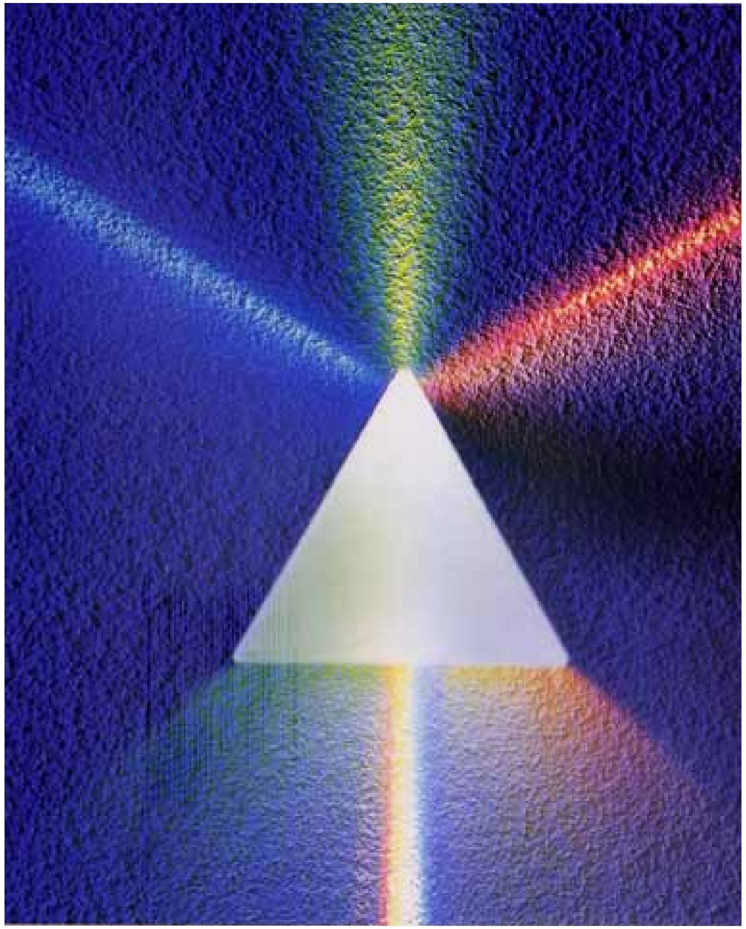
Chemistry

Zumdahl, 7th edition

歐亞書局

CH7 Atomic Structure and Periodicity



Light refracted through a prism.

Contents

Introduction

- In the past 200 years, a great deal of experimental evidence has accumulated to support the atomic model.
- In fact, for the following 20 centuries, no convincing experimental evidence was available to support the existence of atoms.
- The first real scientific data were gathered by Lavoisier and others from quantitative measurements of chemical reactions.

- The results of these stoichiometric experiments led John Dalton to propose the first systematic atomic theory.
- Dalton’s theory, although crude, has stood the test of time extremely well.

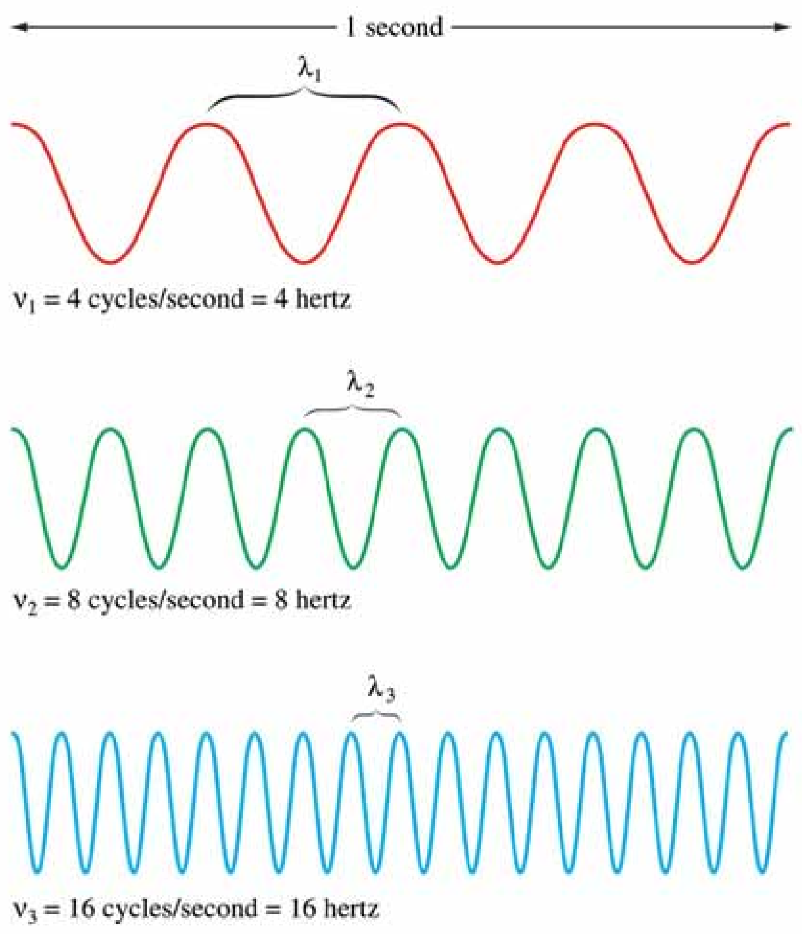
✱ One of the most striking things about the chemistry of the elements is the periodic repetition of properties. There are several groups of elements that show great similarities in chemical behavior.

- A radical new theory called quantum mechanics was developed to account for the behavior of light and atoms.

7.1 Electromagnetic Radiation

- One of the ways that energy travels through space is by **electromagnetic radiation**.
- Waves have three primary characteristics: wavelength, frequency, and speed.
- **Wavelength** (symbolized by the lowercase Greek letter lambda, λ) is the distance between two consecutive peaks or troughs in a wave, as shown in Fig. 7.1.

Figure 7.1



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

- The **frequency** (symbolized by the lowercase Greek letter nu, ν) is defined as the *number of waves (cycles) per second that pass a given point in space*.
- Since all types of electromagnetic radiation travel at the speed of light, short-wavelength radiation must have a high frequency.
- Note that the wave the shortest wavelength (λ_3) has the highest frequency and the wave with the longest wavelength (λ_1) has the lowest frequency.

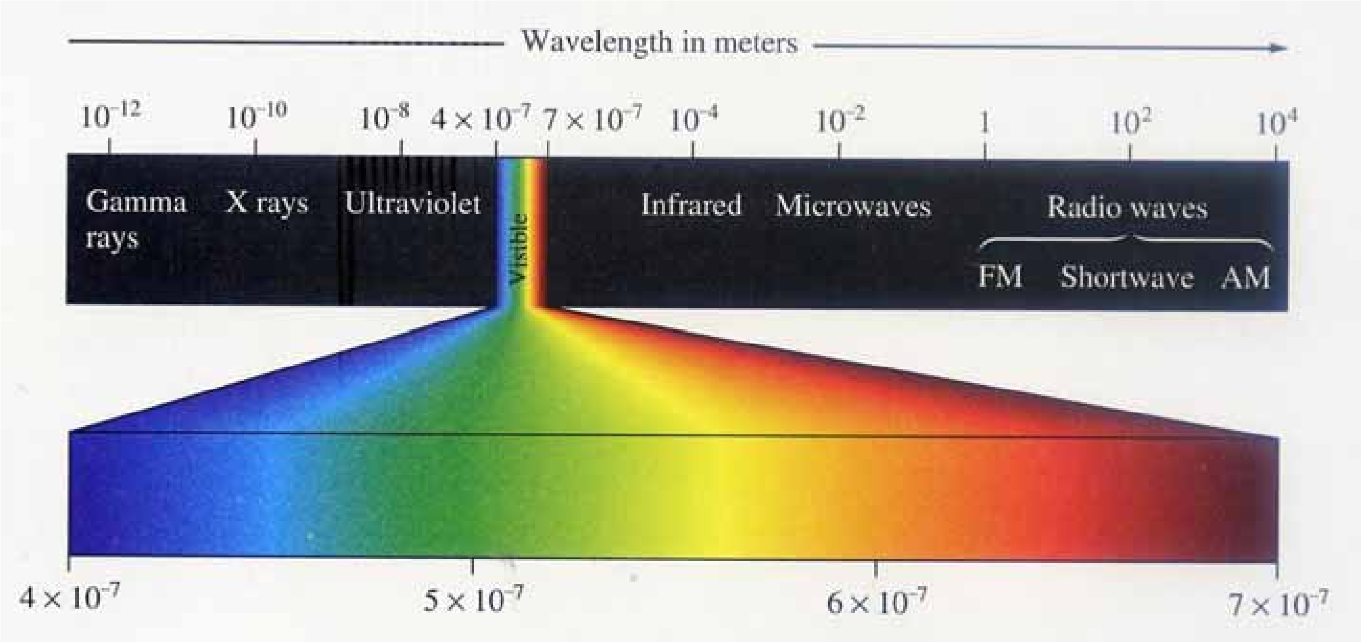
$$\lambda \nu = c$$

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

- Electromagnetic radiation is classified as shown in Fig. 7.2. Radiation provides an important means of energy transfer.

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

Figure 7.2



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

Sample Exercise 7.1

Frequency of Electromagnetic Radiation

The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $Sr(NO_3)_2$ and $SrCO_3$ are heated. (This can be easily demonstrated in the lab by dissolving one of these salts in methanol that contains a little water and igniting the mixture in an evaporating dish.) Calculate the frequency of red light of wavelength 6.50×10^2 nm.

Sample Exercise 7.1

Solution

We can convert wavelength to frequency using the equation

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

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

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

Sample Exercise 7.1

And

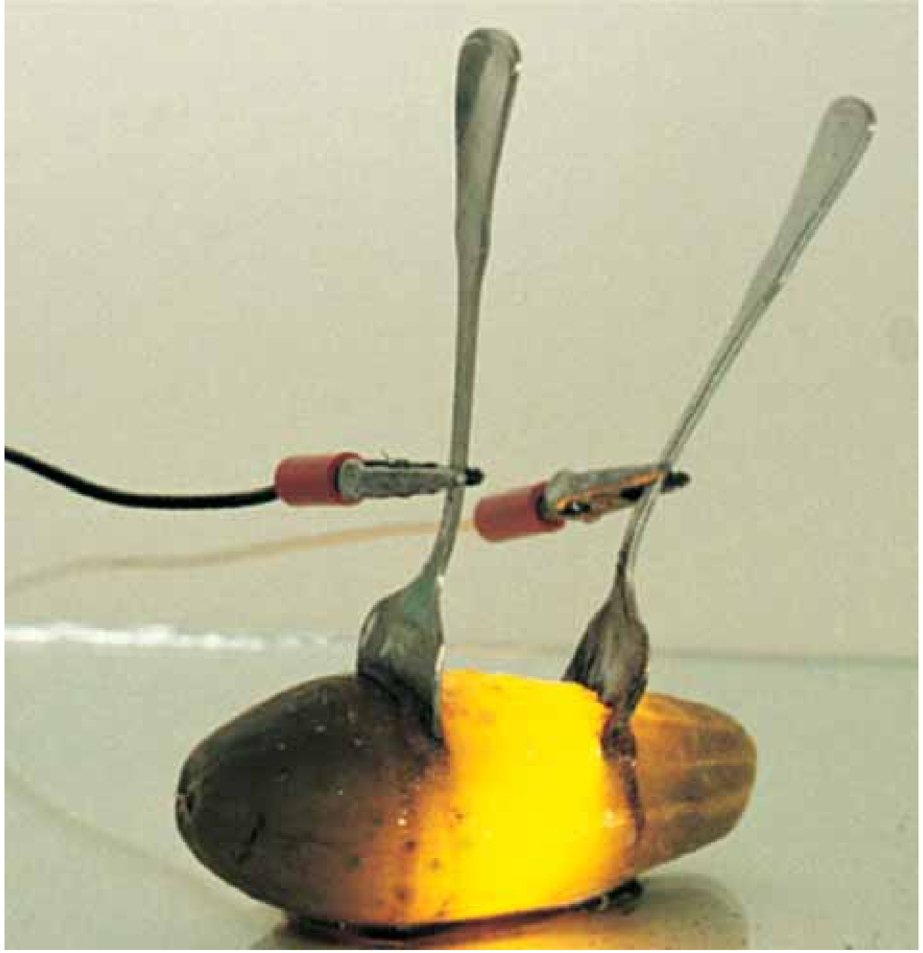
$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{8}\ \cancel{m}/s}{6.50 \times 10^{-7}\ \cancel{m}} = 4.61 \times 10^{14}\ s^{-1} = 4.61$$

See Exercises 7.31 and 7.32

7.2 The Nature of Matter

- Matter was thought to consist of particles, whereas energy in the form of light (electromagnetic radiation) was described as a wave.
- Particles were things that had mass and whose position in space could be specified.
- Waves were described as massless and delocalized; that is, their position in space could not be specified.

- It also was assumed that there was no intermingling of matter and light. Everything known before 1900 seemed to fit neatly into this view.



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

- The first important advance came in 1900 from the German physicist Max Planck (1858-1947).
- Planck could account for these observations only by postulating that energy can be gained or lost only in whole-number multiples of the quantity $h\nu$, where h is a constant called **Planck's constant**, determined by experiment to have the value 6.626×10^{-34} J・s.

- That is, the change in energy for a system ΔE can be represented by the equation

$$\Delta E = h\nu$$

- where *n* is an integer (1, 2, 3, …), *h* is Plack’s constant, and ν is the frequency of the electromagnetic radiation absorbed or emitted.

- Now it seemed clear that energy is in fact **quantized** and can occur only in discrete units of size $h\nu$.
- Each of these small "packets" of energy is called a *quantum*.
- A system can transfer energy only in whole quanta.

Sample Exercise 7.2 The Energy of a Photon

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

Solution

The quantum of energy can be calculated from the equation

$$\Delta E = h\nu$$

Sample Exercise 7.2

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

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

So

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

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

See Exercises 7.33 and 7.34

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

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

- where *h* is Plack’s constant, ν is the frequency of the radiation, and λ is the wavelength of the radiation.

Figure 7.3

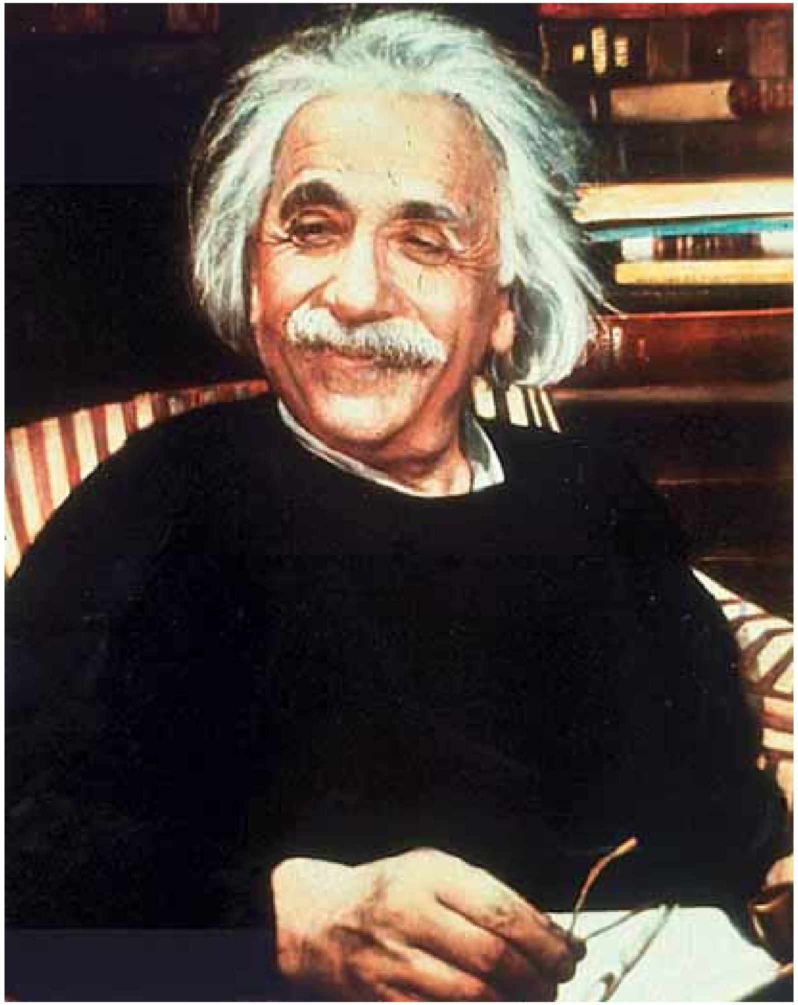


Figure 7.3

Albert Einstein (1879-1955) was born in Germany. Nothing in his early development suggested genius; even at the age of 9 he did not speak clearly, and his school principal replied, “it doesn’t matter; he’ll never make a success of anything.” When he was 10, Einstein entered the Luitpold Gymnaium (high school), which was typical of German schools of that time in being harshly disciplinarian. There he developed a deep suspicion of authority and a skepticism that encouraged him to question and doubt-valuable qualities in a scientist. In 1905, while a patent clerk in Switzerland, Einstein published a paper explaining the photoelectric effect via the quantum theory. For this revolutionary thinking he received a Nobel Prize in 1921. Highly regarded by this time, he worked in Germany until 1933, when Hitler’s

Figure 7.3

persecution of the Jews forced him to come to the United States. He worked at the Instituted for Advanced Studies in Princeton, New Jersey, until his death in 1955.

