$ energy level, giving off the *difference* in energy in the form of light (the 1216-Å transition). Other hydrogen atoms might have their electrons excited to the $n = 3$ level; subsequently some could fall to the $n = 1$ level (the 1026-Å transition). Because higher energy levels become closer and closer in energy, *differences* in energy between successive transitions become smaller and smaller. The corresponding lines in the emission spectrum become closer together and eventually result in a continuum, a series of lines so close together that they are indistinguishable. (b) The emission spectrum of hydrogen. The series of lines produced by the electron falling to the $n = 1$ level is known as the *Lyman series*; it is in the ultraviolet region. A transition in which the electron falls to the $n = 2$ level gives rise to a similar set of lines in the visible region of the spectrum, known as the *Balmer series*. Not shown are series involving transitions to energy levels with higher values of n . (c) The Balmer series shown on an expanded scale. The line at 6563 Å (the $n = 3 \rightarrow n = 2$ transition) is much more intense than the line at 4861 Å (the $n = 4 \rightarrow n = 2$ transition) because the first transition occurs much more frequently than the second. Successive lines in the spectrum become less intense as the series limit is approached because the transitions that correspond to these lines are less probable.

stable state). Going away from the nucleus, the allowable orbits are farther apart in distance, but closer together in energy. Consider the two possible limits of these equations. One limit is when $n = 1$; this describes the electron at the smallest possible distance from the nucleus and at its lowest (most negative) energy. The other limit is for very large values of n , that is, as n approaches infinity. As this limit is approached, the electron is very far from the nucleus, or effectively removed from the atom; the potential energy is as high as possible, approaching zero.

Each line in the emission spectrum represents the *difference in energies* between two allowed energy levels for the electron. When the electron goes from energy level n_2 to energy level n_1 , the difference in energy is given off as a single photon. The energy of this photon can be calculated from Bohr's equation for the energy, as follows.

$$E \text{ of photon} = E_2 - E_1 = \left(-\frac{2.180 \times 10^{-18} \text{ J}}{n_2^2} \right) - \left(-\frac{2.180 \times 10^{-18} \text{ J}}{n_1^2} \right)$$

Factoring out the constant $2.180 \times 10^{-18} \text{ J}$ and rearranging, we get

$$E \text{ of photon} = 2.180 \times 10^{-18} \text{ J} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The Planck equation, $E = hc/\lambda$, relates the energy of the photon to the wavelength of the light, so

$$\frac{hc}{\lambda} = 2.180 \times 10^{-18} \text{ J} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

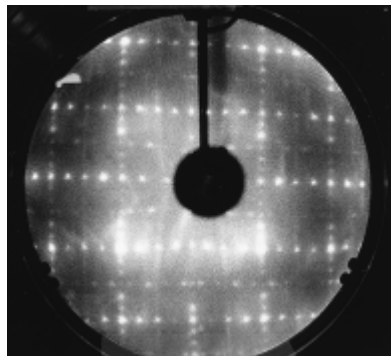
Rearranging for $1/\lambda$, we obtain

$$\frac{1}{\lambda} = \frac{2.180 \times 10^{-18} \text{ J}}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Comparing this to the Balmer-Rydberg equation, Bohr showed that the Rydberg constant is equivalent to $2.180 \times 10^{-18} \text{ J}/hc$. We can use the values for h and c to obtain the same value, $1.097 \times 10^7 \text{ m}^{-1}$, that was obtained by Rydberg on a solely empirical basis. Furthermore, Bohr showed the physical meaning of the two whole numbers n_1 and n_2 ; they represent the two energy states between which the transition takes place. Using this approach, Bohr was able to use fundamental constants to calculate the wavelengths of the observed lines in the hydrogen emission spectrum. Thus, Bohr's application of the idea of quantization of energy to the electron in an atom provided the answer to a half-century-old puzzle concerning the discrete colors given off in the spectrum.


We now accept the fact that electrons occupy only certain energy levels in atoms. In most atoms, some of the energy differences between levels correspond to the energy of visible light. Thus, colors associated with electronic transitions in such elements can be observed by the human eye.

Although the Bohr theory satisfactorily explained the spectra of hydrogen and of other species containing one electron (He^+ , Li^{2+} , etc.) the wavelengths in the observed spectra of more complex species could not be calculated. Bohr's assumption of circular orbits was modified in 1916 by Arnold Sommerfeld (1868–1951), who assumed elliptical orbits. Even so, the Bohr approach was doomed to failure, because it modified classical mechanics to solve a problem that could not be solved by classical mechanics. It was a contrived solution. This failure of classical mechanics set the stage for the development of a new physics, quantum mechanics, to deal with small particles. The Bohr theory, however, did introduce the ideas that only certain energy levels are possible, that these energy levels are



Materials scientists study electron diffraction patterns to learn about the surfaces of solids.

Be careful to distinguish between the letter v , which represents velocity, and the Greek letter nu, ν , which represents frequency. (See Section 5-10.)

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.8, Wave Properties of the Electron.

described by quantum numbers that can have only certain allowed values, and that the quantum numbers indicate something about where and how stable the electrons are in these energy levels. The ideas of modern atomic theory have replaced Bohr's original theory. But his achievement in showing a link between electronic arrangements and Balmer and Rydberg's empirical description of light absorption, and in establishing the quantization of electronic energy, was a very important step toward an understanding of atomic structure.

Two big questions remained about electrons in atoms: (1) How are electrons arranged in atoms? (2) How do these electrons behave? We now have the background to consider how modern atomic theory answers these questions.

5-13 THE WAVE NATURE OF THE ELECTRON

Einstein's idea that light can exhibit both wave properties and particle properties suggested to Louis de Broglie (1892–1987) that very small particles, such as electrons, might also display wave properties under the proper circumstances. In his doctoral thesis in 1925, de Broglie predicted that a particle with a mass m and velocity v should have the wavelength associated with it. The numerical value of this de Broglie wavelength is given by

$$\lambda = h/mv \quad (\text{where } h = \text{Planck's constant})$$

Two years after de Broglie's prediction, C. Davisson (1882–1958) and L. H. Germer (1896–1971) at the Bell Telephone Laboratories demonstrated diffraction of electrons by a crystal of nickel. This behavior is an important characteristic of waves. It shows conclusively that electrons do have wave properties. Davisson and Germer found that the wavelength associated with electrons of known energy is exactly that predicted by de Broglie. Similar diffraction experiments have been successfully performed with other particles, such as neutrons.

EXAMPLE 5-7 de Broglie Equation

(a) Calculate the wavelength in meters of an electron traveling at 1.24×10^7 m/s. The mass of an electron is 9.11×10^{-28} g. (b) Calculate the wavelength of a baseball of mass 5.25 oz traveling at 92.5 mph. Recall that $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$.

Plan

For each calculation, we use the de Broglie equation

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

where

$$\begin{aligned} h \text{ (Planck's constant)} &= 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times \frac{1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{1 \text{ J}} \\ &= 6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}} \end{aligned}$$

For consistency of units, mass must be expressed in kilograms. In part (b), we must also convert the speed to meters per second.

Solution

$$(a) \quad m = 9.11 \times 10^{-28} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 9.11 \times 10^{-31} \text{ kg}$$

Substituting into the de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{(9.11 \times 10^{-31} \text{ kg}) \left(1.24 \times 10^7 \frac{\text{m}}{\text{s}}\right)} = 5.87 \times 10^{-11} \text{ m}$$

Though this seems like a very short wavelength, it is similar to the spacing between atoms in many crystals. A stream of such electrons hitting a crystal gives measurable diffraction patterns.

$$(b) \quad m = 5.25 \text{ oz} \times \frac{1 \text{ lb}}{16 \text{ oz}} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} = 0.149 \text{ kg}$$

$$v = \frac{92.5 \text{ miles}}{\text{h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1.609 \text{ km}}{1 \text{ mile}} \times \frac{1000 \text{ m}}{1 \text{ km}} = 41.3 \frac{\text{m}}{\text{s}}$$

Now, we substitute into the de Broglie equation.

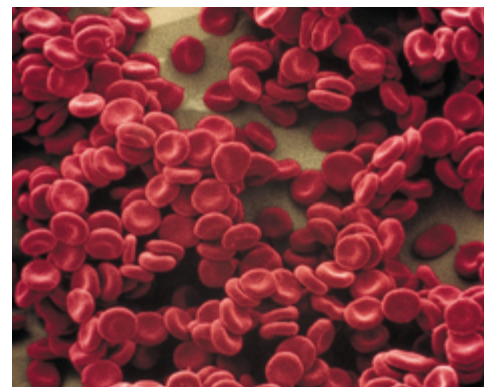
$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{(0.149 \text{ kg}) \left(41.3 \frac{\text{m}}{\text{s}}\right)} = 1.08 \times 10^{-34} \text{ m}$$

This wavelength is far too short to give any measurable effects. Recall that atomic diameters are in the order of 10^{-10} m, which is 24 powers of 10 greater than the baseball “wavelength.”

You should now work Exercise 64.



A modern electron microscope.




A color-enhanced scanning electron micrograph of human red blood cells, magnified 1200 \times .

As you can see from the results of Example 5-7, the particles of the subatomic world behave very differently from the macroscopic objects with which we are familiar. To talk about the behavior of atoms and their particles, we must give up many of our long-held views about the behavior of matter. We must be willing to visualize a world of new and unfamiliar properties, such as the ability to act in some ways like a particle and in other ways like a wave.

The wave behavior of electrons is exploited in the electron microscope. This instrument allows magnification of objects far too small to be seen with an ordinary light microscope.

5-14 THE QUANTUM MECHANICAL PICTURE OF THE ATOM

Through the work of de Broglie, Davisson and Germer, and others, we now know that electrons in atoms can be treated as waves more effectively than as small compact particles traveling in circular or elliptical orbits. Large objects such as golf balls and moving automobiles obey the laws of classical mechanics (Isaac Newton's laws), but very small

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.9, Heisenberg's Uncertainty Principle.

This is like trying to locate the position of a moving automobile by driving another automobile into it.

Recall that $\lambda\nu = c$, so $\nu = c/\lambda$.

particles such as electrons, atoms, and molecules do not. A different kind of mechanics, called **quantum mechanics**, which is based on the *wave* properties of matter, describes the behavior of very small particles much better. Quantization of energy is a consequence of these properties.

One of the underlying principles of quantum mechanics is that we cannot determine precisely the paths that electrons follow as they move about atomic nuclei. The **Heisenberg Uncertainty Principle**, stated in 1927 by Werner Heisenberg (1901–1976), is a theoretical assertion that is consistent with all experimental observations.

It is impossible to determine accurately both the momentum and the position of an electron (or any other very small particle) simultaneously.

Momentum is mass times velocity, mv . Because electrons are so small and move so rapidly, their motion is usually detected by electromagnetic radiation. Photons that interact with electrons have about the same energies as the electrons. Consequently, the interaction of a photon with an electron severely disturbs the motion of the electron. It is not possible to determine simultaneously both the position and the velocity of an electron, so we resort to a statistical approach and speak of the probability of finding an electron within specified regions in space.

With these ideas in mind, we list some basic ideas of quantum mechanics.

1. Atoms and molecules can exist only in certain energy states. In each energy state, the atom or molecule has a definite energy. When an atom or molecule changes its energy state, it must emit or absorb just enough energy to bring it to the new energy state (the quantum condition).

Atoms and molecules possess various forms of energy. Let us focus our attention on their *electronic energies*.