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

The Photoelectric Effect

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

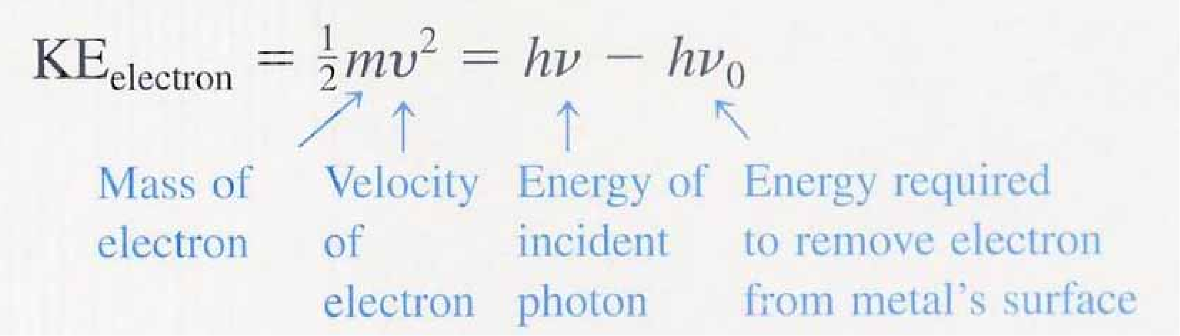
1. Studies in which the frequency of the light is varied show that no electrons are emitted by a given metal below a specific threshold frequency ν_0.
2. For light with frequency lower than the threshold frequency, no electrons are emitted regardless of the intensity of the light.
3. For light with frequency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

4. For light with frequency greater than the threshold frequency, the kinetic energy, of the emitted electrons increase linearly with the frequency of the light.

Minimum energy required to remove an electron

$$= E_0 = h\nu_0$$

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



$$KE_{electron} = \frac{1}{2}mv^2 = h\nu - h\nu_0$$

Mass of electron

Velocity of electron

Energy of incident photon

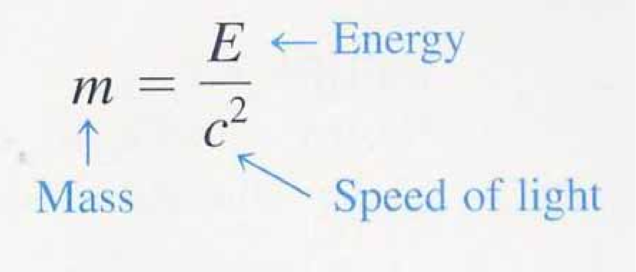
Energy required to remove electron from metal's surface

- In a related development, Einstein derived the famous equation

$$E = mc^2$$

- In his special theory of relativity published in 1905. The main significance of this equation is that energy has mass.

- This is more apparent if we rearrange the equation in the following form:



$$\overset{\text{Mass}}{m} = \frac{E}{c^2}$$

Energy

Mass

Speed of light

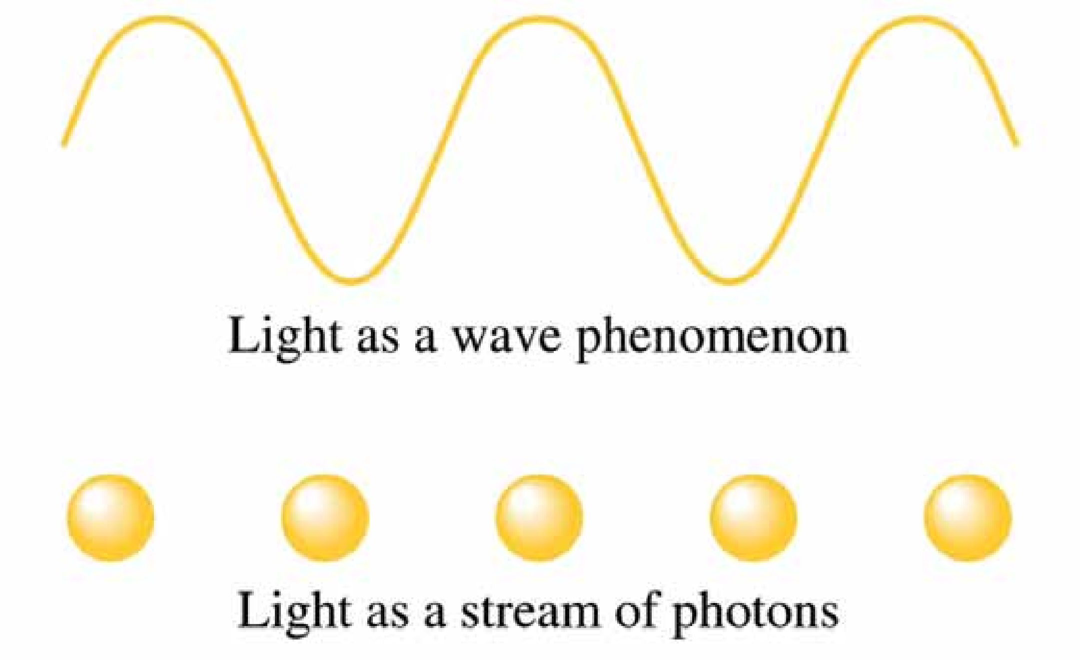
$$\Delta E_{\text{photon}} = \frac{hc}{\lambda}$$

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

- In 1922 American physicist Arthur Compton (1892-1962) performed experiments involving collisions of X rays and electrons that showed that photons do exhibit the apparent mass calculated from the preceding equation.

- The important conclusions from the work of Planck and Einstein as follows:
- Energy is quantized. It can occur only in discrete units called quanta.
- Electromagnetic radiation, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well.
- This phenomenon is sometimes referred to as the dual nature of light and is illustrated in Fig. 7.4.

Figure 7.4



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

- This question was raised in 1923 by a young French physicist named Louis de Broglie (1892-1987).

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

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

Sample Exercise 7.3

Calculations of Wavelength

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

Solution

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

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

since

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

Sample Exercise 7.3

For the electron,

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

For the ball,

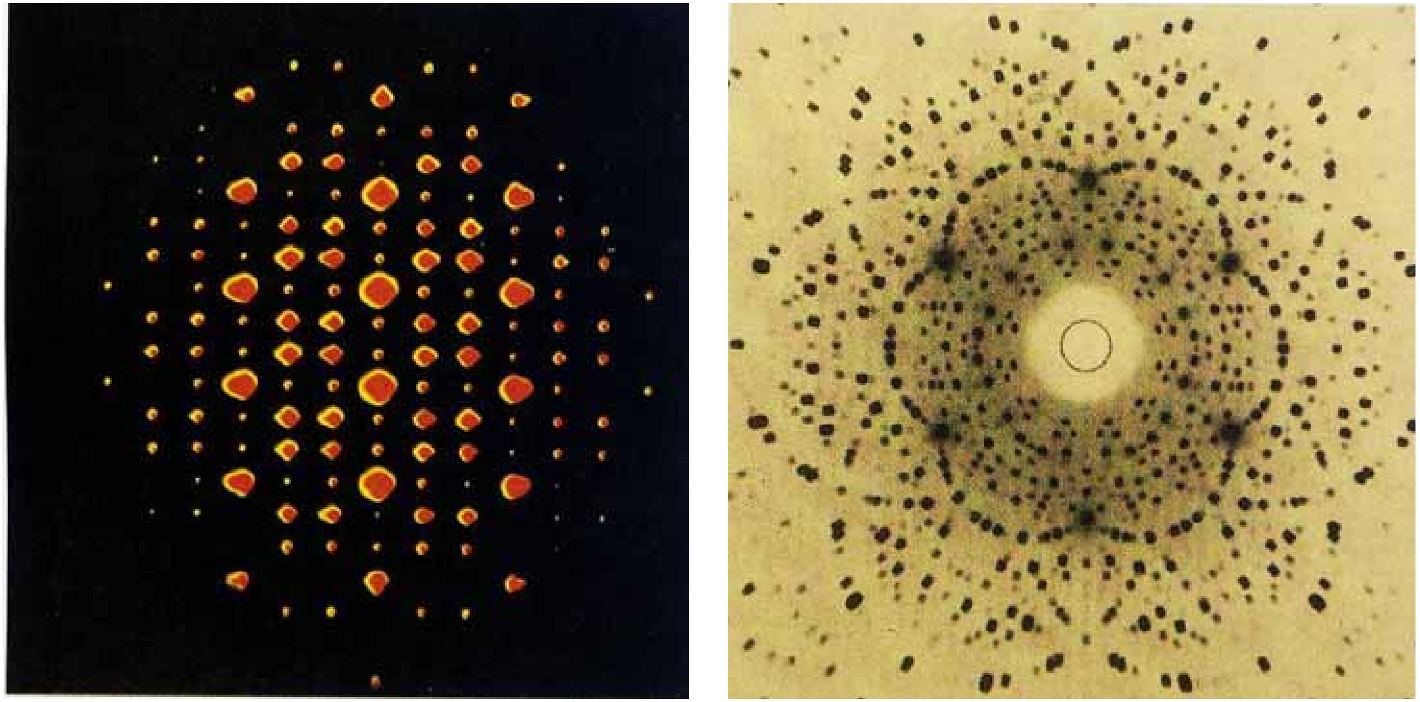
$$\lambda_b = \frac{6.626 \times 10^{-34} \dfrac{\cancel{\text{kg}} \cdot \cancel{\text{m}} \cdot \text{m}}{\cancel{\text{s}}}}{(0.10\ \cancel{\text{kg}})(35\ \cancel{\text{m}}/\cancel{\text{s}})} = 1.9 \times 10^{-34}\ \text{m}$$

See Exercises 7.41 though 7.44

- **Diffraction** results when light is scattered from a regular array of points or lines.
- When X rays are directed onto a crystal of sodium chloride, with its regular array of Na^+ and Cl^- ions, the scattered radiation produces a **diffraction pattern** of bright spots and dark areas on a photographic plate, as shown in Fig. 7.5(a).

- This occurs because the scattered light can interfere constructively (the peaks and troughs of the beams are in phase) to produce a bright spot [Fig. 7.5(b)] or destructively (the peaks and troughs are out of phase) to produce a dark area [Fig. 7.5(c)].

- A diffraction pattern can only be explained in terms of waves.
- Thus this phenomenon provides a test for the postulate that particles such as electrons have wavelengths.
- An experiment to test this idea was carried out in 1927 by C.J. Davisson and L.H. Germer at Bell Laboratories.



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

Figure 7.5

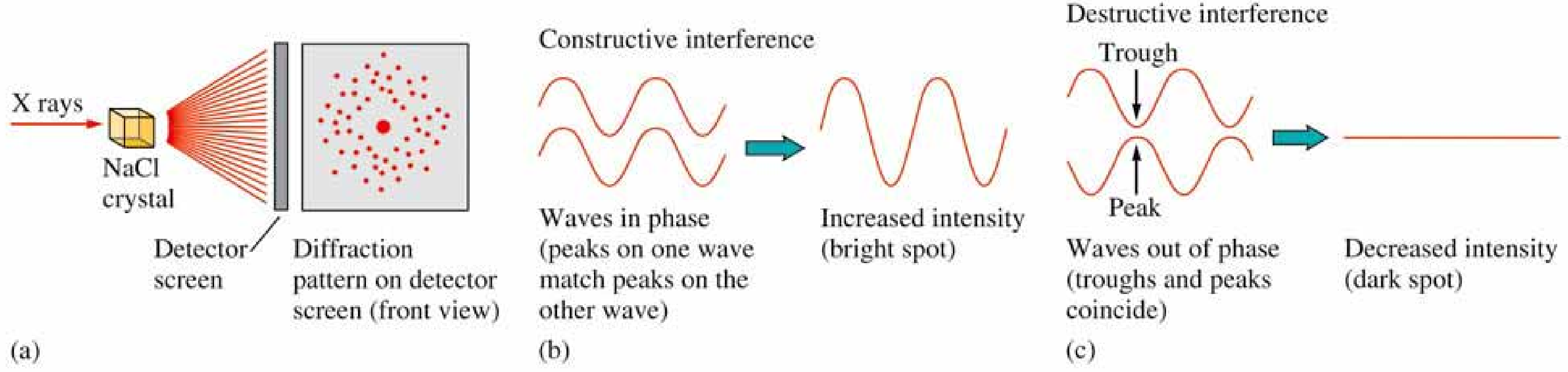

X rays
NaCl crystal
Detector screen
Diffraction pattern on detector screen (front view)
(a)
Constructive interference
Waves in phase (peaks on one wave match peaks on the other wave)
Increased intensity (bright spot)
(b)
Destructive interference
Trough
Peak
Waves out of phase (troughs and peaks coincide)
Decreased intensity (dark spot)
(c)

Figure 7.5

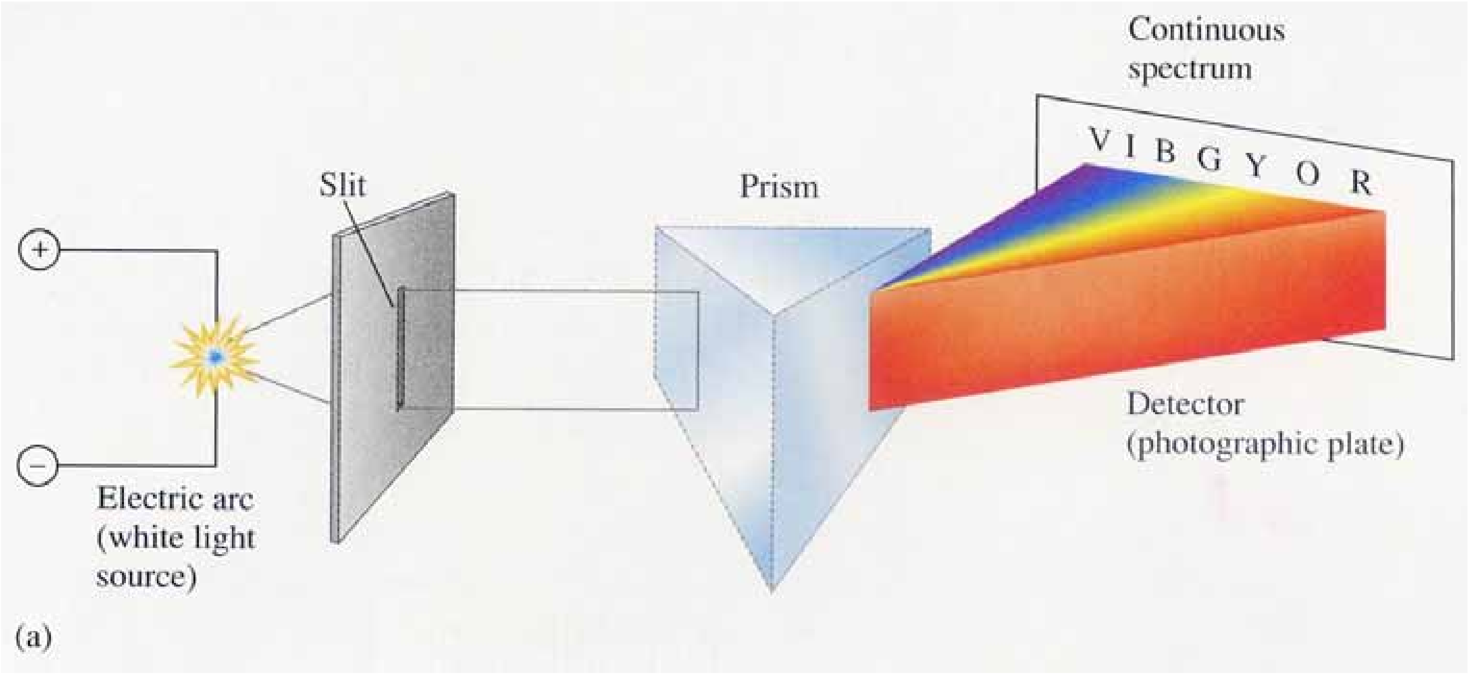
(a) Diffraction occurs when electromagnetic radiation is scattered from a regular array of objects, such as the ions in a crystal of sodium chloride. The large spot in the center is from the main incident beam of X-rays. (b) Bright spots in the diffraction pattern result from constructive interference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

7.3 The Atomic Spectrum of Hydrogen

- The resulting hydrogen atoms are excited; that is , they contain excess energy, which they release by emitting light of various wavelengths to produce what is called the emission spectrum of the hydrogen atom.
- To understand the significance of the hydrogen emission spectrum, we must first describe the **continuous spectrum** that results when white light is passed through a prism, as shown in Fig. 7.6(a).