2. When atoms or molecules emit or absorb radiation (light), they change their energies. The energy change in the atom or molecule is related to the frequency or wavelength of the light emitted or absorbed by the equations:

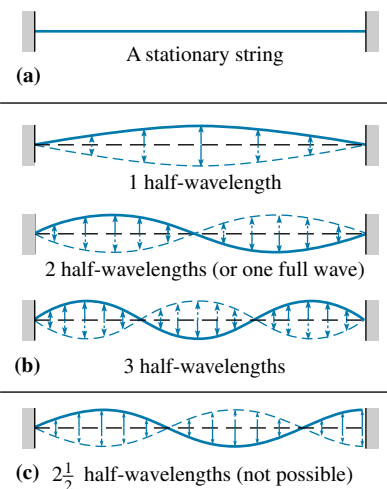
$$\Delta E = h\nu \quad \text{or} \quad \Delta E = hc/\lambda$$

This gives a relationship between the energy change, ΔE , and the wavelength, λ , of the radiation emitted or absorbed. *The energy lost (or gained) by an atom as it goes from higher to lower (or lower to higher) energy states is equal to the energy of the photon emitted (or absorbed) during the transition.*

3. The allowed energy states of atoms and molecules can be described by sets of numbers called *quantum numbers*.

The mathematical approach of quantum mechanics involves treating the electron in an atom as a *standing wave*. A standing wave is a wave that does not travel and therefore has at least one point at which it has zero amplitude, called a node. As an example, consider the various ways that a guitar string can vibrate when it is plucked (Figure 5-18). Because both ends are fixed (nodes), the string can vibrate only in ways in which there is a whole number of *half-wavelengths* in the length of the string (Figure 5-18a). Any possible motion of the string can be described as some combination of these allowed vibrations. In a similar way, we can imagine that the electron in the hydrogen atom behaves as a wave (recall the de Broglie relationship in the last section). The electron can be described by the same

Figure 5-18 When a string that is fixed at both ends—such as (a) a guitar string—is plucked, it has a number of natural patterns of vibration, called normal modes. Because the string is fixed at both ends, the ends must be stationary. Each different possible vibration is a standing wave, and can be described by a wave function. The only waves that are possible are those in which a whole number of half-wavelengths fits into the string length. These allowed waves constitute a harmonic series. Any total motion of the string is some combination of these allowed harmonics. (b) Some of the ways in which a plucked guitar string can vibrate. The position of the string at one extreme of each vibration is shown as a solid line, and at the other extreme as a dashed line. (c) An example of vibration that is *not* possible for a plucked string. In such a vibration, an end of the string would move; this is not possible because the ends are fixed.



kind of standing-wave mathematics that is applied to the vibrating guitar string. In this approach, the electron is characterized by a three-dimensional wave function, ψ . In a given space around the nucleus, only certain “waves” can exist. Each “allowed wave” corresponds to a stable energy state for the electron and is described by a particular set of quantum numbers.

The quantum mechanical treatment of atoms and molecules is highly mathematical. The important point is that each solution of the Schrödinger wave equation (see the following Enrichment section) describes a possible energy state for the electrons in the atom. Each solution is described by a set of **quantum numbers**. These numbers are in accord with those deduced from experiment and from empirical equations such as the Balmer-Rydberg equation. Solutions of the Schrödinger equation also tell us about the shapes and orientations of the probability distributions of the electrons. (The Heisenberg Principle implies that this is how we must describe the positions of the electrons.) These *atomic orbitals* (which are described in Section 5-16) are deduced from the solutions of the Schrödinger equation. The orbitals are directly related to the quantum numbers.

The Schrödinger Equation

In 1926, Erwin Schrödinger (1887–1961) modified an existing equation that described a three-dimensional standing wave by imposing wavelength restrictions suggested by de Broglie’s ideas. The modified equation allowed him to calculate the energy levels in the hydrogen atom. It is a differential equation that need not be memorized or even understood to read this book. A knowledge of differential calculus would be necessary.

$$-\frac{\hbar^2}{8\pi^2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi$$

This equation has been solved exactly only for one-electron species such as the hydrogen atom and the ions He^+ and Li^{2+} . Simplifying assumptions are necessary to solve the equation for more complex atoms and molecules. Chemists and physicists have used their intuition and ingenuity (and modern computers), however, to apply this equation to more complex systems.

In 1928, Paul A. M. Dirac (1902–1984) reformulated electron quantum mechanics to take into account the effects of relativity. This gave rise to a fourth quantum number.



Enrichment

Schrödinger’s equation and wave functions.

5-15 QUANTUM NUMBERS

The solutions of the Schrödinger and Dirac equations for hydrogen atoms give wave functions, ψ , that describe the various states available to hydrogen's single electron. Each of these possible states is described by four quantum numbers. We can use these quantum numbers to designate the electronic arrangements in all atoms, their so-called **electron configurations**. These quantum numbers play important roles in describing the energy levels of electrons and the shapes of the orbitals that describe distributions of electrons in space. The interpretation will become clearer when we discuss atomic orbitals in the following section. For now, let's say that

an **atomic orbital** is a region of space in which the probability of finding an electron is high.

We define each quantum number and describe the range of values it may take.

1. The **principal quantum number**, n , describes the *main energy level*, or shell, an electron occupies. It may be any positive integer:

$$n = 1, 2, 3, 4, \dots$$

2. The **angular momentum quantum number**, ℓ , designates the *shape of the region* in space that an electron occupies. Within a shell (defined by the value of n , the principal quantum number) different sublevels or subshells are possible, each with a characteristic shape. The angular momentum quantum number designates a *sublevel*, or specific *shape* of atomic orbital that an electron may occupy. This number, ℓ , may take integral values from 0 up to and including $(n - 1)$:

$$\ell = 0, 1, 2, \dots, (n - 1)$$

Thus, the maximum value of ℓ is $(n - 1)$. We give a letter notation to each value of ℓ . Each letter corresponds to a different sublevel (subshell).

$$\ell = 0, 1, 2, 3, \dots, (n - 1)$$

$s \quad p \quad d \quad f$

In the first shell, the maximum value of ℓ is zero, which tells us that there is only an s subshell and no p subshell. In the second shell, the permissible values of ℓ are 0 and 1, which tells us that there are only s and p subshells.

3. The **magnetic quantum number**, m_ℓ , designates the specific orbital within a subshell. Orbitals within a given subshell differ in their orientations in space, but not in their energies. Within each subshell, m_ℓ may take any integral values from $-\ell$ through zero up to and including $+\ell$:

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

The maximum value of m_ℓ depends on the value of ℓ . For example, when $\ell = 1$, which designates the p subshell, there are three permissible values of m_ℓ : -1 , 0 , and $+1$. Thus, three distinct regions of space, called atomic orbitals, are associated with a p subshell. We refer to these orbitals as the p_x , p_y , and p_z orbitals (see Section 5-16).



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.11, Shells, Subshells, and Orbitals.

The s , p , d , f designations arise from the characteristics of spectral emission lines produced by electrons occupying the orbitals: s (sharp), p (principal), d (diffuse), and f (fundamental).

TABLE 5-4 Permissible Values of the Quantum Numbers Through $n = 4$

n	ℓ	m_ℓ	m_s	Electron Capacity of Subshell = $4\ell + 2$	Electron Capacity of Shell = $2n^2$
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
	1 (2p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
	1 (3p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (3d)	-2, -1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
	1 (4p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (4d)	-2, -1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
	3 (4f)	-3, -2, -1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of m_ℓ	14	

4. The **spin quantum number**, m_s , refers to the spin of an electron and the orientation of the magnetic field produced by this spin. For every set of n , ℓ , and m_ℓ values, m_s can take the value $+\frac{1}{2}$ or $-\frac{1}{2}$:

$$m_s = \pm\frac{1}{2}$$

The values of n , ℓ , and m_ℓ describe a particular atomic orbital. Each atomic orbital can accommodate no more than two electrons, one with $m_s = +\frac{1}{2}$ and another with $m_s = -\frac{1}{2}$.

Table 5-4 summarizes some permissible values for the four quantum numbers. Spectroscopic evidence confirms the quantum mechanical predictions about the number of atomic orbitals in each shell.

5-16 ATOMIC ORBITALS

Let us now describe the distributions of electrons in atoms. For each neutral atom, we must account for a number of electrons equal to the number of protons in the nucleus, that is, the atomic number of the atom. Each electron is said to occupy an atomic orbital defined by a set of quantum numbers n , ℓ , and m_ℓ . In any atom, each orbital can hold a maximum of two electrons. Within each atom, these atomic orbitals, taken together, can be represented as a diffuse cloud of electrons (Figure 5-19).

The main shell of each atomic orbital in an atom is indicated by the principal quantum number n (from the Schrödinger equation). As we have seen, the principal quantum number takes integral values: $n = 1, 2, 3, 4, \dots$. The value $n = 1$ describes the first, or innermost, shell. These shells have been referred to as electron energy levels. Successive shells are at increasingly greater distances from the nucleus. For example, the $n = 2$ shell is farther from the nucleus than the $n = 1$ shell. The electron capacity of each shell is indicated in the right-hand column of Table 5-4. For a given n , the capacity is $2n^2$.

By the rules of Section 5-15, each shell has an s subshell (defined by $\ell = 0$) consisting of one s atomic orbital (defined by $m_\ell = 0$). We distinguish among orbitals in different



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.12, Quantum Numbers and Orbitals.

As you study the next two sections, keep in mind that the wave function, ψ , for an orbital characterizes two features of an electron in that orbital: (1) *where* (the region in space) the probability of finding the electron is high and (2) *how stable* that electron is (its energy).

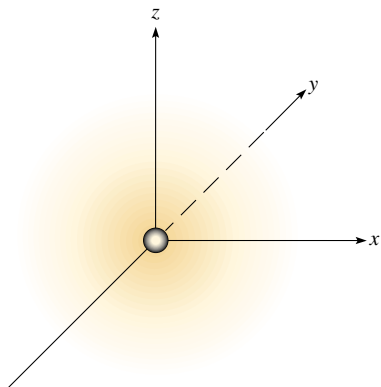


Figure 5-19 An electron cloud surrounding an atomic nucleus. The electron density drops off rapidly but smoothly as distance from the nucleus increases.

principal shells (main energy levels) by using the principal quantum number as a coefficient; $1s$ indicates the s orbital in the first shell, $2s$ is the s orbital in the second shell, $2p$ is a p orbital in the second shell, and so on (Table 5-4).

For each solution to the quantum mechanical equation, we can calculate the electron probability density (sometimes just called the electron density) at each point in the atom. This is the probability of finding an electron at that point. It can be shown that this electron density is proportional to $r^2\psi^2$, where r is the distance from the nucleus.

In the graphs in Figure 5-20, the electron probability density at a given distance from the nucleus is plotted against distance from the nucleus, for s orbitals. It is found that the electron probability density curve is the same regardless of the direction in the atom. We

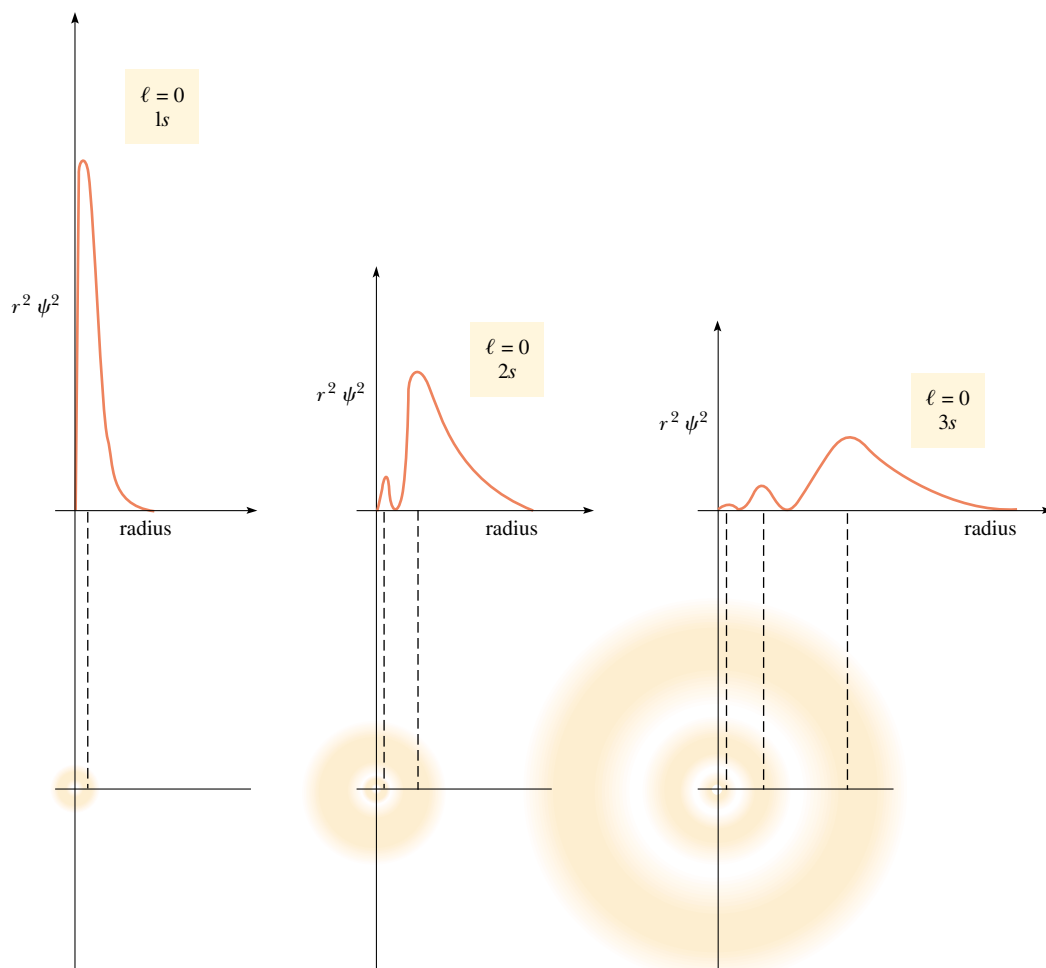


Figure 5-20 Plots of the electron density distributions associated with s orbitals. For any s orbital, this plot is the same in any direction (spherically symmetrical). The sketch below each plot shows a cross-section, in the plane of the atomic nucleus, of the electron cloud associated with that orbital. Electron density is proportional to $r^2\psi^2$.

describe an s orbital as *spherically symmetrical*; that is, it is round like a basketball (Figure 5-21). The electron clouds (electron densities) associated with the $1s$, $2s$, and $3s$ atomic orbitals are shown just below the plots. The electron clouds are three-dimensional, and only cross-sections are shown here. The regions shown in some figures (Figures 5-21 through 5-25) appear to have surfaces or skins only because they are arbitrarily “cut off” so that there is a 90% probability of finding an electron occupying the orbital somewhere within the surfaces.