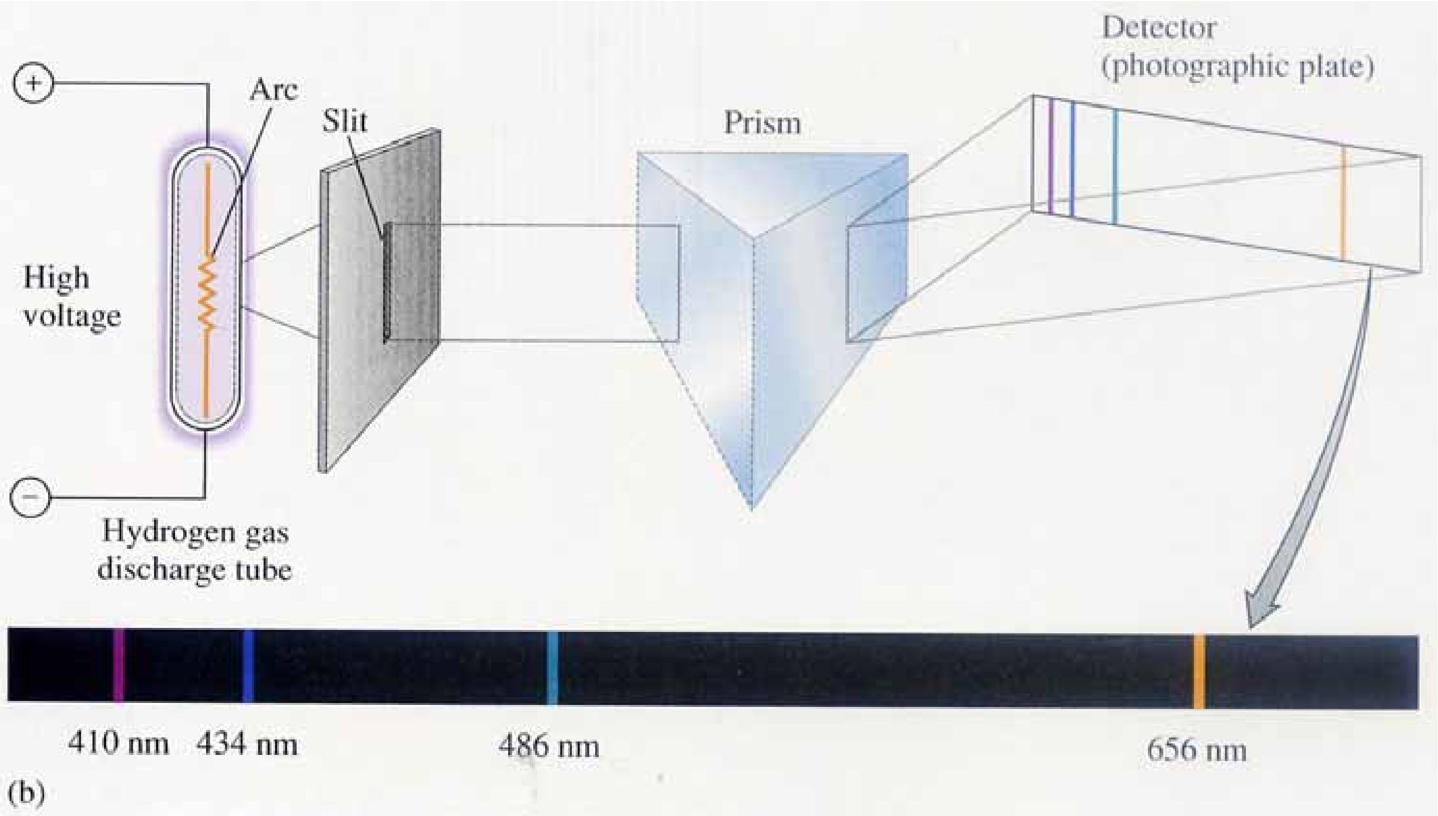
- This spectrum, like contains all the wavelengths of visible light.
- In contrast, when the hydrogen emission spectrum in the visible region is passed through a prism, as shown in Fig. 7.6(b), we see only a few lines, each of which corresponds to a discrete wavelength.
- The hydrogen emission spectrum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

Figure 7.6



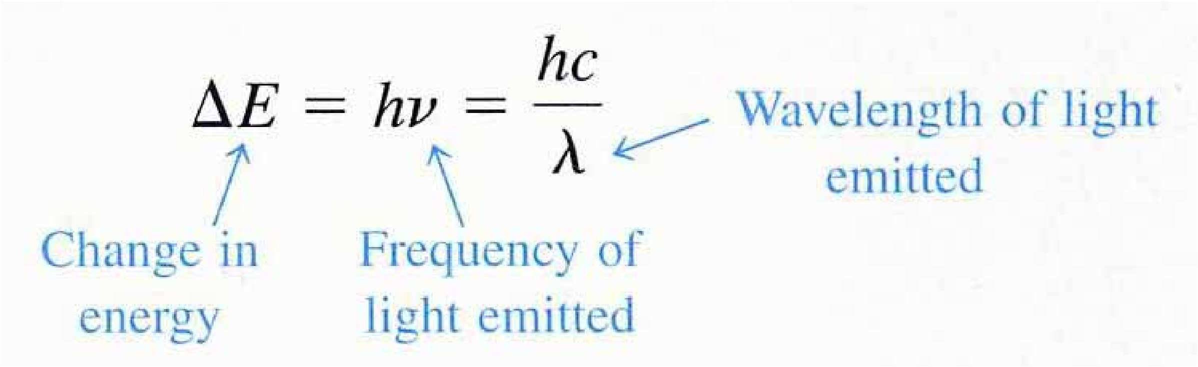
(a) A continuous spectrum containing all wavelengths of visible light (indicated by the initial letters of the colors of the rainbow)

Figure 7.6



(b) The hydrogen line spectrum contains only a few discrete wavelengths.

- What is the significance of the line spectrum of hydrogen?
- It indicates that *only certain energies are allowed for the electron in the hydrogen atom*.
- In other words, the energy of the electron in the hydrogen atom is *quantized.*
- Changes in energy between discrete energy levels in hydrogen will produce only certain wavelengths of emitted light, as shown in Fig. 7.7.



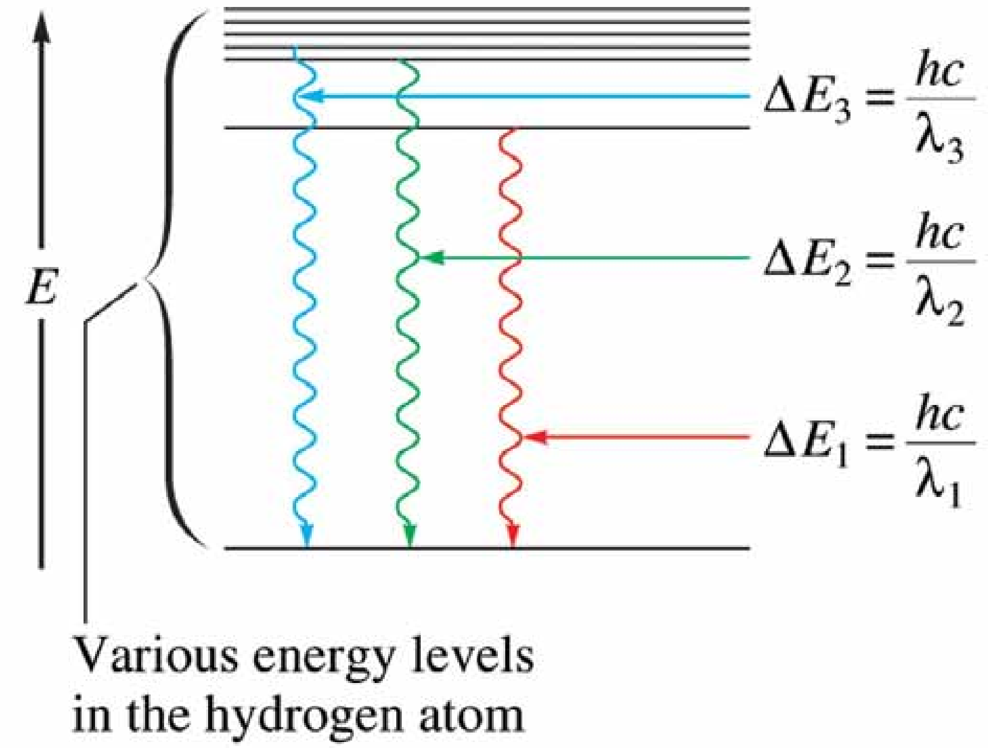
$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Change in energy

Frequency of light emitted

Wavelength of light emitted

Figure 7.7



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

7.4 The Bohr Model

- In 1913, a Danish physicist named Niels Bohr (1885-1962), aware of the experimental results we have just discussed, developed a **quantum model** for the hydrogen atom. Bohr proposed that the *electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits*.
- Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum. The model is represented pictorially in Fig. 7.8.

Figure 7.8

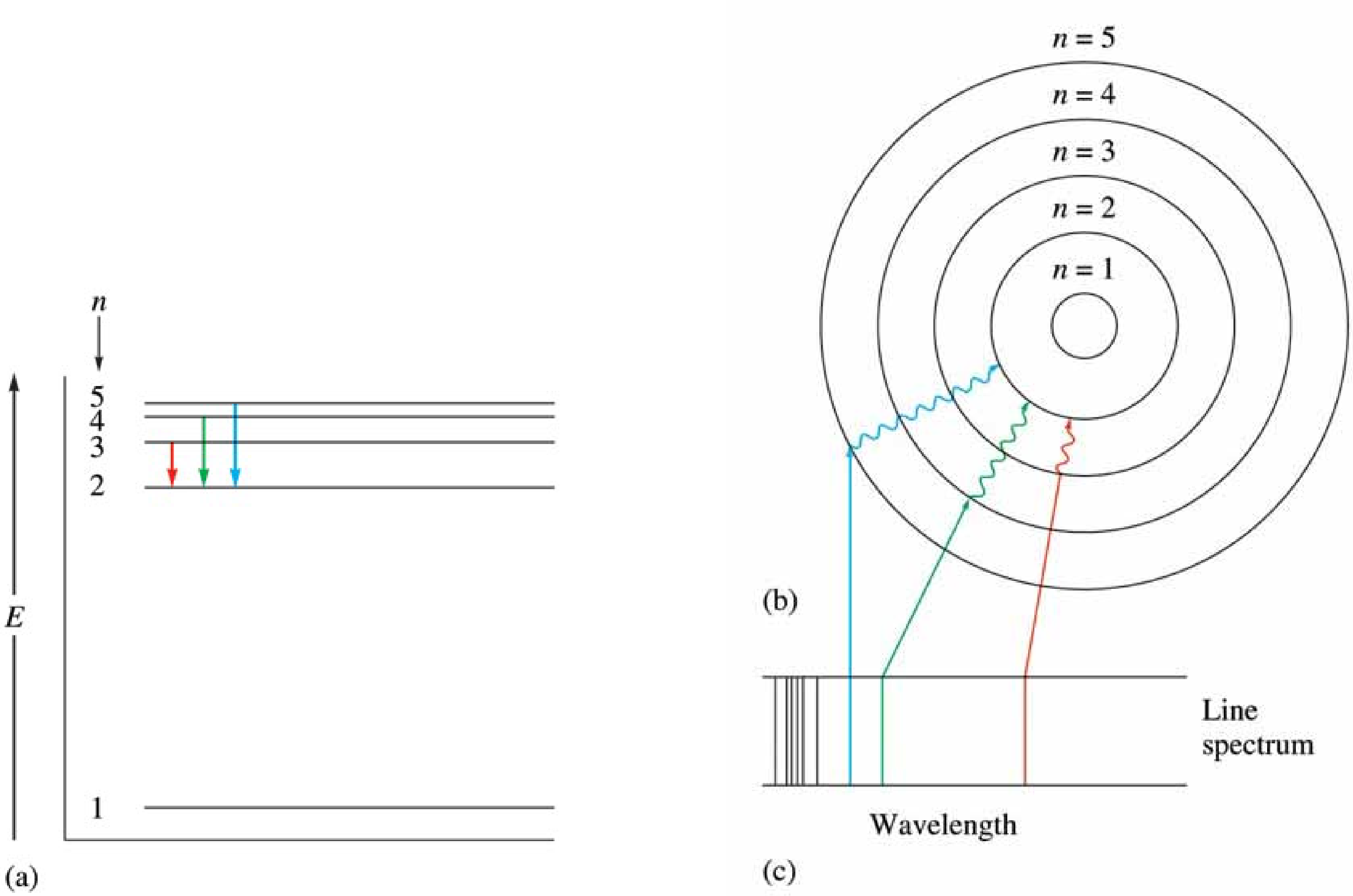


Figure 7.8

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

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

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

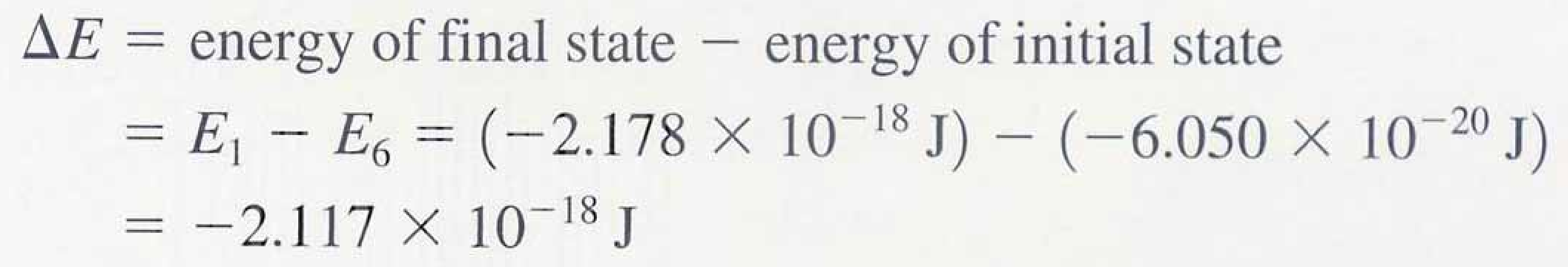
- in which n is an integer (the larger the value of n, the larger is the orbit radius) and *Z* is the nuclear charge.

- Equation (7.1) can be used to calculate the change in energy of an electron when the electron changes orbits. For example, suppose an electron in level n=6 of an excited hydrogen atom falls back to level n=1 as the hydrogen atom returns to its lowest possible energy state, its ground state.