Beginning with the second shell, each shell also contains a p subshell, defined by $\ell = 1$. Each of these subshells consists of a set of *three* p atomic orbitals, corresponding to the three allowed values of m_ℓ (-1 , 0 , and $+1$) when $\ell = 1$. The sets are referred to as $2p$, $3p$, $4p$, $5p$, . . . orbitals to indicate the main shells in which they are found. Each set of atomic p orbitals resembles three mutually perpendicular equal-arm dumbbells (see Figure 5-22). The nucleus defines the origin of a set of Cartesian coordinates with the usual x , y , and z axes (see Figure 5-23a). The subscript x , y , or z indicates the axis along which each of the three two-lobed orbitals is directed. A set of three p atomic orbitals may be represented as in Figure 5-23b.

Beginning at the third shell, each shell also contains a third subshell ($\ell = 2$) composed of a set of *five* d atomic orbitals ($m_\ell = -2, -1, 0, +1, +2$). They are designated $3d$, $4d$, $5d$, . . . to indicate the shell in which they are found. The shapes of the members of a set are indicated in Figure 5-24.

In each of the fourth and larger shells, there is also a fourth subshell, containing a set of *seven* f atomic orbitals ($\ell = 3$, $m_\ell = -3, -2, -1, 0, +1, +2, +3$). These are shown in Figure 5-25.

Thus, we see the first shell contains only the $1s$ orbital; the second shell contains the $2s$ and three $2p$ orbitals; the third shell contains the $3s$, three $3p$, and five $3d$ orbitals; and the fourth shell consists of a $4s$, three $4p$, five $4d$, and seven $4f$ orbitals. All subsequent shells contain s , p , d , and f subshells as well as others that are not occupied in any presently known elements in their lowest energy states.

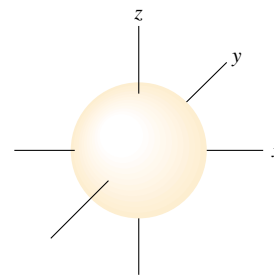



Figure 5-21 The shape of an s orbital.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 7.13, Shapes of Atomic Orbitals.

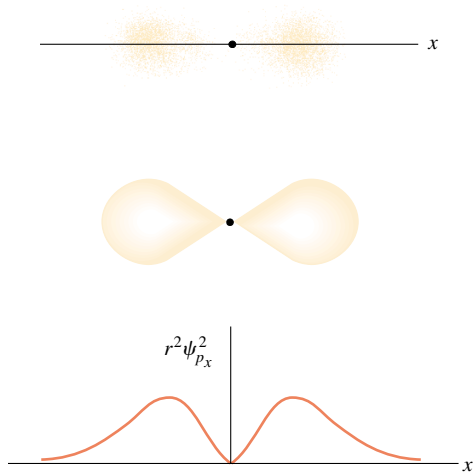


Figure 5-22 Three representations of the shape of a p orbital. The plot at the bottom is along the axis of maximum electron density for this orbital. A plot along any other direction would be different, because a p orbital is *not* spherically symmetrical.

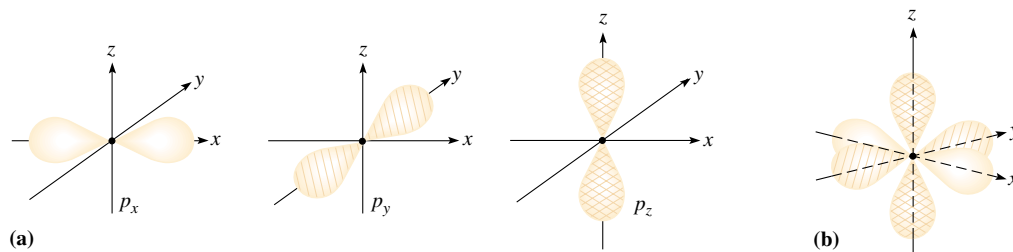


Figure 5-23 (a) The relative directional character of a set of p orbitals. (b) A model of three p orbitals (p_x , p_y , and p_z) of a single set of orbitals. The nucleus is at the center. (The lobes are actually more diffuse (“fatter”) than depicted. See Figure 5-26.)

The sizes of orbitals increase with increasing n and the true shapes of p orbitals are “diffuse,” as shown in Figure 5-26. The directions of p , d , and f orbitals, however, are easier to visualize in drawings such as those in Figures 5-23, 5-24, and 5-25; therefore, these “slender” representations are usually used.

In this section, we haven’t yet discussed the fourth quantum number, the spin quantum number, m_s . Because m_s has two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$, each atomic orbital, defined

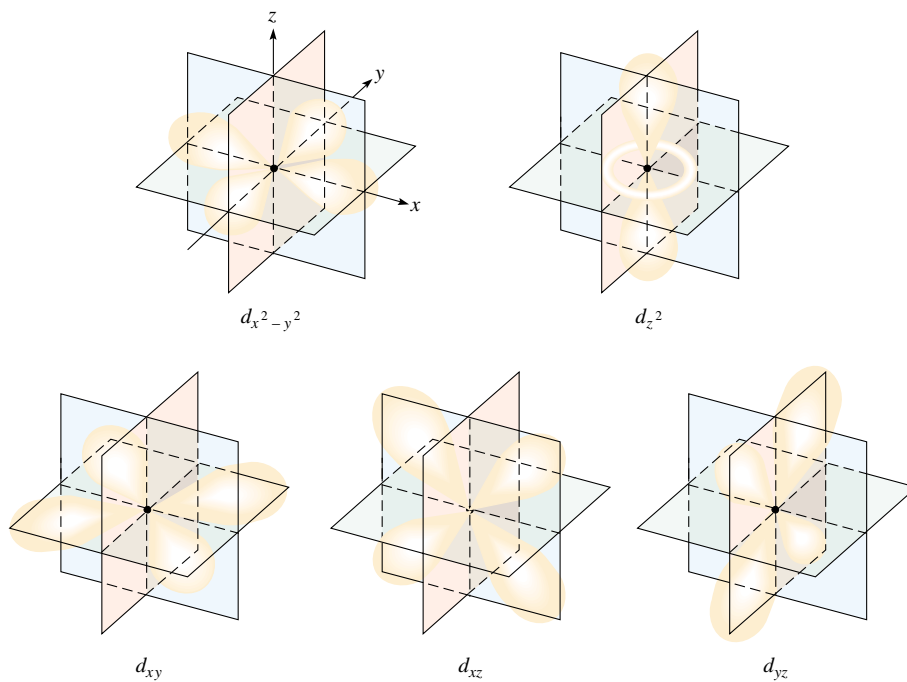


Figure 5-24 Spatial orientation of d orbitals. Note that the lobes of the $d_{x^2-y^2}$ and d_{z^2} orbitals lie along the axes, whereas the lobes of the others lie along diagonals between the axes.

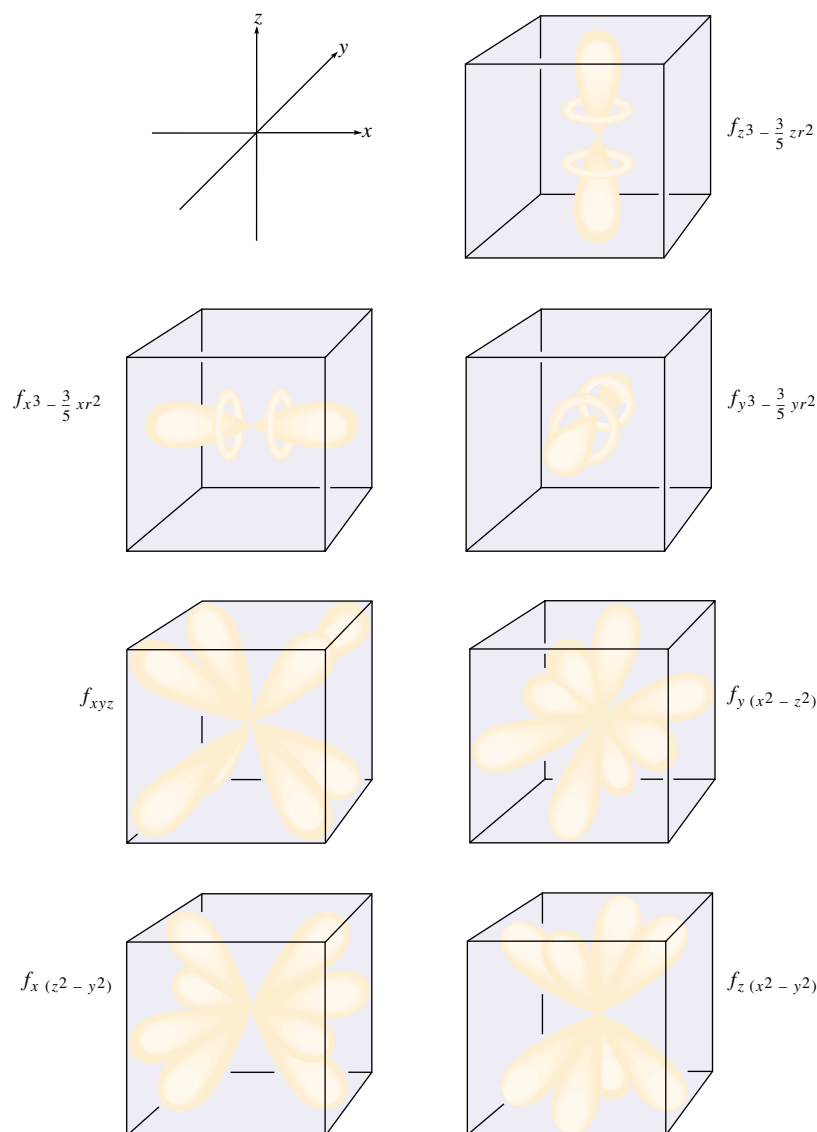


Figure 5-25 Relative directional character of f orbitals. The seven orbitals are shown within cubes as an aid to visualization.

by the values of n , ℓ , and m_ℓ , has a capacity of two electrons. Electrons are negatively charged, and they behave as though they were spinning about axes through their centers, so they act like tiny magnets. The motions of electrons produce magnetic fields, and these can interact with one another. Two electrons in the same orbital having opposite m_s values are said to be **spin-paired**, or simply **paired** (Figure 5-27).

Let us summarize, in tabular form, some of the information we have developed to this point. The principal quantum number n indicates the main shell. The number of subshells per shell is equal to n , the number of atomic orbitals per shell is n^2 , and the maximum number of electrons per shell is $2n^2$, because each atomic orbital can hold two electrons.

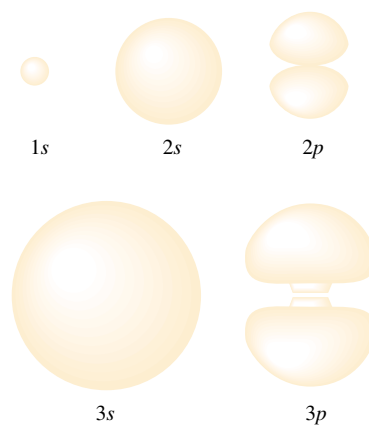
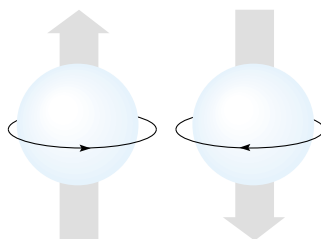


Figure 5-26 Shapes and approximate relative sizes of several orbitals in an atom.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 8.2, Spinning Electrons.



One electron has $m_s = +\frac{1}{2}$;
the other has $m_s = -\frac{1}{2}$.

Figure 5-27 Electron spin. Electrons act as though they spin about an axis through their centers. Because electrons may spin in two directions, the spin quantum number has two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$. Each electron spin produces a magnetic field. When two electrons have opposite spins, the attraction due to their opposite magnetic fields (*gray arrows*) helps to overcome the repulsion of their like charges. This permits two electrons to occupy the same region (orbital).