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

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

- Note that for n=1 electron has a more negative energy than it does for n=6, which means that the electron is more tightly bound in the smallest allowed orbit.
- The change in energy ΔE when the electron falls from $n = 6$ to $n = 1$ is



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

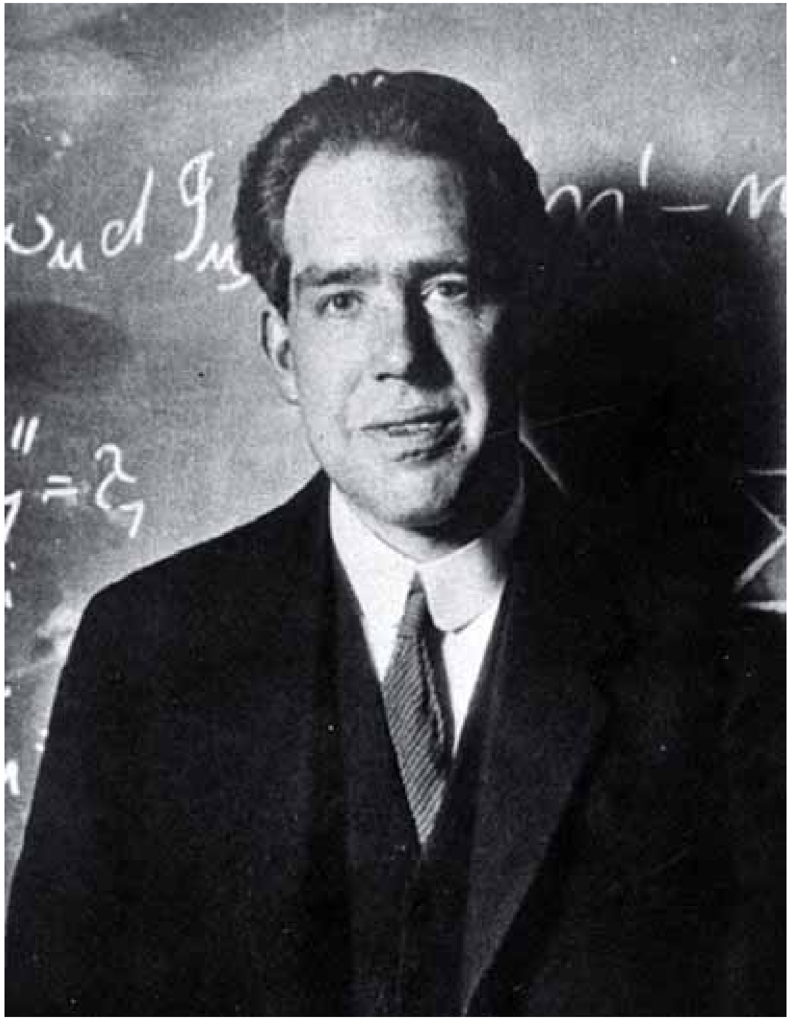
- The negative sign for the change in energy indicates that the atom has lost energy and is now in a more stable state.
- The wavelength of the emitted photon can be calculated from the equation

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

- Where ΔE represents the change in energy of the atom, which equals the energy of the emitted photon.

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

- Note that for this calculation the absolute value of ΔE is used.



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

Sample Exercise 7.4

Energy Quantization in Hydrogen

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

Solution

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

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

Sample Exercise 7.4

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

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

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

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\,\cancel{\mathrm{J}} \cdot \cancel{\mathrm{s}})(2.9979 \times 10^{8}\,\mathrm{m}/\cancel{\mathrm{s}})}{1.633 \times 10^{-18}\,\cancel{\mathrm{J}}}$$

$$= 1.216 \times 10^{-7}\,\mathrm{m}$$

See Exercises 7.45 and 7.46

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

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

Sample Exercise 7.5

Electron Energies

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

Solution

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

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

Sample Exercise 7.5

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

See Exercises 7.51 and 7.52

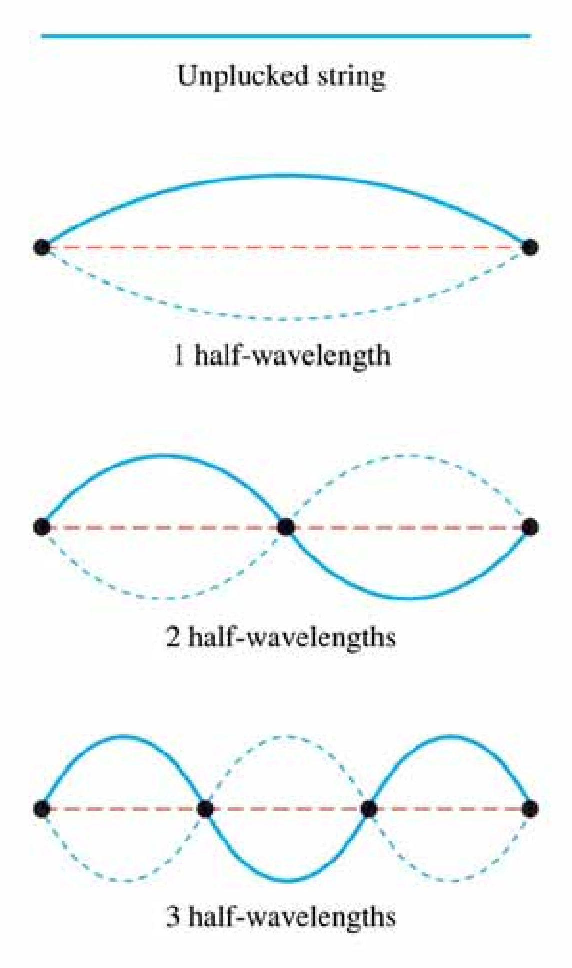
7.5 The Quantum Mechanical Model of the Atom

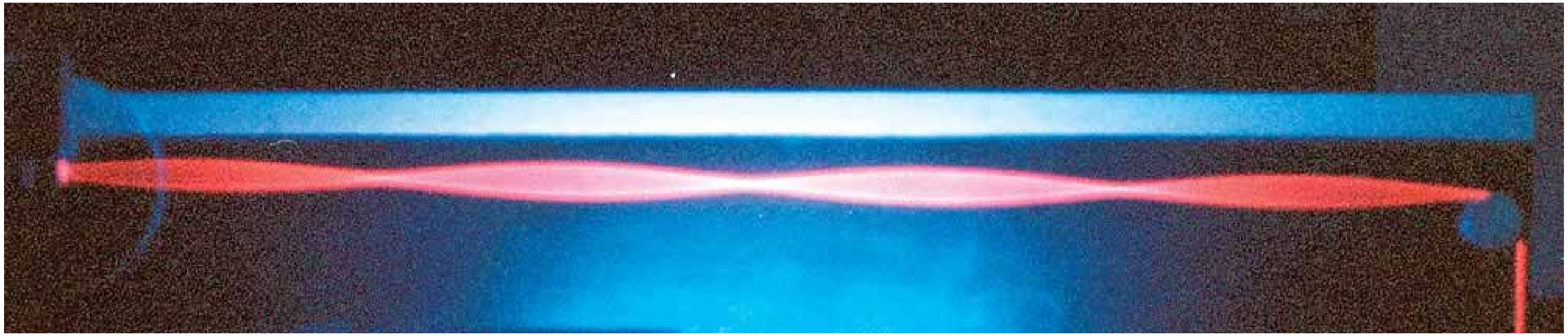
- By the mid-1920s it had become apparent that the Bohr model could not be made to work.
- Three physicists were at the forefront of this effort: Werner Heisenberg (1901-1976), Louis de Broglie (1892-1987), and Erwin Schrödinger (1887-1961).
- The approach they developed became known as *wave mechanics* or, more commonly, *quantum mechanics*.

- The most familiar example of standing waves occurs in association with musical instruments such as guitars or violins, where a string attached at both ends vibrates to produce a musical tone.
- The waves are described as “standing” because they are stationary; the waves do not travel along the length of the string.
- The motions of the string can be explained as a combination of simple waves of the type shown in Fig. 7.9.

Figure 7.9

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



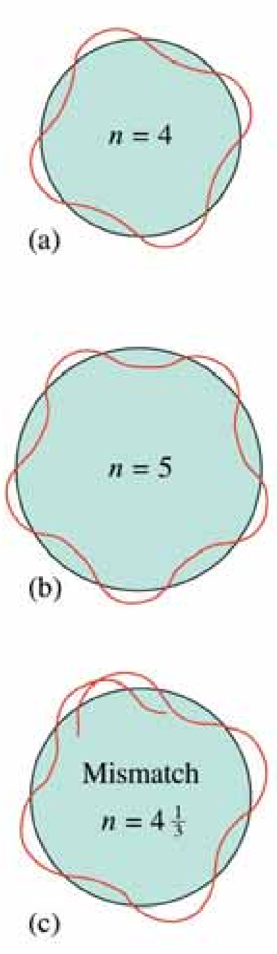


Wave-generating apparatus.

- A similar situation results when the electron in the hydrogen atom is imagined to be a standing wave. As shown in Fig. 7.10, only certain circular orbits have a circumference into which a whole number of wavelengths of the standing electron wave will “fit.”
- It is important to recognize that Schrödinger could not be sure that this idea would work.
- The physical principles for describing standing waves were well known in 1925 when Schrödinger decided to treat the electron in this way.

Figure 7.10

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



- Schrödinger's equation is

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

- where ψ, called the **wave function**, is a function of the coordinates (x, y, and z) of the electron's position in three-dimensional space and $\hat{H}$ represents a set of mathematical instructions called an *operator*.
- When this equation is analyzed, many solutions are found. Each solution consists of a wave function ψ that is characterized by a particular value of E.

- A specific wave function is often called an orbital.
- To illustrate the most important ideas of the **quantum (wave) mechanical model** of the atom, we will first concentrate on the wave function corresponding to the lowest energy for the hydrogen atom.
- This wave function is called the 1*s* orbital.
- An orbital is *not* a Bohr orbit. The electron in the hydrogen 1*s* orbital is not moving around the nucleus in a circular orbit.

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

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

- This is a statement of the **Heisenberg uncertainty principle**.
- Stated mathematically, the uncertainty principle is

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

- where Δx is the uncertainty in a particle’s position, $\Delta(m\upsilon)$ is the uncertainty in a particle’s momentum, and h is Planck’s constant. Thus the minimum uncertainty in the product $\Delta \cdot \Delta(m\upsilon)$ is $h/4\pi$.

The Physical Meaning of a Wave Function

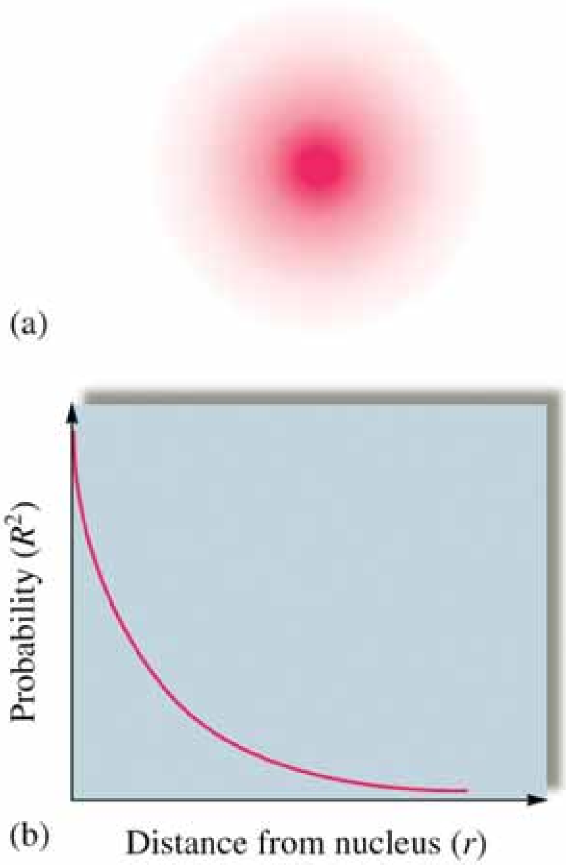
- *The square of the function indicates the probability of finding an electron near a particular point in space.*
- Suppose we have two positions in space, one defined by the coordinates x_1, y_1, and z_1 and the other by the coordinates x_2, y_2, and z_2.
- The relative probability of finding the electron at positions 1 and 2 is given by substituting the values of x, y, and z for the two positions into the wave function, squaring the function value, and computing the following ratio:

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

- The quotient N_1/N_2 is the ratio of the probabilities of finding the electron at positions 1 and 2.
- The square of the wave function is most conveniently represented as a **probability distribution**, in which the intensity of color is used to indicate the probability value near a given point in space. The probability distribution for the hydrogen 1s wave function (orbital) is shown in Fig. 7.11(a).

- This diagram is also known as an *electron density map*; *electron density and electron probability* mean the same thing.
- Another way of representing the electron probability distribution for the 1s wave function is to calculate the probability at points along a line drawn outward in any direction from the nucleus. The result is shown in Fig. 7.11(b).

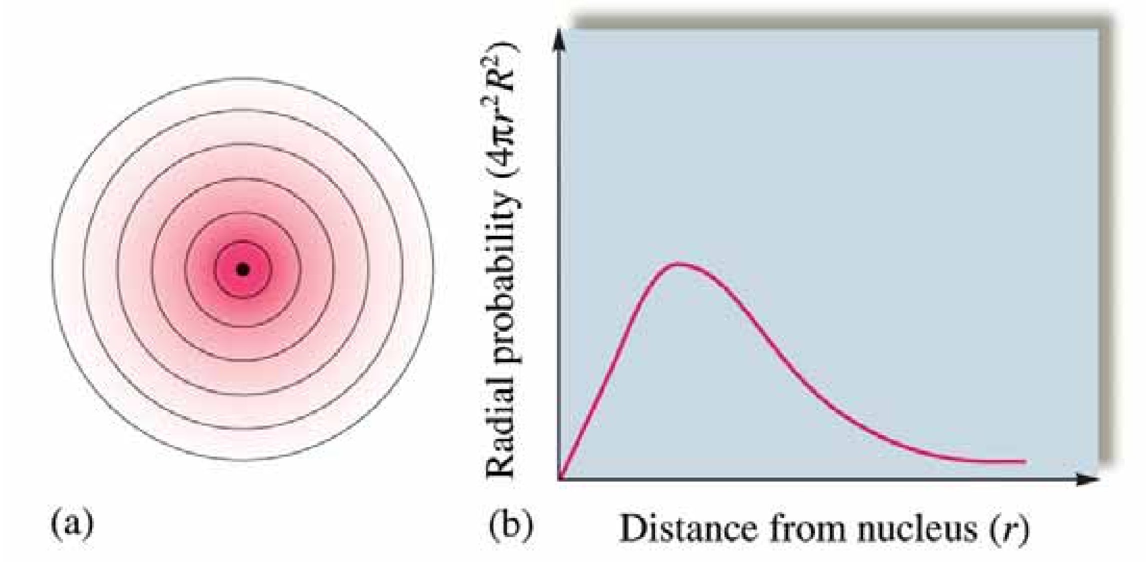
Figure 7.11



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

- Imagine that the space around the hydrogen nucleus is made up of a series of thin spherical shells (rather like layers in an onion), as shown in Fig. 7.12(a).
- When the total probability of finding the electron in each spherical shell is plotted versus the distance from the nucleus, the plot in Fig. 7.12(b) is obtained.
- This graph is called the **radial probability distribution**.

Figure 7.12



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

- One more characteristic of the hydrogen 1s orbital that we must consider is its size. As we can see from Fig. 7.11, the size of this orbital cannot be defined precisely, since the probability never becomes zero.
- So, in fact, the hydrogen 1s orbital has no distinct size.
- *The definition most often used by chemists to describe the size of the hydrogen 1s orbital is the radius of the sphere that encloses* 90% *of the total electron probability*.

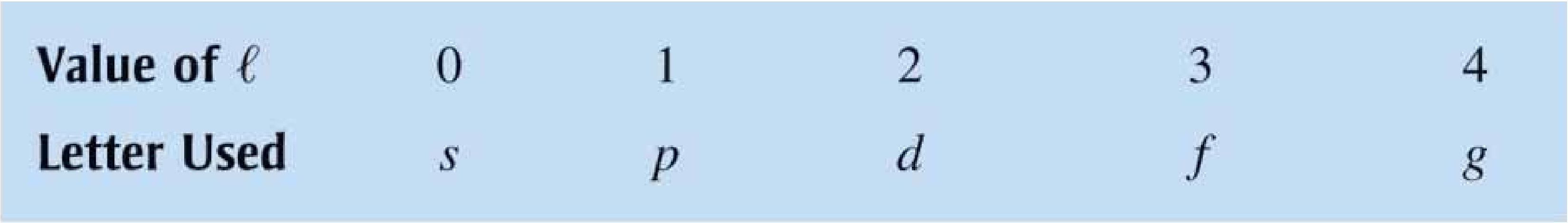
7.6 Quantum Numbers

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

- The **angular momentum quantum number** (**l**) has integral values from 0 to n-1 for each value of n. This quantum number is related to the shape of atomic orbitals. The value of l for a particular orbital is commonly assigned a letter: **l** = 0 is called *s*; **l** = 1 is called *p*; **l** = 2 is called *d*; **l** = 3 is called *f*. This system arises from early spectral studies and is summarized in Table 7.1.