Shell n	Number of Subshells per Shell n	Number of Atomic Orbitals n^2	Maximum Number of Electrons $2n^2$
1	1	1 (1s)	2
2	2	4 (2s, 2p _x , 2p _y , 2p _z)	8
3	3	9 (3s, three 3p's, five 3d's)	18
4	4	16	32
5	5	25	50

5-17 ELECTRON CONFIGURATIONS

The wave function for an atom simultaneously depends on (describes) all of the electrons in the atom. The Schrödinger equation is much more complicated for atoms with more than one electron than for a one-electron species such as a hydrogen atom, and an explicit solution to this equation is not possible even for helium, let alone for more complicated atoms. We must therefore rely on approximations to solutions of the many-electron Schrödinger equation. We shall use one of the most common and useful, called the **orbital approximation**. In this approximation, the electron cloud of an atom is assumed to be the superposition of charge clouds, or orbitals, arising from the individual electrons; these orbitals resemble the atomic orbitals of hydrogen (for which exact solutions are known), which we described in some detail in the previous section. Each electron is described by the same allowed combinations of quantum numbers (n , ℓ , m_ℓ , and m_s) that we used for the hydrogen atom; however, the order of energies of the orbitals is often different from that in hydrogen.

Let us now examine the electronic structures of atoms of different elements. The electronic arrangement that we will describe for each atom is called the **ground state electron configuration**. This corresponds to the isolated atom in its lowest energy, or unexcited, state. Electron configurations for the elements, as determined by experiment, are given in Appendix B. We will consider the elements in order of increasing atomic number, using as our guide the periodic table on the inside front cover of this text.

In describing ground state electron configuration, the guiding idea is that the *total energy* of the atom is as low as possible. To determine these configurations, we use the **Aufbau Principle** as a guide:

The great power of modern computers has allowed scientists to make numerical approximations to this solution to very high accuracy for simple atoms such as helium. As the number of electrons increases, however, even such numerical approaches become quite difficult to apply and interpret. For multielectron atoms, more quantitative approximations are used.

The German verb *aufbauen* means “to build up.”

Each atom is “built up” by (1) adding the appropriate numbers of protons and neutrons as specified by the atomic number and the mass number, and (2) adding the necessary number of electrons into orbitals in the way that gives the lowest *total* energy for the atom.

As we apply this principle, we will focus on the difference in electronic arrangement between a given element and the element with an atomic number that is one lower. In doing this, we emphasize the particular electron that distinguishes each element from the previous one; however, we should remember that this distinction is artificial, because electrons are not really distinguishable. Though we do not always point it out, we *must* keep in mind that the atomic number (the charge on the nucleus) also differs.

The orbitals increase in energy with increasing value of the quantum number n . For a given value of n , energy increases with increasing value of ℓ . In other words, within a particular main shell, the s subshell is lowest in energy, the p subshell is the next lowest, then the d , then the f , and so on. As a result of changes in the nuclear charge and interactions among the electrons in the atom, the order of energies of the orbitals can vary somewhat from atom to atom.

Two general rules help us to predict electron configurations.

1. Electrons are assigned to orbitals in order of increasing value of $(n + \ell)$.
2. For subshells with the same value of $(n + \ell)$, electrons are assigned first to the subshell with lower n .

For example, the $2s$ subshell has $(n + \ell = 2 + 0 = 2)$, and the $2p$ subshell has $(n + \ell = 2 + 1 = 3)$, so we would expect to fill the $2s$ subshell before the $2p$ subshell (rule 1). This rule also predicts that the $4s$ subshell $(n + \ell = 4 + 0 = 4)$ will fill before the $3d$ subshell $(n + \ell = 3 + 2 = 5)$. Rule 2 reminds us to fill $2p$ $(n + \ell = 2 + 1 = 3)$ before $3s$ $(n + \ell = 3 + 0 = 3)$, because $2p$ has a lower value of n . The *usual* order of energies of orbitals of an atom and a helpful device for remembering this order are shown in Figures 5-28 and 5-29.

But we should consider these only as a *guide* to predicting electron arrangements. The observed electron configurations of lowest total energy do not always match those predicted by the Aufbau guide, and we will see a number of exceptions, especially for elements in the B groups of the periodic table.

The electronic structures of atoms are governed by the **Pauli Exclusion Principle**:

No two electrons in an atom may have identical sets of four quantum numbers.

An orbital is described by a particular allowed set of values for n , ℓ , and m_ℓ . Two electrons can occupy the same orbital only if they have opposite spins, m_s . Two such electrons in the same orbital are *paired*. For simplicity, we shall indicate atomic orbitals as $\underline{\quad}$ and show an unpaired electron as \uparrow and spin-paired electrons as $\uparrow\downarrow$. By “unpaired electron” we mean an electron that occupies an orbital singly.

Row 1. The first shell consists of only one atomic orbital, $1s$. This can hold a maximum of two electrons. Hydrogen, as we have already noted, contains just one electron. Helium,

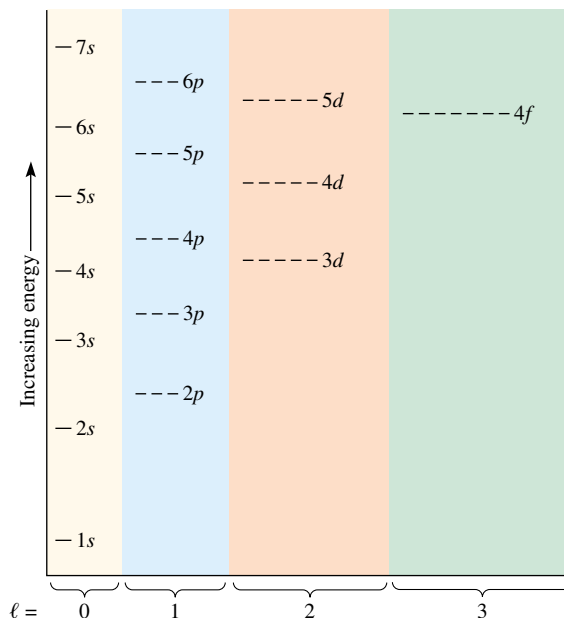
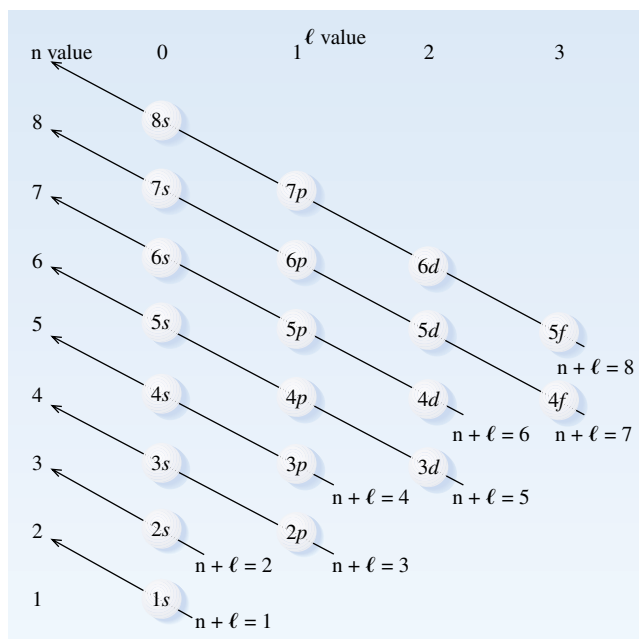


Figure 5-28 The usual order of filling (Aufbau order) of the orbitals of an atom. The relative energies are different for different elements, but the following main features should be noted: (1) The largest energy gap is between the $1s$ and $2s$ orbitals. (2) The energies of orbitals are generally closer together at higher energies. (3) The gap between np and $(n + 1)s$ (e.g., between $2p$ and $3s$ or between $3p$ and $4s$) is fairly large. (4) The gap between $(n - 1)d$ and ns (e.g., between $3d$ and $4s$) is quite small. (5) The gap between $(n - 2)f$ and ns (e.g., between $4f$ and $6s$) is even smaller.

Figure 5-29 An aid to remembering the usual order of filling of atomic orbitals. Write each shell (value of n) on one horizontal line, starting with $n = 1$ at the bottom. Write all like subshells (same ℓ values) in the same vertical column. Subshells are filled in order of increasing $(n + \ell)$. When subshells have the same $(n + \ell)$, the subshell with the lower n fills first. To use the diagram, we follow the diagonal arrows in order, reading bottom to top.



a noble gas, has a filled first main shell (two electrons). The atom is so stable that no chemical reactions of helium are known.

Helium's electrons can be displaced only by very strong forces, as in excitation by high-voltage discharge.

Orbital Notation		Simplified Notation
	1s	
${}^1_1\text{H}$	\uparrow	$1s^1$
${}^2_2\text{He}$	$\uparrow\downarrow$	$1s^2$

In the simplified notation, we indicate with superscripts the number of electrons in each subshell.

Row 2. Elements of atomic numbers 3 through 10 occupy the second period, or horizontal row, in the periodic table. In neon atoms the second main shell is filled completely. Neon, a noble gas, is extremely stable. No reactions of it are known.

	Orbital Notation			Simplified Notation
	1s	2s	2p	
${}^3_3\text{Li}$	$\uparrow\downarrow$	\uparrow		$1s^2 2s^1$ or $[\text{He}] 2s^1$
${}^4_4\text{Be}$	$\uparrow\downarrow$	$\uparrow\downarrow$		$1s^2 2s^2$ or $[\text{He}] 2s^2$
${}^5_5\text{B}$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow — —	$1s^2 2s^2 2p^1$ or $[\text{He}] 2s^2 2p^1$
${}^6_6\text{C}$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow —	$1s^2 2s^2 2p^2$ or $[\text{He}] 2s^2 2p^2$
${}^7_7\text{N}$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \uparrow	$1s^2 2s^2 2p^3$ or $[\text{He}] 2s^2 2p^3$
${}^8_8\text{O}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	$1s^2 2s^2 2p^4$ or $[\text{He}] 2s^2 2p^4$
${}^9_9\text{F}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	$1s^2 2s^2 2p^5$ or $[\text{He}] 2s^2 2p^5$
${}^{10}_{10}\text{Ne}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$1s^2 2s^2 2p^6$ or $[\text{He}] 2s^2 2p^6$

In writing electron configurations of atoms, we frequently simplify the notations. The abbreviation [He] indicates that the 1s orbital is completely filled, $1s^2$, as in helium.

We see that some atoms have unpaired electrons in the same set of energetically equivalent, or **degenerate**, orbitals. We have already seen that two electrons can occupy a given atomic orbital (with the same values of n , ℓ , and m_ℓ) *only* if their spins are paired (have opposite values of m_s). Even with pairing of spins, however, two electrons that are in the same orbital repel each other more strongly than do two electrons in different (but equal-energy) orbitals. Thus, both theory and experimental observations (see the following Enrichment section) lead to **Hund's Rule**:

Electrons occupy all the orbitals of a given subshell singly before pairing begins. These unpaired electrons have parallel spins.

Thus, carbon has two unpaired electrons in its 2p orbitals, and nitrogen has three.



As with helium, neon's electrons can be displaced by high-voltage electric discharge, as is observed in neon signs.

Enrichment

Both paramagnetism and diamagnetism are hundreds to thousands of times weaker than *ferromagnetism*, the effect seen in iron bar magnets.

Paramagnetism and Diamagnetism

Substances that contain unpaired electrons are weakly *attracted* into magnetic fields and are said to be **paramagnetic**. By contrast, those in which all electrons are paired are very weakly repelled by magnetic fields and are called **diamagnetic**. The magnetic effect can be measured by hanging a test tube full of a substance on a balance by a long thread and suspending it above the gap of an electromagnet (Figure 5-30). When the current is switched on, a paramagnetic substance such as copper(II) sulfate is pulled into the strong field. The



Iron displays ferromagnetism.

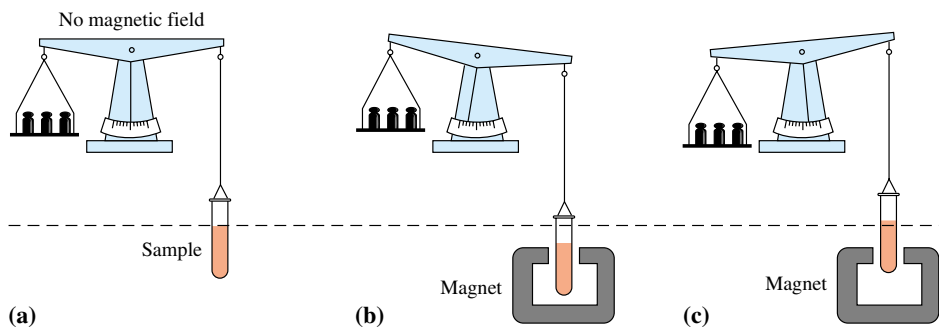



Figure 5-30 Diagram of an apparatus for measuring the paramagnetism of a substance. The tube contains a measured amount of the substance, often in solution. (a) Before the magnetic field is turned on, the position and mass of the sample are determined. (b) When the field is on, a paramagnetic substance is attracted *into* the field. (c) A diamagnetic substance would be repelled *very weakly* by the field.

paramagnetic attraction per mole of substance can be measured by weighing the sample before and after energizing the magnet. The paramagnetism per mole increases with increasing number of unpaired electrons per formula unit. Many transition metals and ions have one or more unpaired electrons and are paramagnetic.

The metals of the iron triad (Fe, Co, and Ni) are the only *free* elements that exhibit **ferromagnetism**. This property is much stronger than paramagnetism; it allows a substance to become permanently magnetized when placed in a magnetic field. This happens as randomly oriented electron spins align themselves with an applied field. To exhibit ferromagnetism, the atoms must be within the proper range of sizes so that unpaired electrons on adjacent atoms can interact cooperatively with one another, but not to the extent that they pair. Experimental evidence suggests that in ferromagnets, atoms cluster together into *domains* that contain large numbers of atoms in fairly small volumes. The atoms within each domain interact cooperatively with one another.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 8.3, Spinning Electrons and Magnetism.

Row 3. The next element beyond neon is sodium. Here we begin to add electrons to the third shell. Elements 11 through 18 occupy the third period in the periodic table.

	Orbital Notation		Simplified Notation
	3s	3p	
$_{11}\text{Na}$	$[\text{Ne}] \uparrow$		$[\text{Ne}] 3s^1$
$_{12}\text{Mg}$	$[\text{Ne}] \uparrow\downarrow$		$[\text{Ne}] 3s^2$
$_{13}\text{Al}$	$[\text{Ne}] \uparrow\downarrow$	$\uparrow _ _$	$[\text{Ne}] 3s^2 3p^1$
$_{14}\text{Si}$	$[\text{Ne}] \uparrow\downarrow$	$\uparrow \uparrow _$	$[\text{Ne}] 3s^2 3p^2$
$_{15}\text{P}$	$[\text{Ne}] \uparrow\downarrow$	$\uparrow \uparrow \uparrow$	$[\text{Ne}] 3s^2 3p^3$
$_{16}\text{S}$	$[\text{Ne}] \uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$	$[\text{Ne}] 3s^2 3p^4$
$_{17}\text{Cl}$	$[\text{Ne}] \uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow$	$[\text{Ne}] 3s^2 3p^5$
$_{18}\text{Ar}$	$[\text{Ne}] \uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$[\text{Ne}] 3s^2 3p^6$

Although the third shell is not yet filled (the *d* orbitals are still empty), argon is a noble gas. All noble gases except helium have ns^2np^6 electron configurations (where *n* indicates the largest occupied shell). The noble gases are quite unreactive.

Rows 4 and 5. It is an experimentally observed fact that *an electron occupies the available orbital that gives the atom the lowest total energy*. It is observed that filling the 4*s* orbitals before electrons enter the 3*d* orbitals *usually* leads to a lower total energy for the atom than some other arrangements. We therefore fill the orbitals in this order (see Figure 5-28). According to the Aufbau order (recall Figures 5-28 and 5-29), 4*s* fills before 3*d*. In general, *the (n + 1)s orbital fills before the nd orbital*. This is sometimes referred to as the *(n + 1) rule*.

After the 3*d* sublevel is filled to its capacity of 10 electrons, the 4*p* orbitals fill next, taking us to the noble gas krypton. Then the 5*s* orbital, the five 4*d* orbitals, and the three 5*p* orbitals fill to take us to xenon, a noble gas.

Let us now examine the electronic structure of the 18 elements in the fourth period in some detail. Some of these have electrons in *d* orbitals.

		Orbital Notation			
		3d	4s	4p	Simplified Notation
19K	[Ar]		\uparrow		[Ar] 4s ¹
20Ca	[Ar]		$\uparrow\downarrow$		[Ar] 4s ²
21Sc	[Ar]	\uparrow — — —	$\uparrow\downarrow$		[Ar] 3d ¹ 4s ²
22Ti	[Ar]	\uparrow \uparrow — —	$\uparrow\downarrow$		[Ar] 3d ² 4s ²
23V	[Ar]	\uparrow \uparrow \uparrow —	$\uparrow\downarrow$		[Ar] 3d ³ 4s ²
24Cr	[Ar]	\uparrow \uparrow \uparrow \uparrow \uparrow	\uparrow		[Ar] 3d ⁵ 4s ¹
25Mn	[Ar]	\uparrow \uparrow \uparrow \uparrow \uparrow	$\uparrow\downarrow$		[Ar] 3d ⁵ 4s ²
26Fe	[Ar]	$\uparrow\downarrow$ \uparrow \uparrow \uparrow \uparrow	$\uparrow\downarrow$		[Ar] 3d ⁶ 4s ²
27Co	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow \uparrow	$\uparrow\downarrow$		[Ar] 3d ⁷ 4s ²
28Ni	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow	$\uparrow\downarrow$		[Ar] 3d ⁸ 4s ²
29Cu	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	\uparrow		[Ar] 3d ¹⁰ 4s ¹
30Zn	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$		[Ar] 3d ¹⁰ 4s ²
31Ga	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow — —	[Ar] 3d ¹⁰ 4s ² 4p ¹
32Ge	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow —	[Ar] 3d ¹⁰ 4s ² 4p ²
33As	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \uparrow	[Ar] 3d ¹⁰ 4s ² 4p ³
34Se	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	[Ar] 3d ¹⁰ 4s ² 4p ⁴
35Br	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	[Ar] 3d ¹⁰ 4s ² 4p ⁵
36Kr	[Ar]	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	[Ar] 3d ¹⁰ 4s ² 4p ⁶

End-of-chapter Exercises 81–111 provide much valuable practice in writing electron configurations.

As you study these electron configurations, you should be able to see how most of them are predicted from the Aufbau order. However, as we fill the 3d set of orbitals, from ₂₁Sc to ₃₀Zn, we see that these orbitals are not filled quite regularly. As the 3d orbitals are filled, their energies get closer to that of the 4s orbital and eventually become lower. If the order of filling of electrons on chromium gave the expected configuration, it would be: [Ar] 4s²3d⁴. Chemical and spectroscopic evidence indicates, however, that the configuration of Cr has only one electron in the 4s orbital, [Ar] 4s¹3d⁵. For this element, the 4s and 3d orbitals are nearly equal in energy. Six electrons in these six orbitals of nearly the same energy are more stable with the electrons all unpaired, [Ar] 3d \uparrow \uparrow \uparrow \uparrow \uparrow 4s \uparrow rather than the predicted order [Ar] 3d \uparrow \uparrow \uparrow \uparrow — 4s $\uparrow\downarrow$.

The next elements, Mn to Ni, have configurations as predicted by the Aufbau order, presumably because forming a pair of electrons in the larger 4s orbital is easier than in a smaller, less diffuse, 3d orbital. By the time Cu is reached, the energy of 3d is sufficiently lower than that of 4s, so that the total energy of the configuration [Ar] 4s¹3d¹⁰ is lower than that of [Ar] 4s²3d⁹.

We notice that the exceptions for Cr and Cu give half-filled or filled sets of equivalent orbitals (d⁵ and d¹⁰, respectively), and this is also true for several other exceptions to the Aufbau order. You may wonder why such an exception does not occur in, for example, ₁₄Si or ₃₂Ge, where we could have an s¹p³ configuration that would have half-filled sets of s and p orbitals. It does not occur because of the very large energy gap between ns and np orbitals. There is some evidence that does, however, suggest an enhanced stability of half-filled sets of p orbitals.



Problem-Solving Tip: Exceptions to the Aufbau Order

In Appendix B, you will find a number of exceptions to the electron configurations predicted from the Aufbau Principle. You should realize that statements such as the Aufbau Principle and the (n + 1) rule merely represent general guidelines and should

The electron configurations of elements 1 through 109 are given in Appendix B.

not be viewed as hard-and-fast rules; the *total energy* of the atom is as low as possible. Some of the reasons for exceptions are

1. The Aufbau order of orbital energies is based on calculations for the hydrogen atom, which contains only one electron. The orbital energies also depend on additional factors such as the nuclear charge and interactions of electrons in different occupied orbitals.
2. The energy scale varies with the atomic number.
3. Some orbitals are very close together, so their order can change, depending on the occupancies of other orbitals.

Some types of exceptions to the Aufbau order are general enough to remember easily, for example, those based on the special stability of filled or half-filled sets of orbitals. Other exceptions are quite unpredictable. Your instructor may expect you to remember some of the exceptions.

Let us now write the quantum numbers to describe each electron in an atom of nitrogen. Keep in mind the fact that Hund's Rule must be obeyed. Thus, there is only one (unpaired) electron in each $2p$ orbital in a nitrogen atom.

EXAMPLE 5-8 *Electron Configurations and Quantum Numbers*

Write an acceptable set of four quantum numbers for each electron in a nitrogen atom.

Plan

Nitrogen has seven electrons, which occupy the lowest energy orbitals available. Two electrons can occupy the first shell, $n = 1$, in which there is only one s orbital; when $n = 1$, then ℓ must be zero, and therefore $m_\ell = 0$. The two electrons differ only in spin quantum number, m_s . The next five electrons can all fit into the second shell, for which $n = 2$ and ℓ may be either 0 or 1. The $\ell = 0$ (s) subshell fills first, and the $\ell = 1$ (p) subshell is occupied next.

Solution

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration
1,2	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right\}$	0	0	$\left\{ \begin{array}{l} +\frac{1}{2} \\ -\frac{1}{2} \end{array} \right\}$	$1s^2$
3,4	$\left\{ \begin{array}{l} 2 \\ 2 \end{array} \right\}$	0	0	$\left\{ \begin{array}{l} +\frac{1}{2} \\ -\frac{1}{2} \end{array} \right\}$	$2s^2$
5, 6, 7	$\left\{ \begin{array}{l} 2 \\ 2 \\ 2 \end{array} \right\}$	1	$\left\{ \begin{array}{l} -1 \\ 0 \\ +1 \end{array} \right\}$	$\left\{ \begin{array}{l} +\frac{1}{2} \text{ or } -\frac{1}{2} \\ +\frac{1}{2} \text{ or } -\frac{1}{2} \\ +\frac{1}{2} \text{ or } -\frac{1}{2} \end{array} \right\}$	$\left. \begin{array}{l} 2p_x^1 \\ 2p_y^1 \\ 2p_z^1 \end{array} \right\} \text{ or } 2p^3$

Electrons are indistinguishable. We have numbered them 1, 2, 3, and so on as an aid to counting them.

In the lowest energy configurations, the three $2p$ electrons either have $m_s = +\frac{1}{2}$ or all have $m_s = -\frac{1}{2}$.

EXAMPLE 5-9 *Electron Configurations and Quantum Numbers*

Write an acceptable set of four quantum numbers for each electron in a chlorine atom.

Plan

Chlorine is element number 17. Its first seven electrons have the same quantum numbers as those of nitrogen in Example 5-8. Electrons 8, 9, and 10 complete the filling of the $2p$ subshell

($n = 2, \ell = 1$) and therefore also the second energy level. Electrons 11 through 17 fill the $3s$ subshell ($n = 3, \ell = 0$) and partially fill the $3p$ subshell ($n = 3, \ell = 1$).

Solution

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration
1, 2	1	0	0	$\pm\frac{1}{2}$	$1s^2$
3, 4	2	0	0	$\pm\frac{1}{2}$	$2s^2$
5–10	2	1	-1	$\pm\frac{1}{2}$	$2p^6$
		1	0	$\pm\frac{1}{2}$	
		1	+1	$\pm\frac{1}{2}$	
11, 12	3	0	0	$\pm\frac{1}{2}$	$3s^2$
13–17	3	1	-1	$\pm\frac{1}{2}$	$3p^5$
		1	0	$\pm\frac{1}{2}$	
		1	+1	$\pm\frac{1}{2}$ or $-\frac{1}{2}^*$	

*The $3p$ orbital with only a single electron can be any one of the set, not necessarily the one with $m_\ell = +1$.

You should now work Exercises 104 and 108.

5-18 THE PERIODIC TABLE AND ELECTRON CONFIGURATIONS

In this section, we view the *periodic table* (see inside front cover and Section 4-1) from a modern, much more useful perspective—as a systematic representation of the electron configurations of the elements. In the periodic table, elements are arranged in blocks based on the kinds of atomic orbitals that are being filled (Figure 5-31). The periodic tables in this text are divided into “A” and “B” groups. The A groups contain elements in which s and p orbitals are being filled. Elements within any particular A group have similar electron configurations and chemical properties, as we shall see in the next chapter. The B groups are those in which there are one or two electrons in the s orbital of the outermost occupied shell, and the d orbitals, one shell smaller, are being filled.