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

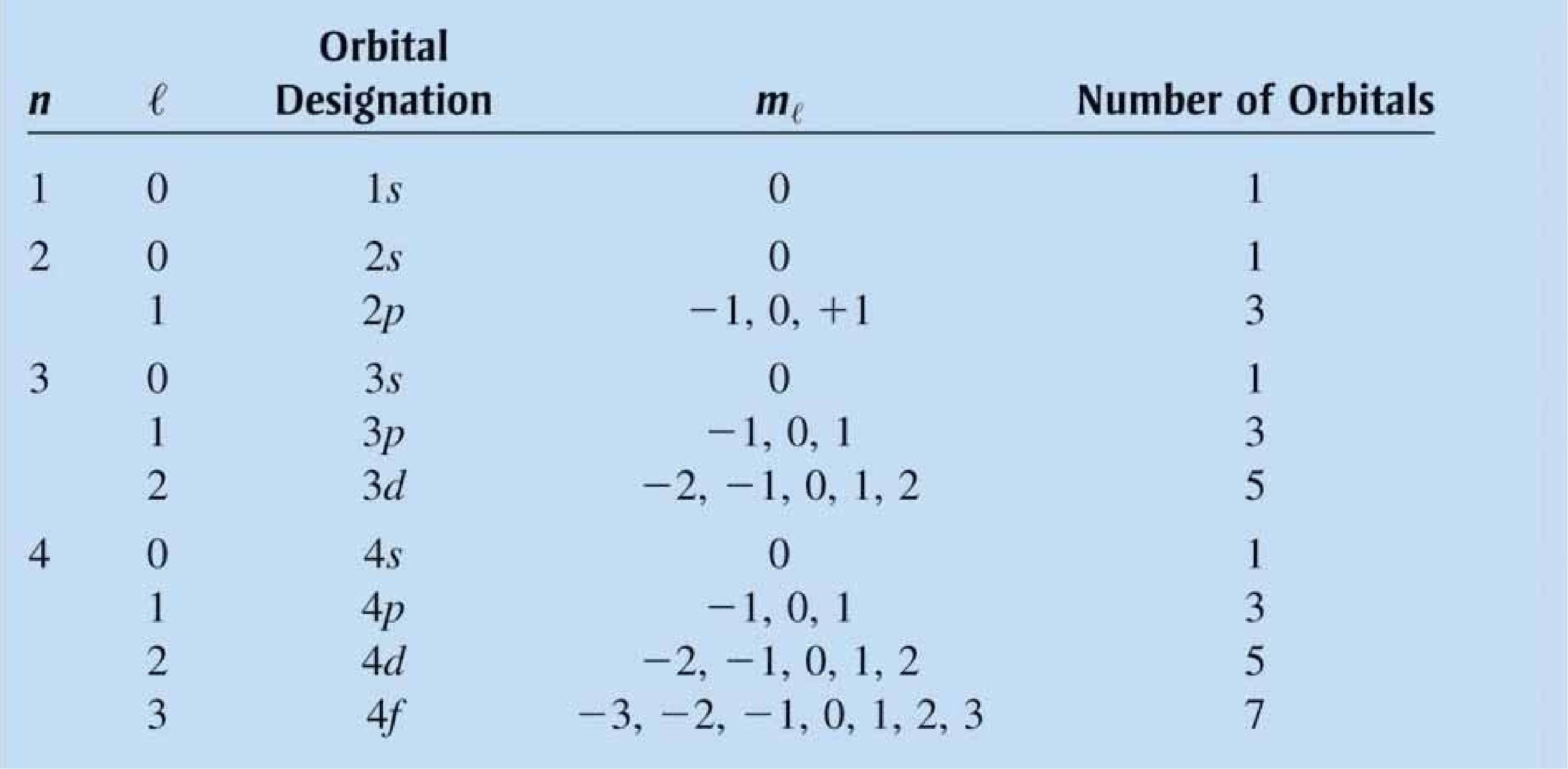
TABLE 7.1 The Angular Momentum Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals



Value of ℓ	0	1	2	3	4
Letter Used	*s*	*p*	*d*	*f*	*g*

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

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



n	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1*s*	0	1
2	0	2*s*	0	1
	1	2*p*	−1, 0, +1	3
3	0	3*s*	0	1
	1	3*p*	−1, 0, 1	3
	2	3*d*	−2, −1, 0, 1, 2	5
4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

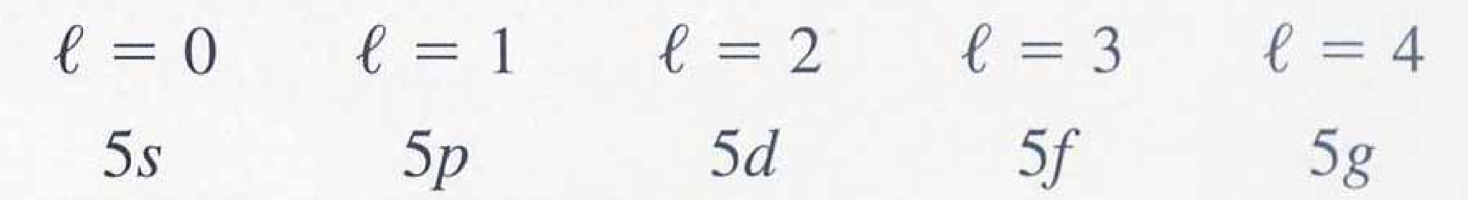
Sample Exercise 7.6

Electron Subshells

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

Solution

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



$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
5*s*	5*p*	5*d*	5*f*	5*g*

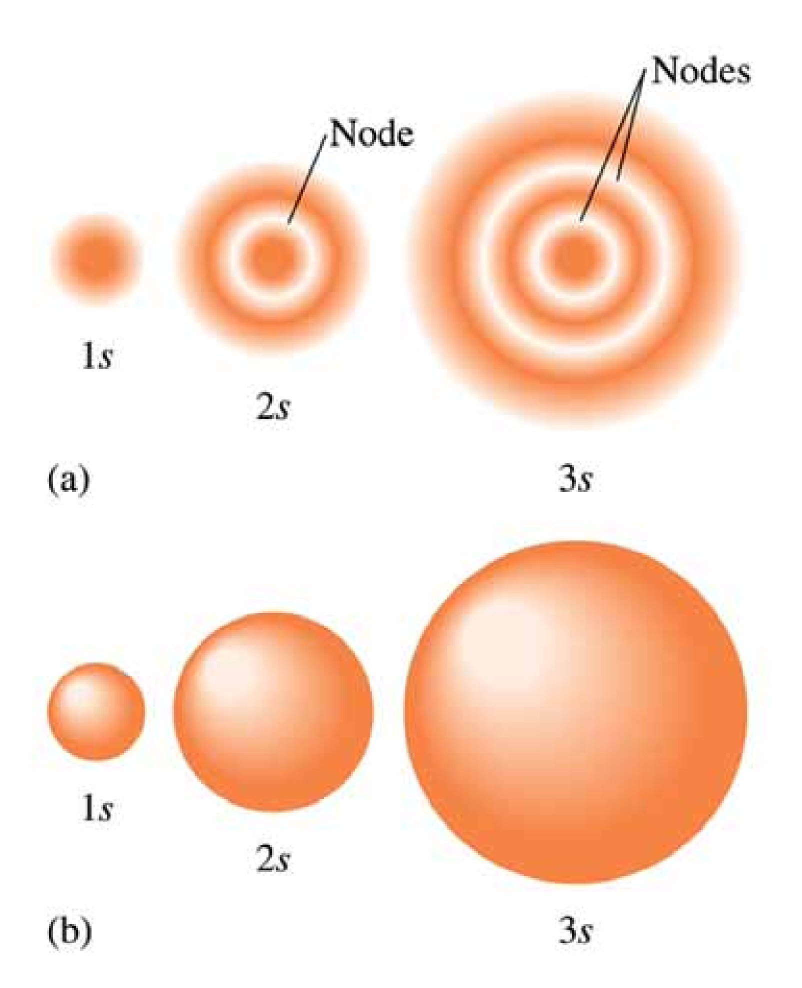
See Exercises 7.57 through 7.59

7.7 Orbital Shapes and Energies

- These two types of representations for the hydrogen 1*s*, 2*s*, and 3*s* orbitals are shown in Fig. 7.13.
- Note the characteristic spherical shape of each of the s orbitals.
- Note also that the 2*s* and 3*s* orbitals contain areas of high probability separated by areas of zero probability. These latter areas are called **nodal surfaces**, or simply **nodes**.

Figure 7.13

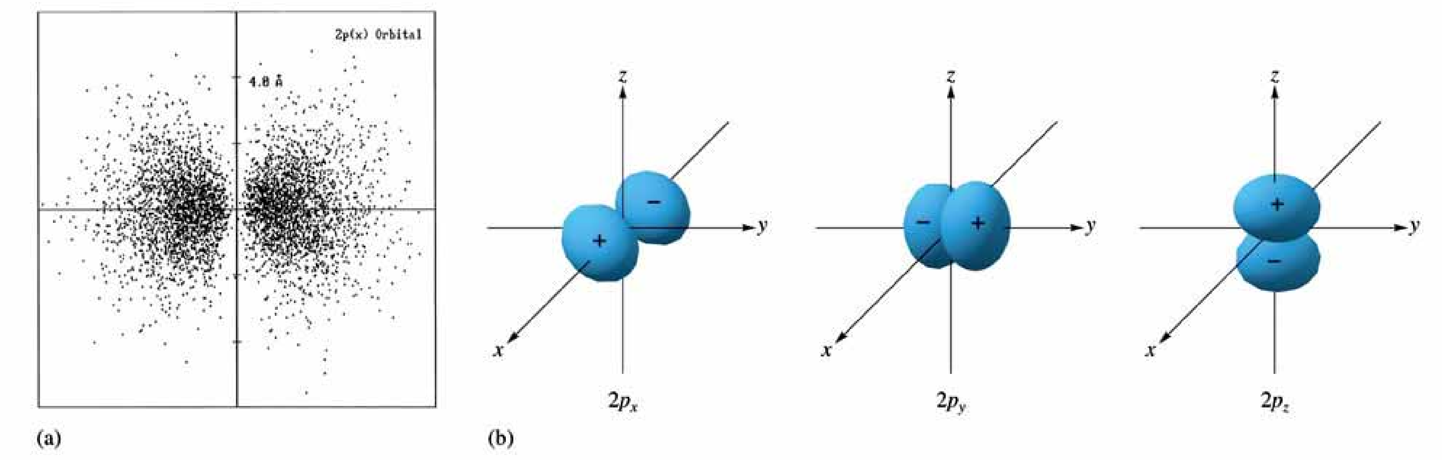
Two representations of the hydrogen 1s, 2s, and 3s orbitals. (a) The electron probability distribution. (b) The surface that contains 90% of the total electron probability (the size of the orbital, by definition).



- The two types of representations for the 2*p* orbitals (there are no 1*p* orbitals) are shown in Fig. 7.14.
- Note that the *p* orbitals are not spherical like *s* orbitals but have two *lobes* separated by a node at the nucleus.
- At this point it is useful to remember that mathematical functions have signs.
- This behavior is indicated in Fig. 7.14(b) by the positive and negative signs inside their boundary surfaces.

- It is important to understand that these are mathematical signs, not charges.
- Just as a sine wave has alternating positive and negative phases, so too p orbitals have positive and negative phases.
- The phases of the p_x, p_y, and p_z orbitals are indicated in Fig. 7.14(b).

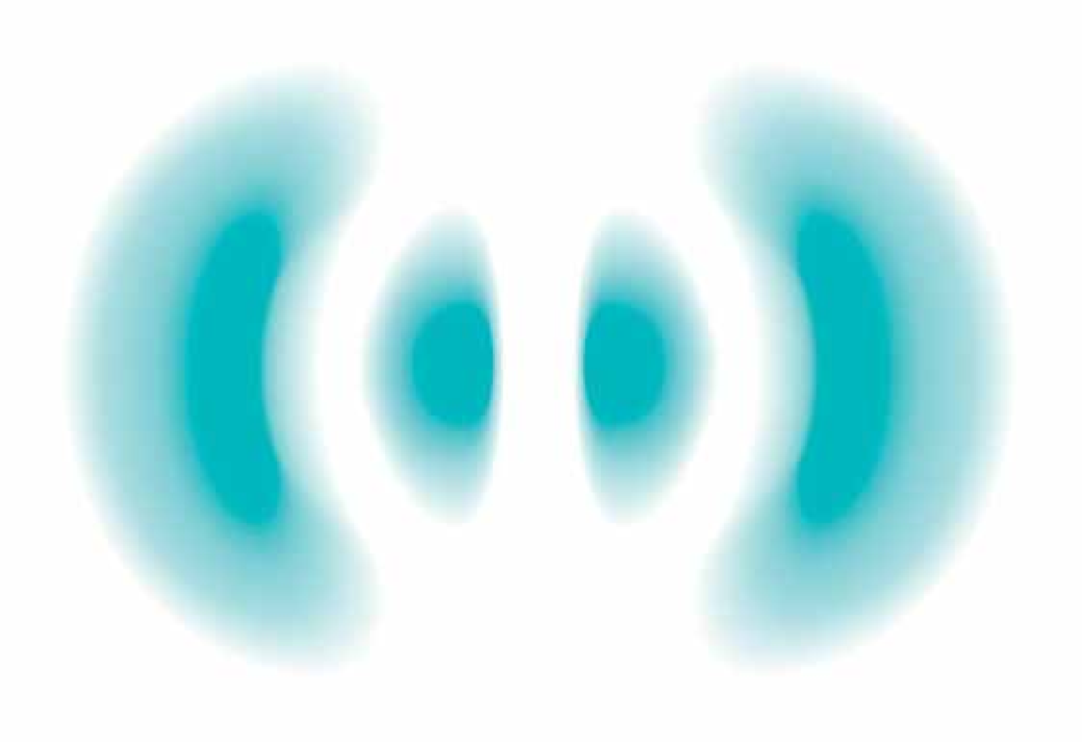
Figure 7.14



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

- The $3p$ orbitals have a more complex probability distribution than that of the $2p$ orbitals (see Fig. 7.15),
- The d orbitals ($\mathbf{l} = 2$) first occur in level $n = 3$. The five $3d$ orbitals have the shapes shown in Fig. 7.16.
- The d orbitals have two different fundamental shapes.
- The f orbitals first occur in level $n = 4$.
- Figure 7.17 shows representations of the $4f$ orbitals ($\mathbf{l} = 3$) along with their designations.