Lithium, sodium, and potassium, elements of the leftmost column of the periodic table (Group IA), have a single electron in their outermost s orbital (ns^1). Beryllium and magnesium, of Group IIA, have two electrons in their outermost shell, ns^2 , while boron and aluminum (Group IIIA) have three electrons in their outermost shell, ns^2np^1 . Similar observations can be made for other A group elements.

The electron configurations of the A group elements and the noble gases can be predicted reliably from Figures 5-28 and 5-29. However, there are some more pronounced irregularities in the B groups below the fourth period. In the heavier B group elements, the higher energy subshells in different principal shells have energies that are very nearly equal (Figure 5-29). It is easy for an electron to jump from one orbital to another of nearly the same energy, even in a different set. This is because the orbital energies are *perturbed* (change slightly) as the nuclear charge changes, and an extra electron is added in going from one element to the next. This phenomenon gives rise to other irregularities that are analogous to those of Cr and Cu, described earlier.

Group	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII B			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
Period 1	1 H 1s																1 H	2 He 1s
Period 2	3 Li 2s	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne 2p
Period 3	11 Na 3s	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar 3p
Period 4	19 K 4s	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn 3d	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr 4p
Period 5	37 Rb 5s	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd 4d	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe 5p
Period 6	55 Cs 6s	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg 5d	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn 6p
Period 7	87 Fr 7s	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112 6d						

6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu 4f
7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr 5f

Figure 5-31 A periodic table colored to show the kinds of atomic orbitals (subshells) being filled and the symbols of blocks of elements. The electronic structures of the A group elements are quite regular and can be predicted from their positions in the periodic table, but many exceptions occur in the *d* and *f* blocks. The colors in this figure are the same as those in Figure 5-28.

Hydrogen and helium are shown here in their usual positions in the periodic table. These may seem somewhat unusual based just on their electron configurations. We should remember, however, that the first shell ($n = 1$) can hold a maximum of only two electrons. This shell is entirely filled in helium, so He behaves as a noble gas, and we put it in the column with the other noble gases (Group VIIIA). Hydrogen has one electron that is easily lost, like the metals in Group IA, so we put it in Group IA even though it is not a metal. Furthermore, hydrogen is one electron short of a noble gas configuration (He), so we could also place it with the other such elements in Group VIIA.

We can extend the information in Figure 5-31 to indicate the electron configurations that are represented by each *group* (column) of the periodic table. Table 5-5 shows this interpretation of the periodic table, along with the most important exceptions (A more complete listing of electron configurations is given in Appendix B.) We can use this interpretation of the periodic table to write, quickly and reliably, the electron configurations for elements.

TABLE 5-5 The *s*, *p*, *d*, and *f* Blocks of the Periodic Table*

		GROUPS																															
		IA	IIA	IIIB	IVB VB VIB VIIIB						VIII B			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA												
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)														
	<i>s</i> orbital block																																
	s^1 s^2																																
<i>n</i> = 1		1 H																	2 He														
<i>n</i> = 2		3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne										
<i>n</i> = 3		11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar														
<i>n</i> = 4		19 K	20 Ca	21 Sc											29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr											
<i>n</i> = 5		37 Rb	38 Sr	39 Y											47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe											
<i>n</i> = 6		55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
<i>n</i> = 7		87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112						
<i>n</i> = 6	LANTHANIDE SERIES																					4 <i>f</i> subshell being filled											
<i>n</i> = 7	ACTINIDE SERIES																					5 <i>f</i> subshell being filled											

**n* is the principal quantum number. The d^1s^2, d^2s^2, \dots designations represent known configurations. They refer to $(n - 1)d$ and ns orbitals. Several exceptions to the configurations indicated above each group are shown in gray.

EXAMPLE 5-10 Electron Configurations

Use Table 5-5 to determine the electron configurations of (a) magnesium, Mg; (b) germanium, Ge; and (c) molybdenum, Mo.

Plan

We will use the electron configurations indicated in Table 5-5 for each group. Each *period* (row) begins filling a new shell (new value of *n*). Elements to the right of the *d* orbital block have the *d* orbitals in the $(n - 1)$ shell already filled. We often find it convenient to collect all sets of orbitals with the same value of *n* together, to emphasize the number of electrons in the *outermost* shell, that is, the shell with the highest value of *n*.

Solution

(a) Magnesium, Mg, is in Group IIA, which has the general configuration s^2 ; it is in Period 3 (third row). The last filled noble gas configuration is that of neon, or [Ne]. The electron configuration of Mg is [Ne] $3s^2$.

(b) Germanium, Ge, is in Group IVA, for which Table 5-5 shows the general configuration s^2p^2 . It is in Period 4 (the fourth row), so we interpret this as $4s^24p^2$. The last filled noble gas configuration is that of argon, Ar, accounting for 18 electrons. In addition, Ge lies beyond the

d orbital block, so we know that the $3d$ orbitals are completely filled. The electron configuration of Ge is $[\text{Ar}] 4s^2 3d^{10} 4p^2$ or $[\text{Ar}] 3d^{10} 4s^2 4p^2$.

(c) Molybdenum, Mo, is in Group VIB, with the general configuration $d^5 s^1$; it is in Period 5, which begins with $5s$ and is beyond the noble gas krypton. The electron configuration of Mo is $[\text{Kr}] 5s^1 4d^5$ or $[\text{Kr}] 4d^5 5s^1$. The electron configuration of molybdenum is analogous to that of chromium, Cr, the element just above it. The configuration of Cr was discussed in Section 5-17 as one of the exceptions to the Aufbau order of filling.

You should now work Exercise 106.

EXAMPLE 5-11 Unpaired Electrons

Determine the number of unpaired electrons in an atom of tellurium, Te.

Plan

Te is in Group VIA in the periodic table, which tells us that its configuration is $s^2 p^4$. All other shells are completely filled, so they contain only paired electrons. We need only to find out how many unpaired electrons are represented by $s^2 p^4$.

Solution

The notation $s^2 p^4$ is a short representation for $s \uparrow\downarrow p \uparrow\downarrow \uparrow \uparrow$. This shows that an atom of Te contains two unpaired electrons.

You should now work Exercises 100 and 102.

The periodic table has been described as “the chemist’s best friend.” Chemical reactions involve loss, gain, or sharing of electrons. In this chapter, we have seen that the fundamental basis of the periodic table is that it reflects similarities and trends in electron configurations. It is easy to use the periodic table to determine many important aspects of electron configurations of atoms. Practice until you can use the periodic table with confidence to answer many questions about electron configurations. As we continue our study, we will learn many other useful ways to interpret the periodic table. We should always keep in mind that the many trends in chemical and physical properties that we correlate with the periodic table are ultimately based on the trends in electron configurations.

Key Terms

Absorption spectrum The spectrum associated with absorption of electromagnetic radiation by atoms (or other species) resulting from transitions from lower to higher energy states.

Alpha (α) particle A helium ion with a $2+$ charge; an assembly of two protons and two neutrons.

amu See *Atomic mass unit*.

Angular momentum quantum number (ℓ) The quantum mechanical solution to a wave equation that designates the subshell, or set of orbitals (s, p, d, f), within a given main shell in which an electron resides.

Anode In a cathode-ray tube, the positive electrode.

Atomic mass unit An arbitrary mass unit defined to be exactly one-twelfth the mass of the carbon-12 isotope.

Atomic number The integral number of protons in the nucleus; defines the identity of an element.

Atomic orbital The region or volume in space in which the probability of finding electrons is highest.

Aufbau (“building up”) Principle A guide for predicting the order in which electrons fill subshells and shells in atoms.

Balmer-Rydberg equation An empirical equation that relates wavelengths in the hydrogen emission spectrum to integers.

Canal ray A stream of positively charged particles (cations) that moves toward the negative electrode in a cathode-ray tube; observed to pass through canals in the negative electrode.

Cathode In a cathode-ray tube, the negative electrode.

- Cathode ray** The beam of electrons going from the negative electrode toward the positive electrode in a cathode-ray tube.
- Cathode-ray tube** A closed glass tube containing a gas under low pressure, with electrodes near the ends and a luminescent screen at the end near the positive electrode; produces cathode rays when high voltage is applied.
- Continuous spectrum** The spectrum that contains all wavelengths in a specified region of the electromagnetic spectrum.
- d* orbitals** Beginning in the third shell, a set of five degenerate orbitals per shell, higher in energy than *s* and *p* orbitals in the same shell.
- Degenerate orbitals** Two or more orbitals that have the same energy.
- Diamagnetism** *Weak* repulsion by a magnetic field; associated with all electrons being paired.
- Electromagnetic radiation** Energy that is propagated by means of electric and magnetic fields that oscillate in directions perpendicular to the direction of travel of the energy.
- Electron** A subatomic particle having a mass of 0.00054858 amu and a charge of $1-$.
- Electron configuration** The specific distribution of electrons in the atomic orbitals of atoms and ions.
- Electron transition** The transfer of an electron from one energy level to another.
- Emission spectrum** The spectrum associated with emission of electromagnetic radiation by atoms (or other species) resulting from electron transitions from higher to lower energy states.
- Excited state** Any energy state other than the ground state of an atom, ion, or molecule.
- f* orbitals** Beginning in the fourth shell, a set of seven degenerate orbitals per shell, higher in energy than *s*, *p*, and *d* orbitals in the same shell.
- Ferromagnetism** The property that allows a substance to become permanently magnetized when placed in a magnetic field; exhibited by iron, cobalt, and nickel.
- Frequency (ν)** The number of crests of a wave that pass a given point per unit time.
- Fundamental particles** Subatomic particles of which all matter is composed; protons, electrons, and neutrons are fundamental particles.
- Ground state** The lowest energy state or most stable state of an atom, molecule, or ion.
- Group** A vertical column in the periodic table; also called a family.
- Heisenberg Uncertainty Principle** It is impossible to determine accurately both the momentum and position of an electron simultaneously.
- Hund's Rule** Each orbital of a given subshell is occupied by a single electron before pairing begins. See *Aufbau Principle*.
- Isotopes** Two or more forms of atoms of the same element with different masses; that is, atoms containing the same number of protons but different numbers of neutrons.
- Line spectrum** An atomic emission or absorption spectrum.
- Magnetic quantum number (m_l)** Quantum mechanical solution to a wave equation that designates the particular orbital within a given subshell (*s*, *p*, *d*, *f*) in which an electron resides.
- Mass number** The integral sum of the numbers of protons and neutrons in an atom.
- Mass spectrometer** An instrument that measures the charge-to-mass ratios of charged particles.
- Natural radioactivity** Spontaneous decomposition of an atom.
- Neutron** A subatomic nuclear particle having a mass of 1.0087 amu and no charge.
- Nucleus** The very small, very dense, positively charged center of an atom containing protons and neutrons, except for ${}^1_1\text{H}$.
- Nuclide symbol** The symbol for an atom, ${}^A_Z E$, in which *E* is the symbol for an element, *Z* is its atomic number, and *A* is its mass number.
- p* orbitals** Beginning with the second shell, a set of three degenerate mutually perpendicular, equal-arm, dumbbell-shaped atomic orbitals per shell.
- Pairing of electrons** Interaction of two electrons with opposite m_s values in the same orbital ($\uparrow\downarrow$).
- Paramagnetism** Attraction toward a magnetic field, stronger than diamagnetism, but still very weak compared with ferromagnetism; due to presence of unpaired electrons.
- Pauli Exclusion Principle** No two electrons in the same atom may have identical sets of four quantum numbers.
- Period** A horizontal row in the periodic table.
- Photoelectric effect** Emission of an electron from the surface of a metal, caused by impinging electromagnetic radiation of certain minimum energy; the resulting current increases with increasing intensity of radiation.
- Photon** A "packet" of light or electromagnetic radiation; also called a quantum of light.
- Principal quantum number (*n*)** The quantum mechanical solution to a wave equation that designates the main shell, or energy level, in which an electron resides.
- Proton** A subatomic particle having a mass of 1.0073 amu and a charge of $1+$, found in the nuclei of atoms.
- Quantum** A "packet" of energy. See *Photon*.
- Quantum mechanics** A mathematical method of treating particles on the basis of quantum theory, which assumes that energy (of small particles) is not infinitely divisible.
- Quantum numbers** Numbers that describe the energies of electrons in atoms; they are derived from quantum mechanical treatment.
- Radiant energy** See *Electromagnetic radiation*.
- s* orbital** A spherically symmetrical atomic orbital; one per shell.
- Spectral line** Any of a number of lines corresponding to definite wavelengths in an atomic emission or absorption spectrum; these lines represent the energy difference between two energy levels.
- Spectrum** Display of component wavelengths of electromagnetic radiation.
- Spin quantum number (m_s)** The quantum mechanical solution to a wave equation that indicates the relative spins of electrons.
- Wavelength (λ)** The distance between two identical points of a wave.

Exercises

Particles and the Nuclear Atom

- List the three fundamental particles of matter, and indicate the mass and charge associated with each.
- (a) How do we know that canal rays have charges opposite in sign to cathode rays? What are canal rays? (b) Why are cathode rays from all samples of gases identical, whereas canal rays are not?
- *3. The following data are measurements of the charges on oil droplets using an apparatus similar to that used by Millikan:

$13.458 \times 10^{-19} \text{ C}$	$17.308 \times 10^{-19} \text{ C}$
$15.373 \times 10^{-19} \text{ C}$	$28.844 \times 10^{-19} \text{ C}$
$17.303 \times 10^{-19} \text{ C}$	$11.545 \times 10^{-19} \text{ C}$
$15.378 \times 10^{-19} \text{ C}$	$19.214 \times 10^{-19} \text{ C}$

Each should be a whole-number ratio of some fundamental charge. Using these data, determine the value of the fundamental charge.

- *4. Suppose we discover a new positively charged particle, which we call the "whizatron." We want to determine its charge.
 - What modifications would we have to make to the Millikan oil-drop apparatus to carry out the corresponding experiment on whizatrons?
 - In such an experiment, we observe the following charges on five different droplets:

$5.76 \times 10^{-19} \text{ C}$	$7.20 \times 10^{-19} \text{ C}$
$2.88 \times 10^{-19} \text{ C}$	$10.08 \times 10^{-19} \text{ C}$
$8.64 \times 10^{-19} \text{ C}$	

What is the charge on the whizatron?

- Outline Rutherford's contribution to understanding the nature of atoms.
- Why was Rutherford so surprised that some of the α -particles were scattered backward in the gold foil experiment?

- Summarize Moseley's contribution to our knowledge of the structure of atoms.
- The approximate radius of a hydrogen atom is 0.0529 nm, and that of a proton is $1.5 \times 10^{-15} \text{ m}$. Assuming both the hydrogen atom and the proton to be spherical, calculate the fraction of the space in an atom of hydrogen that is occupied by the nucleus. $V = (4/3)\pi r^3$ for a sphere.
- The approximate radius of a neutron is $1.5 \times 10^{-15} \text{ m}$, and the mass is $1.675 \times 10^{-27} \text{ kg}$. Calculate the density of a neutron. $V = (4/3)\pi r^3$ for a sphere.

Atom Composition, Isotopes, and Atomic Weights

- Arrange the following in order of increasing ratio of charge to mass: $^{12}\text{C}^+$, $^{12}\text{C}^{2+}$, $^{14}\text{N}^+$, $^{14}\text{N}^{2+}$.
- Refer to Exercise 10. Suppose all of these high-energy ions are present in a mass spectrometer. For which one will its path be changed (a) the most and (b) the least by increasing the external magnetic field?
- Estimate the percentage of the total mass of a $^{65}_{29}\text{Cu}$ atom that is due to (a) electrons, (b) protons, and (c) neutrons by *assuming* that the mass of the atom is simply the sum of the masses of the appropriate numbers of subatomic particles.
- (a) How are isotopic abundances determined experimentally? (b) How do the isotopes of a given element differ?
- Define and illustrate the following terms clearly and concisely: (a) atomic number, (b) isotope, (c) mass number, (d) nuclear charge.
- Write the composition of one atom of each of the three isotopes of silicon: ^{28}Si , ^{29}Si , ^{30}Si .
- Write the composition of one atom of each of the four isotopes of sulfur: ^{32}S , ^{33}S , ^{34}S , ^{36}S .
- Complete Chart A for neutral atoms.
- Complete Chart B for neutral atoms.

Chart A

Kind of Atom	Atomic Number	Mass Number	Isotope	Number of Protons	Number of Electrons	Number of Neutrons
			$^{21}_{10}\text{Ne}$			
chlorine		35				
	28	58				
		40		18		

Chart B

Kind of Atom	Atomic Number	Mass Number	Isotope	Number of Protons	Number of Electrons	Number of Neutrons
selenium						40
			$^{11}_5\text{B}$			
					35	46
		104			45	

- *19. Prior to 1962, the atomic weight scale was based on the assignment of an atomic weight of exactly 16 amu to the *naturally occurring* mixture of oxygen. The atomic weight of cobalt is 58.9332 amu on the carbon-12 scale. What was it on the older scale?
20. Determine the number of protons, neutrons, and electrons in each of the following species: (a) $^{40}_{20}\text{Ca}$; (b) $^{45}_{21}\text{Sc}$; (c) $^{91}_{40}\text{Zr}$; (d) $^{39}_{19}\text{K}^+$; (e) $^{65}_{30}\text{Zn}^{2+}$; (f) $^{108}_{47}\text{Ag}^+$.
21. Determine the number of protons, neutrons, and electrons in each of the following species: (a) $^{34}_{16}\text{S}^+$; (b) $^{93}_{41}\text{Nb}$; (c) $^{27}_{13}\text{Al}$; (d) $^{63}_{29}\text{Cu}^+$; (e) $^{56}_{26}\text{Fe}^{2+}$; (f) $^{55}_{26}\text{Fe}^{3+}$.
22. What is the symbol of the species composed of each of the following sets of subatomic particles? (a) $24p$, $27n$, $24e$; (b) $20p$, $20n$, $18e$; (c) $34p$, $44n$, $34e$; (d) $53p$, $74n$, $54e$.
23. What is the symbol of the species composed of each of the following sets of subatomic particles? (a) $94p$, $150n$, $94e$; (b) $79p$, $118n$, $76e$; (c) $34p$, $45n$, $36e$; (d) $52p$, $76n$, $54e$.
24. The atomic weight of lithium is 6.941 amu. The two naturally occurring isotopes of lithium have the following masses: ^6Li , 6.01512 amu; ^7Li , 7.01600 amu. Calculate the percent of ^6Li in naturally occurring lithium.
25. The atomic weight of rubidium is 85.4678 amu. The two naturally occurring isotopes of rubidium have the following masses: ^{85}Rb , 84.9118 amu; ^{87}Rb , 86.9092 amu. Calculate the percent of ^{85}Rb in naturally occurring rubidium.
26. Bromine is composed of $^{79}_{35}\text{Br}$, 78.9183 amu, and $^{81}_{35}\text{Br}$, 80.9163 amu. The percent composition of a sample is 50.69% Br-79 and 49.31% Br-81. Based on this sample, calculate the atomic weight of bromine.
27. What is the atomic weight of a hypothetical element that consists of the following isotopes in the indicated relative abundances?

Isotope	Isotopic Mass (amu)	% Natural Abundance
1	94.9	12.4
2	95.9	73.6
3	97.9	14.0

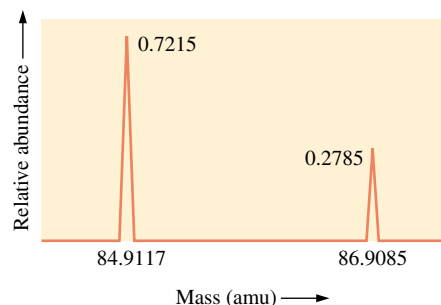
28. Naturally occurring iron consists of four isotopes with the abundances indicated here. From the masses and relative abundances of these isotopes, calculate the atomic weight of naturally occurring iron.

Isotope	Isotopic Mass (amu)	% Natural Abundance
^{54}Fe	53.9396	5.82
^{56}Fe	55.9349	91.66
^{57}Fe	56.9354	2.19
^{58}Fe	57.9333	0.33

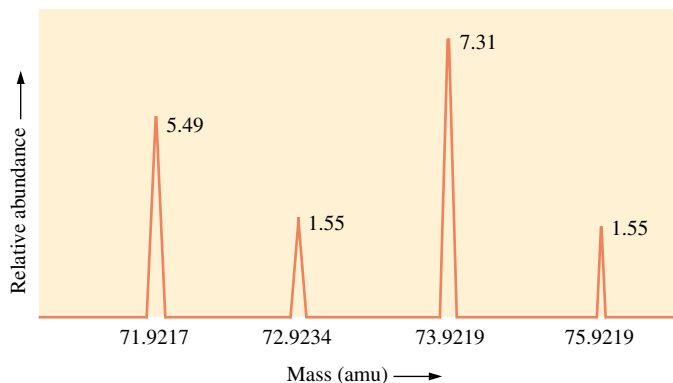
29. Calculate the atomic weight of nickel from the following information.

Isotope	Isotopic Mass (amu)	% Natural Abundance
^{58}Ni	57.9353	67.88
^{60}Ni	59.9332	26.23
^{61}Ni	60.9310	1.19
^{62}Ni	61.9283	3.66
^{64}Ni	63.9280	1.08

30. The atomic weight of copper is 63.546 amu. The two naturally occurring isotopes of copper have the following masses: ^{63}Cu , 62.9298 amu; ^{65}Cu , 64.9278 amu. Calculate the percent of ^{63}Cu in naturally occurring copper.
31. Silver consists of two naturally occurring isotopes: ^{107}Ag , which has a mass of 106.90509 amu, and ^{109}Ag , which has a mass of 108.9047 amu. The atomic weight of silver is 107.8682 amu. Determine the percent abundance of each isotope in naturally occurring silver.
32. Refer to Table 5-3 *only* and calculate the atomic weights of oxygen and chlorine. Do your answers agree with the atomic weights given in that table?
33. The following is a mass spectrum of the $1+$ charged ions of an element. Calculate the atomic weight of the element. What is the element?



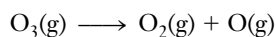
34. Suppose you measure the mass spectrum of the $1+$ charged ions of germanium, atomic weight 72.61 amu. Unfortunately, the recorder on the mass spectrometer jams at the beginning and again at the end of your experiment. You obtain only the following partial spectrum, which *may or may not be complete*. From the information given here, can you tell whether one of the germanium isotopes is missing? If one is missing, at which end of the plot should it appear?



35. Calculate the atomic weight of silicon using the following data for the percent natural abundance and mass of each isotope: (a) 92.23% ^{28}Si (27.9769 amu); (b) 4.67% ^{29}Si (28.9765 amu); (c) 3.10% ^{30}Si (29.9738 amu).
36. Calculate the atomic weight of chromium using the following data for the percent natural abundance and mass of each isotope: (a) 4.35% ^{50}Cr (49.9461 amu); (b) 83.79% ^{52}Cr (51.9405 amu); (c) 9.50% ^{53}Cr (52.9406 amu); (d) 2.36% ^{54}Cr (53.9389 amu).

Electromagnetic Radiation

37. Calculate the wavelengths, in meters, of radiation of the following frequencies: (a) $5.60 \times 10^{15} \text{ s}^{-1}$; (b) $2.11 \times 10^{14} \text{ s}^{-1}$; (c) $3.89 \times 10^{12} \text{ s}^{-1}$.
38. Calculate the frequency of radiation of each of the following wavelengths: (a) 8973 Å; (b) 492 nm; (c) 4.92 cm; (d) $4.55 \times 10^{-9} \text{ cm}$.
39. What is the energy of a photon of each of the radiations in Exercise 37? Express your answer in joules per photon. In which regions of the electromagnetic spectrum do these radiations fall?
40. Excited lithium ions emit radiation at a wavelength of 670.8 nm in the visible range of the spectrum. (This characteristic color is often used as a qualitative analysis test for the presence of Li^+ .) Calculate (a) the frequency and (b) the energy of a photon of this radiation. (c) What color is this light?
41. Calculate the energy, in joules per photon, of X-rays having a wavelength of 3.0 Å. How does the energy of these X-rays compare with the energy calculated for yellow light in Example 5-5?
42. Ozone in the upper atmosphere absorbs ultraviolet radiation, which induces the following chemical reaction:



What is the energy of a 3400-Å photon that is absorbed? What is the energy of a mole of these photons?

- *43. During photosynthesis, chlorophyll- α absorbs light of wavelength 440 nm and emits light of wavelength

670 nm. What is the energy available for photosynthesis from the absorption–emission of a mole of photons?



Photosynthesis.