Figure 7.15



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

Figure 7.16

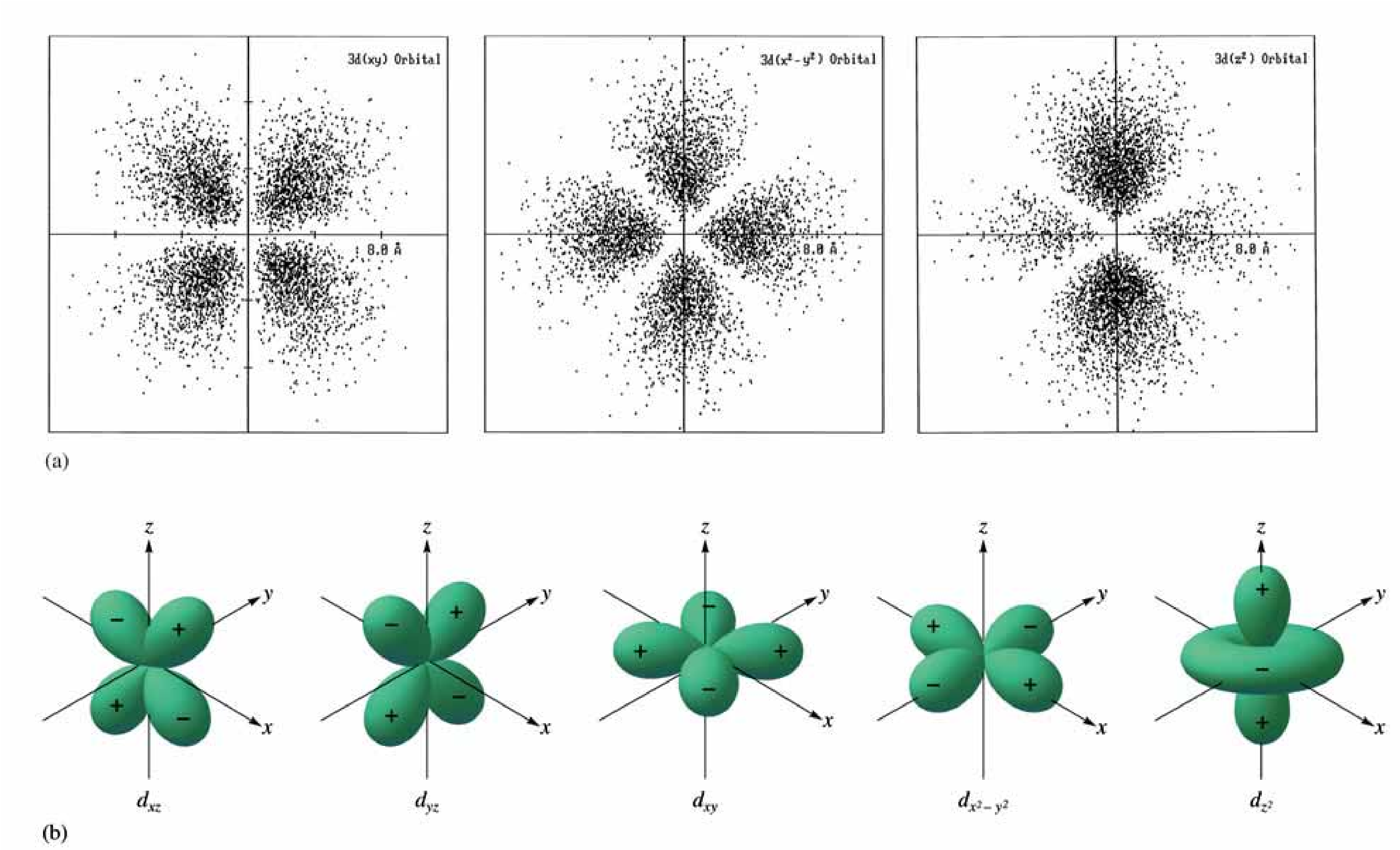
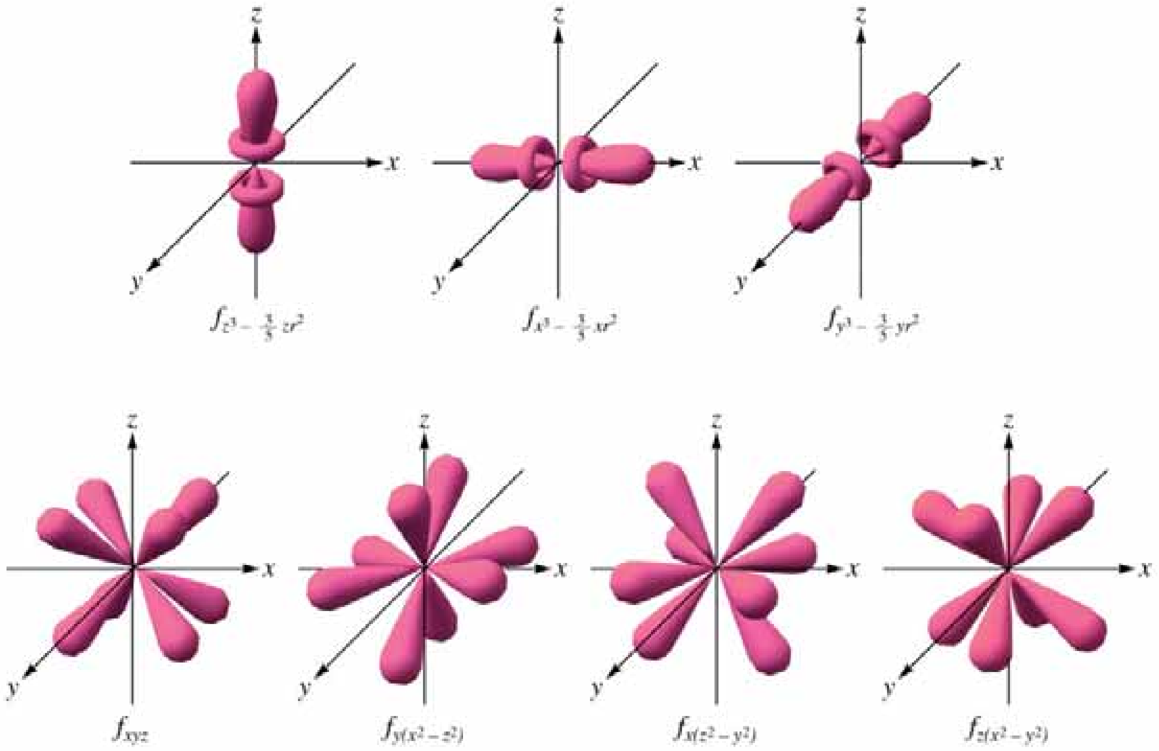

3d(xy) Orbital
8.0 Å
3d(x²-y²) Orbital
8.0 Å
3d(z²) Orbital
8.0 Å
(a)
z
y
x
−
+
+
−
d_{xz}
z
y
x
−
+
+
−
d_{yz}
z
y
x
−
+
+
−
d_{xy}
z
y
x
+
−
−
+
$d_{x^2-y^2}$
z
y
x
+
−
+
d_{z^2}
(b)

Figure 7.16

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

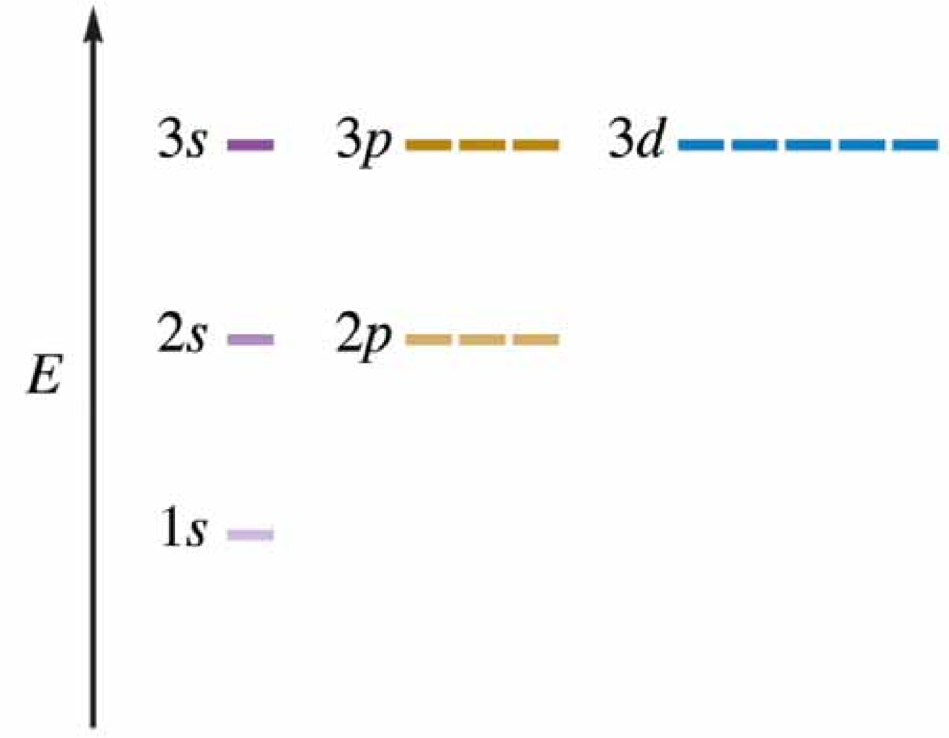
Figure 7.17



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

- Thus all orbitals with the same value of n have the same energy-they are said to be **degenerate**.
- This is shown in Fig. 7.18, where the energies for the orbitals in the first three quantum levels for hydrogen are shown.
- In the lowest energy state, the *ground state*, the electron resides in the 1s orbital. If energy is put into the atom, the electron can be transferred to a higher-energy orbital, producing an *excited state*.

Figure 7.18



Orbital energy levels for the hydrogen atom.

A Summary of the Hydrogen Atom

- In the quantum (wave) mechanical model, the electron is viewed as a standing wave. This representation leads to a series of wave functions (orbitals) that describe the possible energies and spatial distributions available to the electron.
- In agreement with the Heisenberg uncertainty principle, the model cannot specify the detailed electron motions. Instead, the square of the wave function represents the probability distribution of the electron in that orbital. This allows us to picture orbitals in terms of probability distributions, or electron density maps.
- The size of an orbital is arbitrarily defined as the surface that contains 90% of the total electron probability.

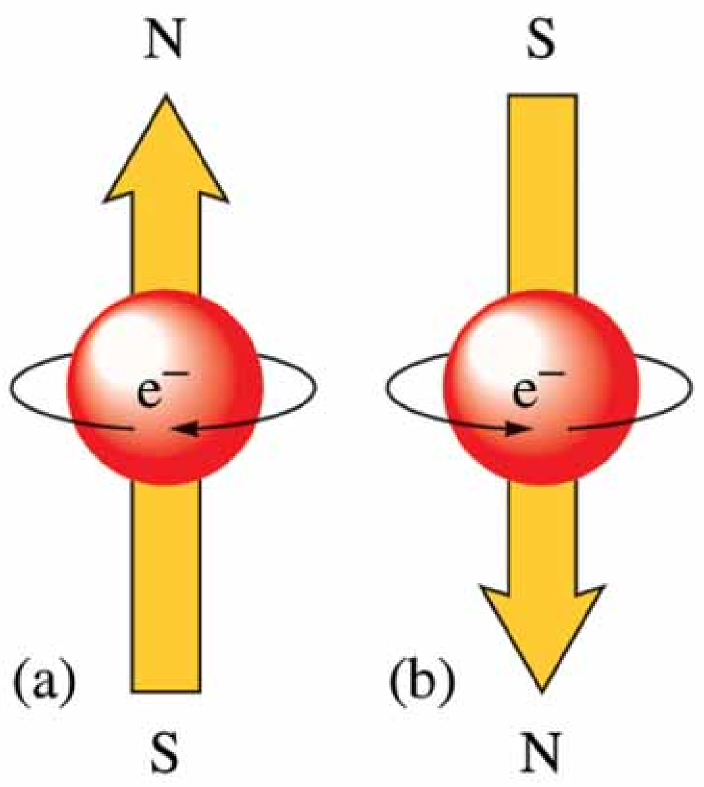
- The hydrogen atom has many types of orbitals. In the ground state, the single electron resides in the 1s orbital. The electron can be excited to higher-energy orbitals if energy is put into the atom.

7.8 Electron Spin and the Pauli Principle

- The concept of **electron spin** was developed by Samuel Goudsmit and George Uhlenbeck.
- A spinning charge produces a magnetic moment, the electron could have two spin states, thus producing the two oppositely directed magnetic moments (see Fig. 7.19).
- The new quantum number adopted to describe this phenomenon, called the **electron spin quantum number** (m_s), can have only one of two values, +1/2 and –1/2.

Figure 7.19

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



- Austrian physicist Wolfgang Pauli (1900-1958): *In a given atom on two electrons can have the same set of four quantum numbers* (n, $\mathbf{l}$, $m_{\mathbf{l}}$, and m_s).
- This is called the **Pauli exclusion principle**.
- Since electrons in the same orbital have the same values of n, $\mathbf{l}$ and $m_{\mathbf{l}}$, this postulate says that they must have different values of m_s.

- Then, since only two values of m_s are allowed, *an orbital can hold only two electrons, and they must have opposite spins*.
- This principle will have important consequences as we use the atomic model to account for the electron arrangements of the atoms in the periodic table.

7.9 Polyelectronic Atoms

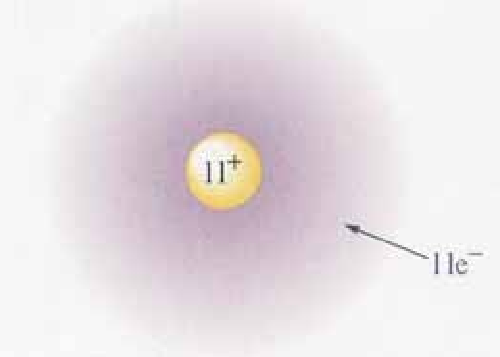
- **polyelectronic atoms** : atoms with more than one electron, let’s consider helium, which has two protons in its nucleus and two electrons:

- Three energy contributions must be considered in the description of the helium atom:

(1) the kinetic energy of the electrons as they move around the nucleus, (2) the potential energy of attraction between the nucleus and the electrons, and (3) the potential energy of repulsion between the two electrons.

- *Electron correlation problem*: Since the electron pathways are unknown, the electron repulsions cannot be calculated exactly.
- To treat these systems using the quantum mechanical model, we must make approximations.
- Most commonly, the approximation used is to treat each electron as if it were moving in a *field of charge that is the net result of the nuclear attraction and the average repulsions of all the other electrons*.

- The sodium atom has 11 electrons:



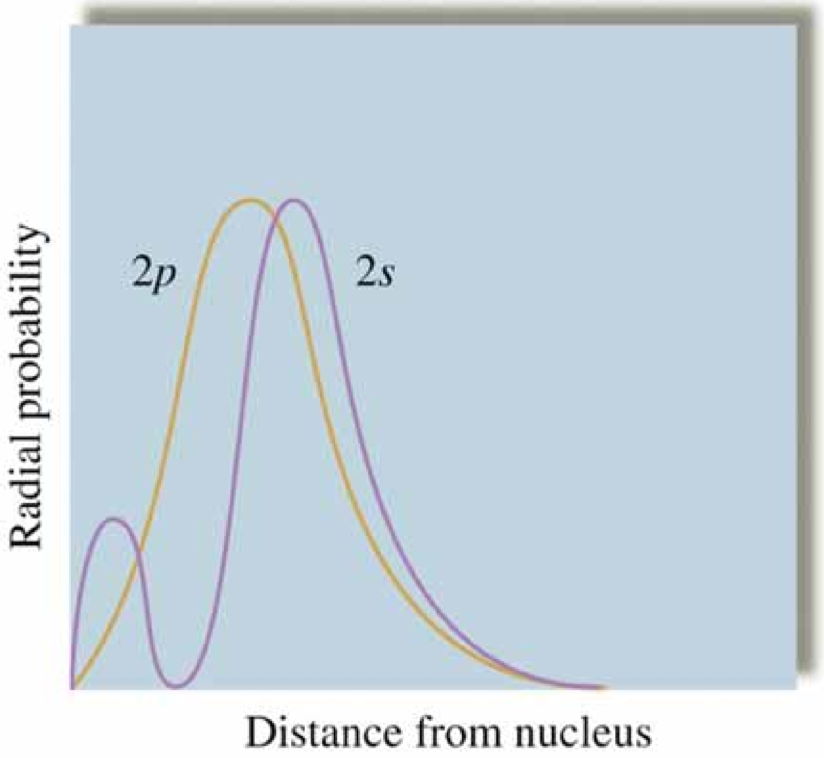
- The electron clearly is attracted to the highly charges nucleus. The electron also feels the repulsions caused by the other 10 electrons.
- The net effect is that the electron is not bound nearly as tightly to the nucleus as it would be if the other electrons were not present.

- The electron is *screened* or *shielded* from the nuclear charge by the repulsions of the other electrons.
- This picture of polyelectronic atoms leads to *hydrogenlike orbitals* for these atoms.
- One especially important difference between polyelectronic atoms and the hydrogen atom is that for hydrogen all the orbitals in a given principal quantum level have the same energy (they are said to be *degenerate*).

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

- In other words, when electrons are placed in a particular quantum level, they “prefer” the orbitals in the other s, p, d, and then f.
- 2s orbital has a lower energy than the 2*p* orbital in a polyelectronic atom by looking at the probability profiles of these orbitals (see Fig. 7.20).
- Notice that the 2*p* orbital has its maximum probability closer to the nucleus than for the 2*s*.

Figure 7.20



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

- This *penetration effect* causes an electron in a 2*s* orbital to be attracted to the nucleus more strongly than an electron in a 2*p* orbital.
- That is, the 2*s* orbital is lower in energy than the 2*p* orbitals in a polyelectronic atom.
- The same thing happens in the other principal quantum levels as well.
- Figure 7.21 shows the radial probability profiles for the 3*s*, 3*p*, and 3*d* orbitals. Note again the hump in the 3*s* profile very near the nucleus.