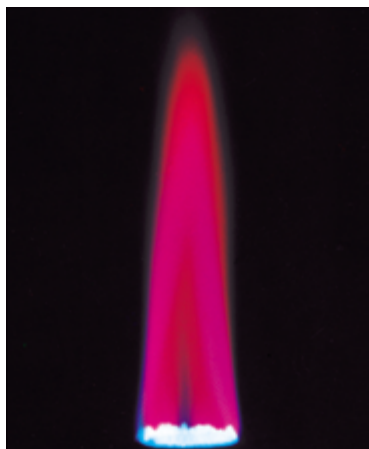
44. Classical music radio station KMFA in Austin broadcasts at a frequency of 89.5 MHz. What is the wavelength of its signal in meters?
45. Describe the following terms clearly and concisely in relation to electromagnetic radiation: (a) wavelength, (b) frequency, (c) amplitude, (d) color.
- *46. Assume that 10^{-17} J of light energy is needed by the interior of the human eye to “see” an object. How many photons of green light (wavelength = 495 nm) are needed to generate this minimum energy?
- *47. The human eye receives a $2.500 \times 10^{-14} \text{ J}$ signal consisting of photons of orange light, $\lambda = 6150 \text{ Å}$. How many photons reach the eye?
48. Alpha Centauri is the star closest to our solar system. It is 4.3 light-years away. How many miles in this? A light-year is the distance that light travels (in a vacuum) in one year. Assume that space is essentially a vacuum.

The Photoelectric Effect

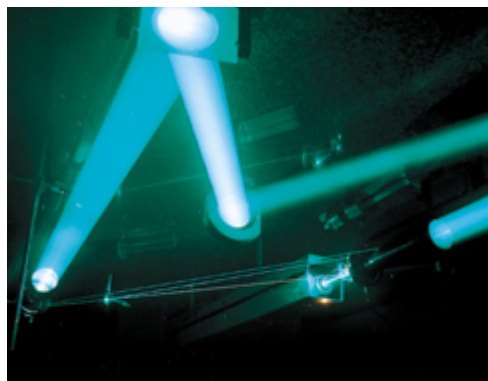
49. What evidence supports the idea that electromagnetic radiation is (a) wave-like; (b) particle-like?
50. Describe the influence of frequency and intensity of electromagnetic radiation on the current in the photoelectric effect.
- *51. Cesium is often used in “electric eyes” for self-opening doors in an application of the photoelectric effect. The amount of energy required to ionize (remove an electron from) a cesium atom is 3.89 electron volts ($1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$). Show by calculation whether a beam of yellow light with wavelength 5830 Å would ionize a cesium atom.
- *52. Refer to Exercise 51. What would be the wavelength, in nanometers, of light with just sufficient energy to ionize a cesium atom? What color would this light be?

Atomic Spectra and the Bohr Theory

53. (a) Distinguish between an atomic emission spectrum and an atomic absorption spectrum. (b) Distinguish between a continuous spectrum and a line spectrum.
54. Prepare a sketch similar to Figure 5-16b that shows a ground energy state and three excited energy states. Using vertical arrows, indicate the transitions that would correspond to the absorption spectrum for this system.
55. Why is the Bohr model of the hydrogen atom referred to as the solar system model?
- *56. If each atom in one mole of atoms emits a photon of wavelength $5.50 \times 10^3 \text{ \AA}$, how much energy is lost? Express the answer in kJ/mol. As a reference point, burning one mole (16 g) of CH_4 produces 819 kJ of heat.
57. What is the Balmer-Rydberg equation? Why is it called an empirical equation?
58. Hydrogen atoms absorb energy so that the electrons are excited to the energy level $n = 7$. Electrons then undergo these transitions: (1) $n = 7 \rightarrow n = 1$; (2) $n = 7 \rightarrow n = 2$; (3) $n = 2 \rightarrow n = 1$. Which of these transitions will produce the photon with (a) the smallest energy; (b) the highest frequency; (c) the shortest wavelength? (d) What is the frequency of a photon resulting from the transition $n = 6 \rightarrow n = 1$?
- *59. Five energy levels of the He atom are given in joules per atom above an *arbitrary* reference energy: (1) 6.000×10^{-19} ; (2) 8.812×10^{-19} ; (3) 9.381×10^{-19} ; (4) 10.443×10^{-19} ; (5) 10.934×10^{-19} . Construct an energy level diagram for He and find the energy of the photon (a) absorbed for the electron transition from level 1 to level 5 and (b) emitted for the electron transition from level 4 to level 1.
60. The following are prominent lines in the visible region of the emission spectra of the elements listed. The lines can be used to identify the elements. What color is the light responsible for each line? (a) lithium, 4603 \AA ; (b) neon, 540.0 nm; (c) calcium, 6573 \AA ; (d) potassium, $\nu = 3.90 \times 10^{14} \text{ Hz}$.



61. Hydrogen atoms have an absorption line at 1026 \AA . What is the frequency of the photons absorbed, and what is the energy difference, in joules, between the ground state and this excited state of the atom?
- *62. An argon laser emits blue light with a wavelength of 488.0 nm. How many photons are emitted by this laser in 2.00 seconds, operating at a power of 515 milliwatts? One watt (a unit of power) is equal to 1 joule/second.



Lasers.

The Wave-Particle View of Matter

63. (a) What evidence supports the idea that electrons are particle-like? (b) What evidence supports the idea that electrons are wave-like?
64. (a) What is the de Broglie wavelength of a proton moving at a speed of $2.50 \times 10^7 \text{ m/s}$? The proton mass is $1.67 \times 10^{-24} \text{ g}$. (b) What is the de Broglie wavelength of a stone with a mass of 30.0 g moving at $2.00 \times 10^3 \text{ m/h}$ ($\approx 100 \text{ mph}$)? (c) How do the wavelengths in parts (a) and (b) compare with the typical radii of atoms? (See the atomic radii in Figure 6-1).
65. What is the wavelength corresponding to a neutron of mass $1.67 \times 10^{-27} \text{ kg}$ moving at 2360 m/s?
66. What is the velocity of an α -particle (a helium nucleus) that has a de Broglie wavelength of 0.529 \AA ?

Quantum Numbers and Atomic Orbitals

67. (a) What is a quantum number? What is an atomic orbital? (b) How many quantum numbers are required to specify a single atomic orbital? What are they?
68. How are the possible values for the angular momentum quantum number for a given electron restricted by the value of n ?
69. Without giving the ranges of possible values of the four quantum numbers, n , ℓ , m_ℓ , and m_s , describe briefly what information each one gives.

70. An electron is in one of the $3p$ orbitals. What are the possible values of the quantum numbers n , ℓ , m_ℓ , and m_s for the electron?
71. What is the maximum number of electrons in an atom that can have the following quantum numbers? (a) $n = 3$; (b) $n = 3$ and $\ell = 1$; (c) $n = 3$, $\ell = 1$, and $m_\ell = -1$; (d) $n = 3$, $\ell = 1$, $m_\ell = -1$, and $m_s = -\frac{1}{2}$.
72. What is the maximum number of electrons in an atom that can have the following quantum numbers? (a) $n = 3$ and $\ell = 1$; (b) $n = 3$ and $\ell = 2$; (c) $n = 3$, $\ell = 2$ and $m_\ell = -1$; (d) $n = 3$, $\ell = 1$, and $m_\ell = -1$; (e) $n = 3$, $\ell = 2$, $m_\ell = 0$, and $m_s = -\frac{1}{2}$.
73. What are the values of n and ℓ for the following subshells? (a) $1s$; (b) $4s$; (c) $3p$; (d) $3d$; (e) $4f$.
74. How many individual orbitals are there in the third shell? Write out n , ℓ , and m_ℓ quantum numbers for each one, and label each set by the s , p , d , f designations.
75. (a) Write the possible values of ℓ when $n = 5$. (b) Write the allowed number of orbitals (1) with the quantum numbers $n = 4$, $\ell = 3$; (2) with the quantum number $n = 4$; (3) with the quantum numbers $n = 4$, $\ell = 2$, $m_\ell = 0$; (4) with the quantum numbers $n = 6$, $\ell = 5$.
76. Write the subshell notations that correspond to (a) $n = 3$, $\ell = 0$; (b) $n = 3$, $\ell = 1$; (c) $n = 7$, $\ell = 0$; (d) $n = 3$, $\ell = 2$.
77. What values can m_ℓ take for (a) a $3d$ orbital, (b) a $1s$ orbital, and (c) a $3p$ orbital?
78. How many orbitals in any atom can have the given quantum number or designation? (a) $4p$; (b) $3p$; (c) $3p_x$; (d) $n = 5$; (e) $6d$; (f) $5d$; (g) $5f$; (h) $7s$.
79. The following incorrect sets of quantum numbers in the order n , ℓ , m_ℓ , m_s are written for paired electrons or for one electron in an orbital. Correct them, assuming n values are correct. (a) $1, 0, 0, +\frac{1}{2}, +\frac{1}{2}$; (b) $2, 2, 1, \pm\frac{1}{2}$; (c) $3, 2, 3, \pm\frac{1}{2}$; (d) $3, 1, 2, +\frac{1}{2}$; (e) $2, 1, -1, 0$; (f) $3, 0, -1, -\frac{1}{2}$.
80. (a) How are a $1s$ orbital and a $2s$ orbital in an atom similar? How do they differ? (b) How are a $2p_x$ orbital and a $2p_y$ orbital in an atom similar? How do they differ?
- electron in an s orbital. Identify the group in which most of these are found in the periodic table.
85. List the elements having an atomic number of 20 or less that have one or more unpaired p orbital electrons. Indicate the group to which each of these elements belongs in the periodic table.
86. Identify the element, or elements possible, given only the number of electrons in the outermost shell and the principal quantum number of that shell. (a) 1 electron, first shell; (b) 2 electrons, second shell; (c) 3 electrons, third shell; (d) 2 electrons, seventh shell; (e) 4 electrons, fourth shell; (f) 8 electrons, sixth shell.
87. Give the ground state electron configurations for the elements of Exercise 81 using shorthand notation—that is, $1s^2 2s^2 2p^6$, and so on.
88. Give the ground state electron configurations for the elements of Exercise 82 using shorthand notation—that is, $1s^2 2s^2 2p^6$, and so on.
89. State the Pauli Exclusion Principle. Would any of the following electron configurations violate this rule: (a) $1s^2$; (b) $1s^2 2p^7$; (c) $1s^3$? Explain.
90. State Hund's Rule. Would any of the following electron configurations violate this rule: (a) $1s^2$; (b) $1s^2 2s^2 2p_x^2$; (c) $1s^2 2s^2 2p_x^1 2p_y^1$; (d) $1s^2 2s^2 2p_x^1 2p_z^1$; (e) $1s^2 2p_x^2 2p_y^1 2p_z^1$? Explain.
- *91. Classify each of the following atomic electron configurations as (i) a ground state, (ii) an excited state, or (iii) a forbidden state: (a) $1s^2 2s^2 2p^5 3s^1$; (b) $[\text{Kr}] 4d^{10} 5s^3$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$; (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$; (e) $1s^2 2s^2 2p^{10} 3s^2 3p^5$.
92. Which of the elements with atomic numbers of 10 or less are paramagnetic when in the atomic state?
93. Semiconductor industries depend on such elements as Si, Ga, As, Ge, Al, Cd, and Se. Write the predicted electron configuration of each element.
94. The manufacture of high-temperature ceramic superconductors depends on such elements as Cu, O, La, Y, Ba, Tl, and Bi. Write the predicted electron configuration of each element. (Consult Appendix B if necessary.)
95. In nature, potassium and sodium are often found together. (a) Write the electron configurations for potassium and for sodium. (b) How are they similar? (c) How do they differ?
96. Which elements are represented by the following electron configurations?
 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
 (b) $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 6d^1 7s^2$
 (c) $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$
 (d) $[\text{Kr}] 4d^5 5s^2$
 (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
97. Repeat Exercise 96 for
 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
 (b) $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^2$
 (d) $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$

Electron Configurations and the Periodic Table

You should be able to use the positions of elements in the periodic table to answer the exercises in this section.

81. Draw representations of ground state electron configurations using the orbital notation ($\uparrow\downarrow$) for the following elements. (a) N; (b) Fe; (c) Cl; (d) Rh.
82. Draw representations of ground state electron configurations using the orbital notation ($\uparrow\downarrow$) for the following elements. (a) P; (b) Ni; (c) Ga; (d) Zr.
83. Determine the number of electrons in the outer occupied shell of each of the following elements, and indicate the principal quantum number of that shell. (a) Na; (b) Al; (c) Ca; (d) Sr; (e) Ba; (f) Br.
84. With the help of Appendix B, list the symbols for the first eight elements, by atomic number, that have an unpaired

122. When compounds of barium are heated in a flame, green light of wavelength 554 nm is emitted. How much energy is lost when one mole of barium atoms each emit one photon of this wavelength?
123. A 60-watt light bulb consumes energy at the rate of $60 \text{ J}\cdot\text{s}^{-1}$. Much of the light is emitted in the infrared region, and less than 5% of the energy appears as visible light. Calculate the number of visible photons emitted per second. Make the simplifying assumptions that 5.0% of the light is visible and that all visible light has a wavelength of 550 nm (yellow-green).