Figure 7.21

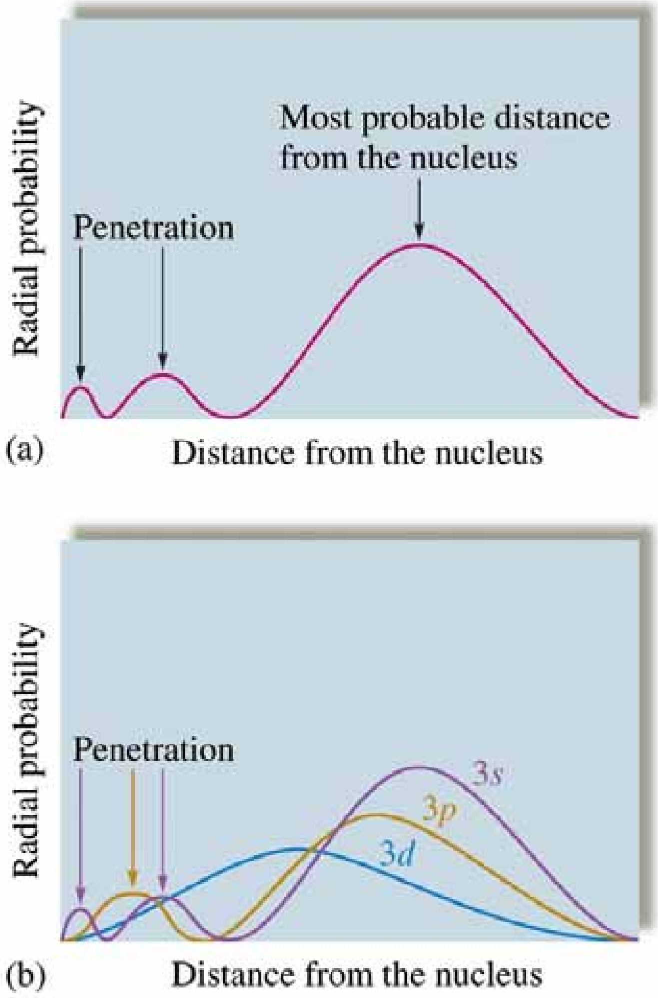

Radial probability
Most probable distance from the nucleus
Penetration
(a)
Distance from the nucleus
Radial probability
Penetration
3s
3p
3d
(b)
Distance from the nucleus

Figure 7.21

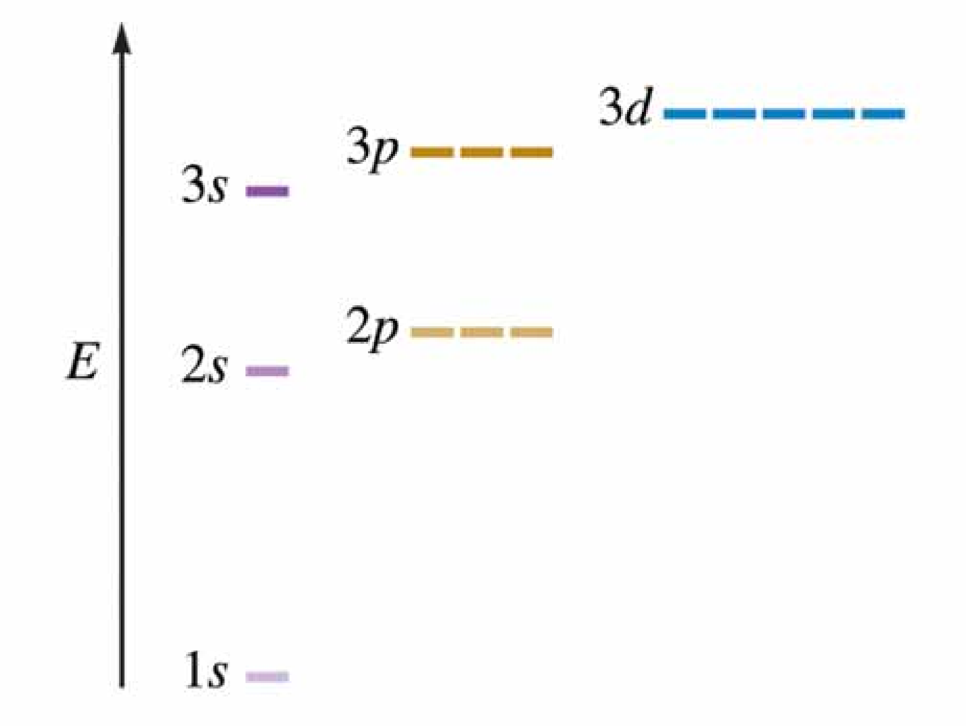
(a) The radial probability distribution for an electron in a 3*s* orbital. Although a 3*s* electron is mostly found far from the nucleus, there is a small but significant probability (shown by the arrows) of its being found close to the nucleus. The 3*s* electron penetrates the shield of inner electrons.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

- The relative energies of the orbitals for $n = 3$ are

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

- A summary diagram of the orders of the orbital energies for polyelectronic atoms is represented in Fig. 7.22.

Figure 7.22



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

7.10 The History of the Periodic Table

- The modern periodic table contains a tremendous amount of useful information.
- The periodic table was originally constructed to represent the patterns observed in the chemical properties of the elements.
- The first chemist to recognize patterns was Johann Dobereiner (1780-1849), who found several groups of three elements that have similar properties, for example, chlorine, bromine, and iodine.

- The next notable attempt was made by the English chemist John Newlands, who in 1864 suggested that elements should be arranged in octaves, based on the idea that certain properties seemed to repeat for every eighth element in a way similar to the musical scale, which repeats for every eighth tone.
- The present form of the periodic table was conceived independently by two chemists: the German Julius Lothar Meyer (1830-1895) and Dmitri Ivanovich Mendeleev (1834-1907), a Russian (Fig. 7.23).

Figure 7.23

Figure 7.23

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

Figure 7.23

chemistry, he eventually arranged the elements in the form of the periodic table.

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

- In 1872 when Mendeleev first published his table (see Fig. 7.24), the elements gallium, scandium, and germanium were unknown.
- The data for germanium (which Mendeleev called “ekasilicon”) are shown in Table 7.3.
- Using his table, Mendeleev also was able to correct several values for atomic masses.
- The original atomic mass of 76 for indium was bases on the assumption that indium oxide had the formula InO.

Figure 7.24

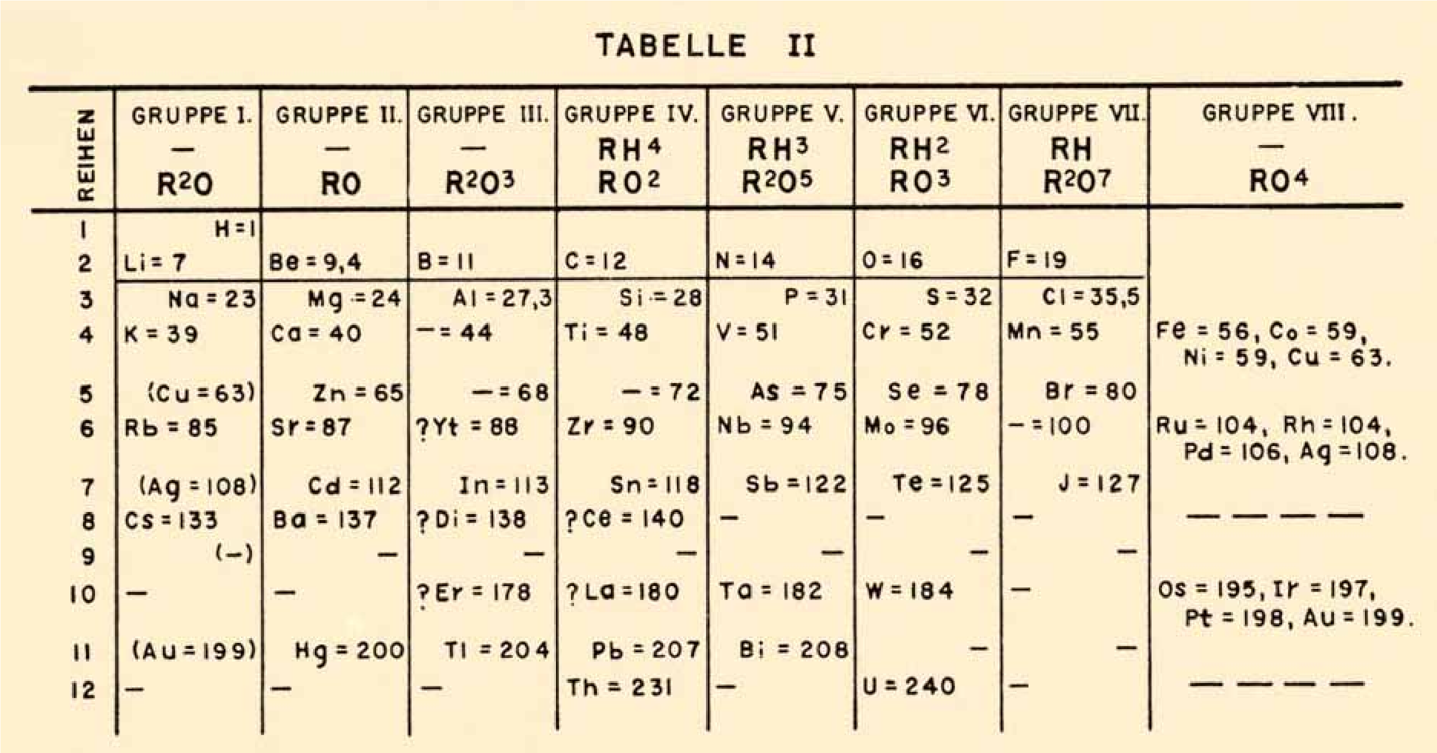
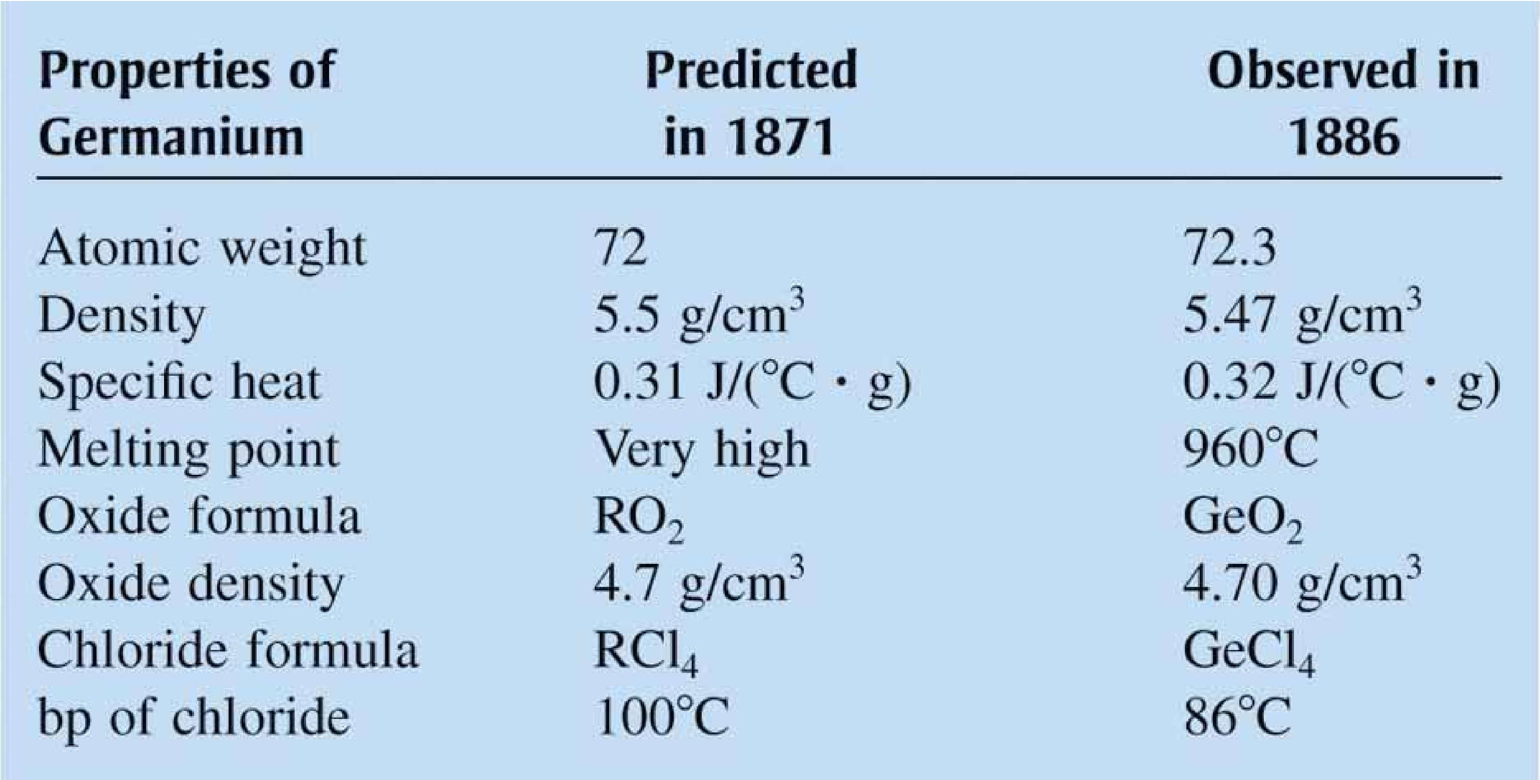


TABELLE II

REIHEN	GRUPPE I. — R^2O	GRUPPE II. — RO	GRUPPE III. — R^2O^3	GRUPPE IV. RH^4 RO^2	GRUPPE V. RH^3 R^2O^5	GRUPPE VI. RH^2 RO^3	GRUPPE VII. RH R^2O^7	GRUPPE VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

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

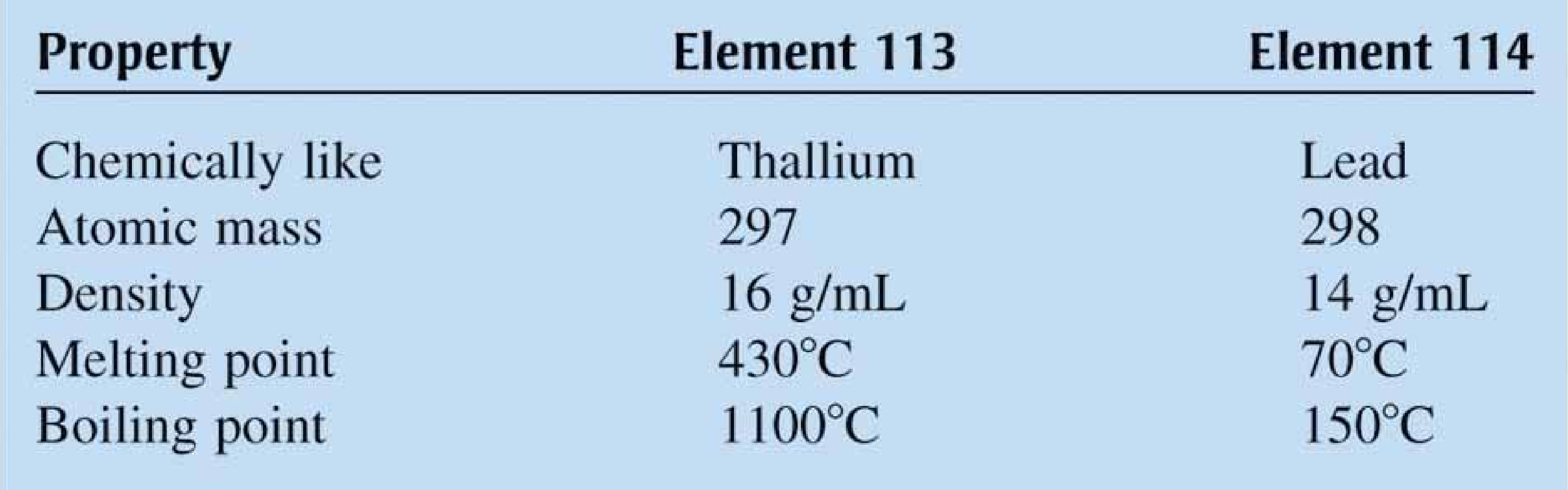
TABLE 7.3 Comparison of the Properties of Germanium as Predicted by Mendeleev and as Actually Observed



Properties of Germanium	**Predicted in 1871**	**Observed in 1886**
Atomic weight	72	72.3
Density	5.5 g/cm^3	5.47 g/cm^3
Specific heat	0.31 J/(°C · g)	0.32 J/(°C · g)
Melting point	Very high	960°C
Oxide formula	RO_2	GeO_2
Oxide density	4.7 g/cm^3	4.70 g/cm^3
Chloride formula	RCl_4	$GeCl_4$
bp of chloride	100°C	86°C

- This atomic mass placed indium, which has metallic properties, among the nonmetals.
- Mendeleev assumed the atomic mass was probably incorrect formula, indium has an atomic mass of approximately 113, placing the element among the metals.
- It is still used to predict the properties of elements recently discovered, as shown in Table 7.4.

TABLE 7.4 Predicted Properties of Elements 113 and 114

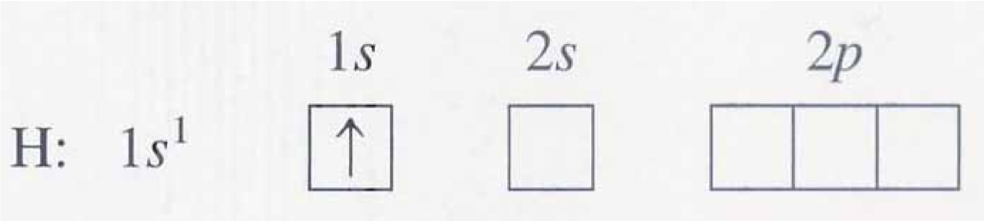


Property	Element 113	Element 114
Chemically like	Thallium	Lead
Atomic mass	297	298
Density	16 g/mL	14 g/mL
Melting point	430°C	70°C
Boiling point	1100°C	150°C

7.11 The Aufbau Principle and the Periodic Table

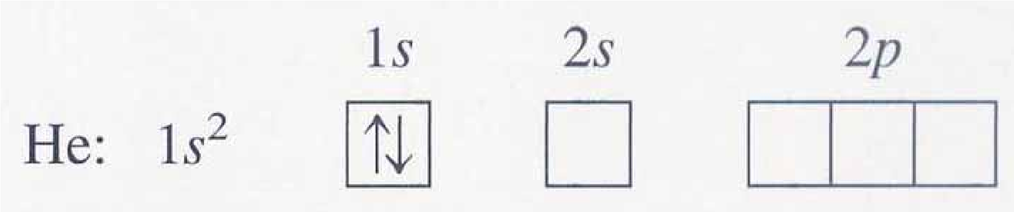
- Our main assumption here is that all atoms have the same type of orbitals as have been described for the hydrogen atom.
- *As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these hydrogenlike orbitals*.
- This is called the **aufbau principle**.

- Hydrogen has one electron, which occupies the 1s orbital in its ground state. The configuration for hydrogen is written as 1s1, which can be represented by the following orbital diagram:

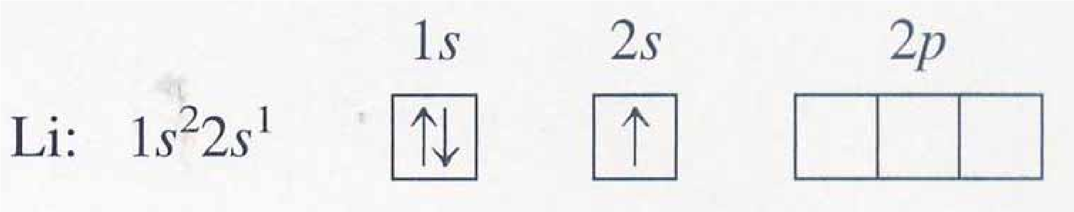


- The arrow represents an electron spinning in a particular direction.

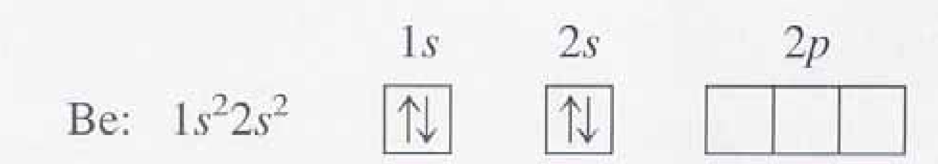
- The next element, *helium*, has two electrons.



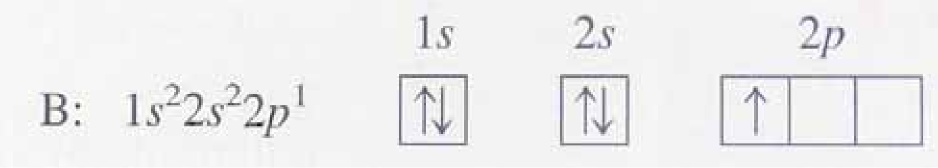
- *Lithium* has three electrons, two of which can go into the 1s orbital before the orbital is filled.



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

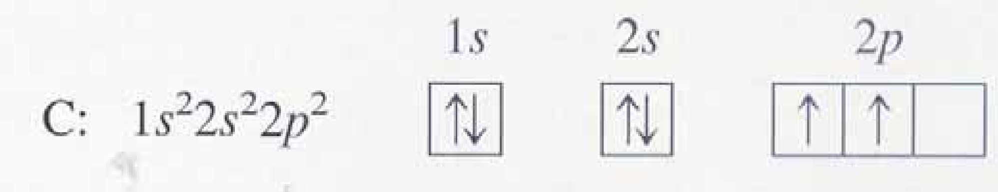


- Boron has five electrons, four of which occupy the 1*s* and 2*s* orbitals. The fifth electron goes into the second type of orbital with $n = 2$, the 2*p* orbitals:

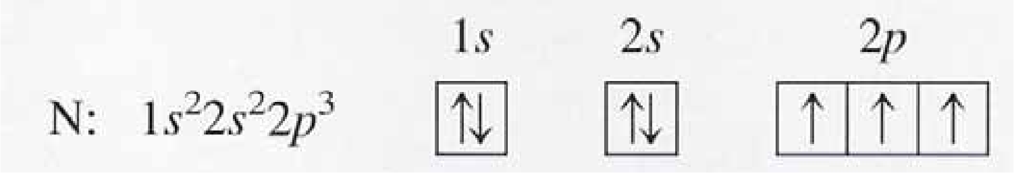


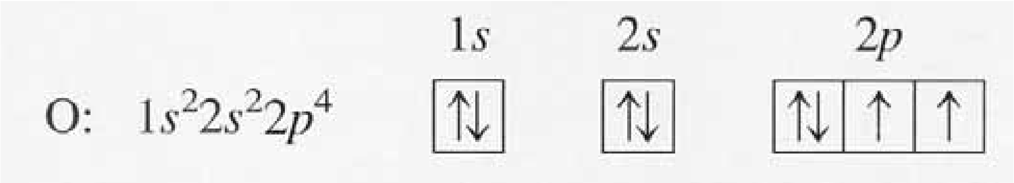
- Carbon is the next element and has six electrons. Two electrons occupy the 1*s* orbital, two occupy the 2*s* orbital, and two occupy 2*p* orbitals.
- This behavior is summarized by **Hund's rule** (named for the German physicist F. H. Hund), which states that *the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate orbitals*.

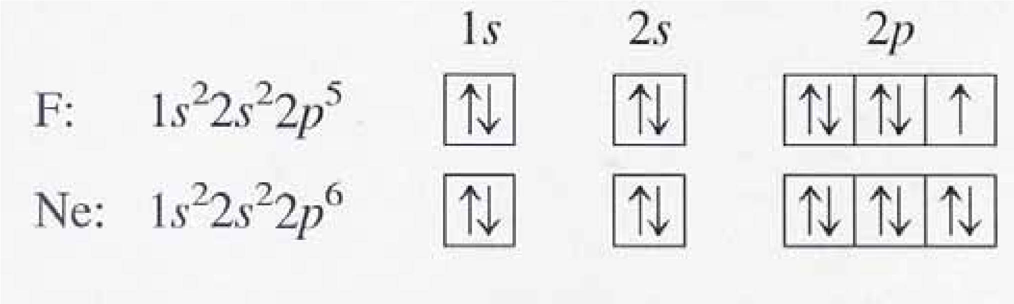
- The configuration for carbon could be written $1s^2 2s^2 2p^1 2p^1$ to indicate that the electrons occupy separate $2p$ orbitals.
- However, the configuration is usually given as $1s^2 2s^2 2p^2$, and it is understood that the electrons are in different $2p$ orbitals.
- The orbital diagram for carbon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



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

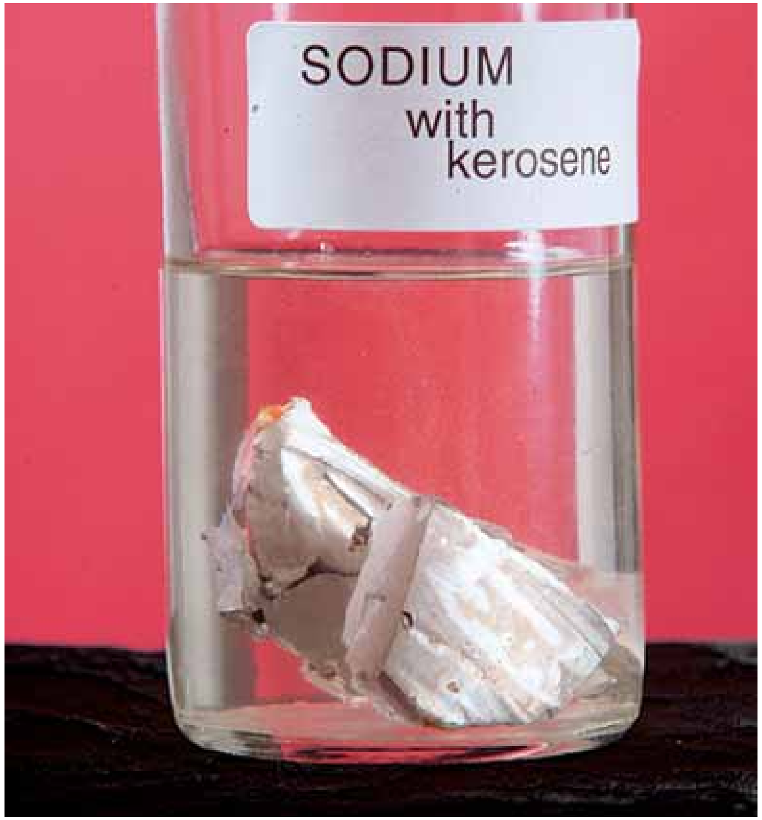






- Figure 7.25 summarizes the electron configurations of the first 18 elements by giving the number of electrons in the type of orbital occupied last.
- At this point it is useful to introduce the concept of **valence electrons**, *the electrons in the outermost principal quantum level of an atom*.
- The valence electrons of the nitrogen atom, for example, are the $2s$ and $2p$ electrons.

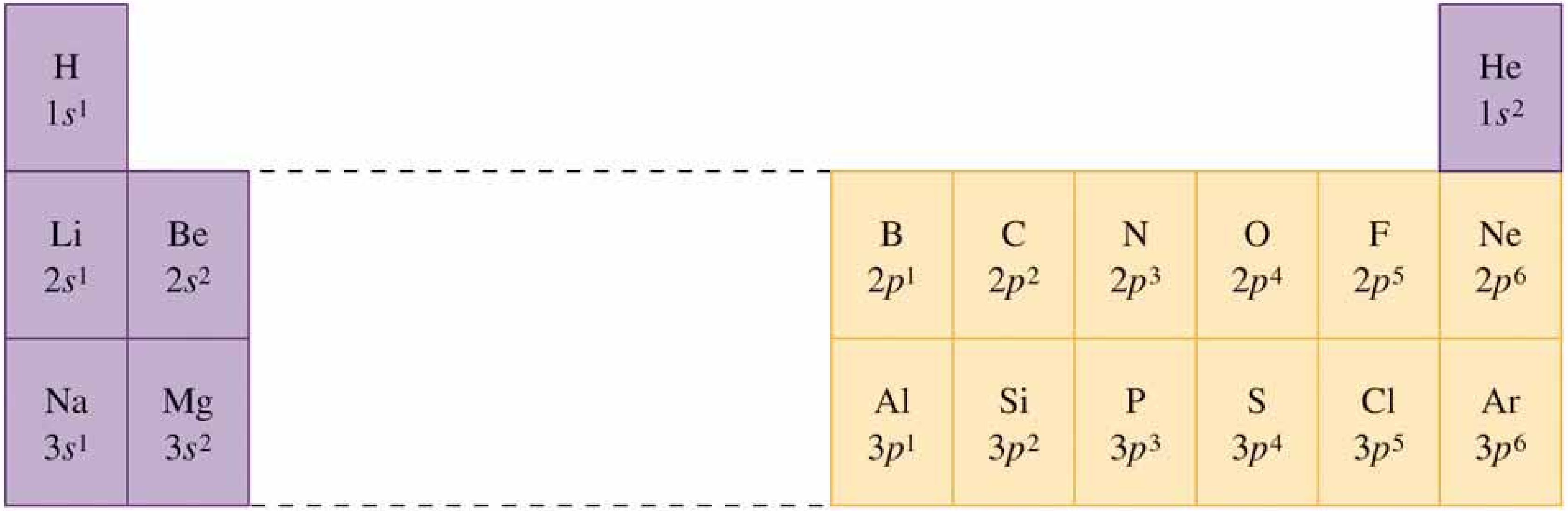
- Valence electrons are the most important electrons to chemists because they are involved in bonding, as we will see in the next two chapters. The inner electrons are known as **core electrons**.
- Note in Fig. 7.25 that a very important pattern is developing: *The elements in the same group (vertical column of the periodic table) have the same valence electron configuration*.



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

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

Figure 7.25



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

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

- The electron configuration of potassium is

$$\text{K:}\quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 \qquad \text{or} \qquad [\text{Ar}]4s^1$$

$$\text{Ca:}\quad [\text{Ar}]4s^2$$

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

$$\text{Sc:}\quad [\text{Ar}]4s^2 3d^1$$

Ti: $[\mathrm{Ar}]4s^2 3d^2$

V: $[\mathrm{Ar}]4s^2 3d^3$

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

Mn: $[\mathrm{Ar}]4s^2 3d^5$ Co: $[\mathrm{Ar}]4s^2 3d^7$
Fe: $[\mathrm{Ar}]4s^2 3d^6$ Ni: $[\mathrm{Ar}]4s^2 3d^8$

Cu: $[\mathrm{Ar}]4s^1 3d^{10}$

Zn: $[\mathrm{Ar}]4s^2 3d^{10}$

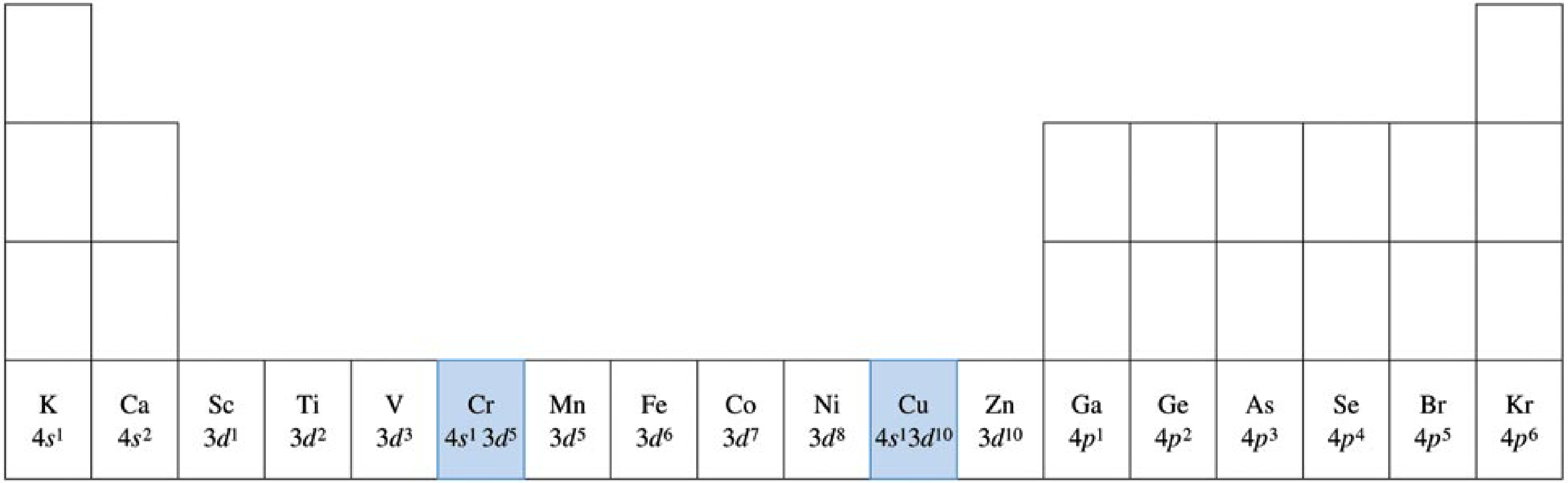
Calcium metal.

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

- The configurations of the transition metals are shown in Fig. 7.26.
- The entire periodic table is represented in Fig. 2.27 in terms of which orbitals are being filled. The valence electron configurations are given in Fig. 7.28. From these two figures, note the following additional points:

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

Figure 7.26



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

Electron configurations for potassium through krypton. The transition metals (scandium through zinc) have the general configuration $[Ar]4s^2 3d^n$, except for chromium and copper.

Figure 7.27

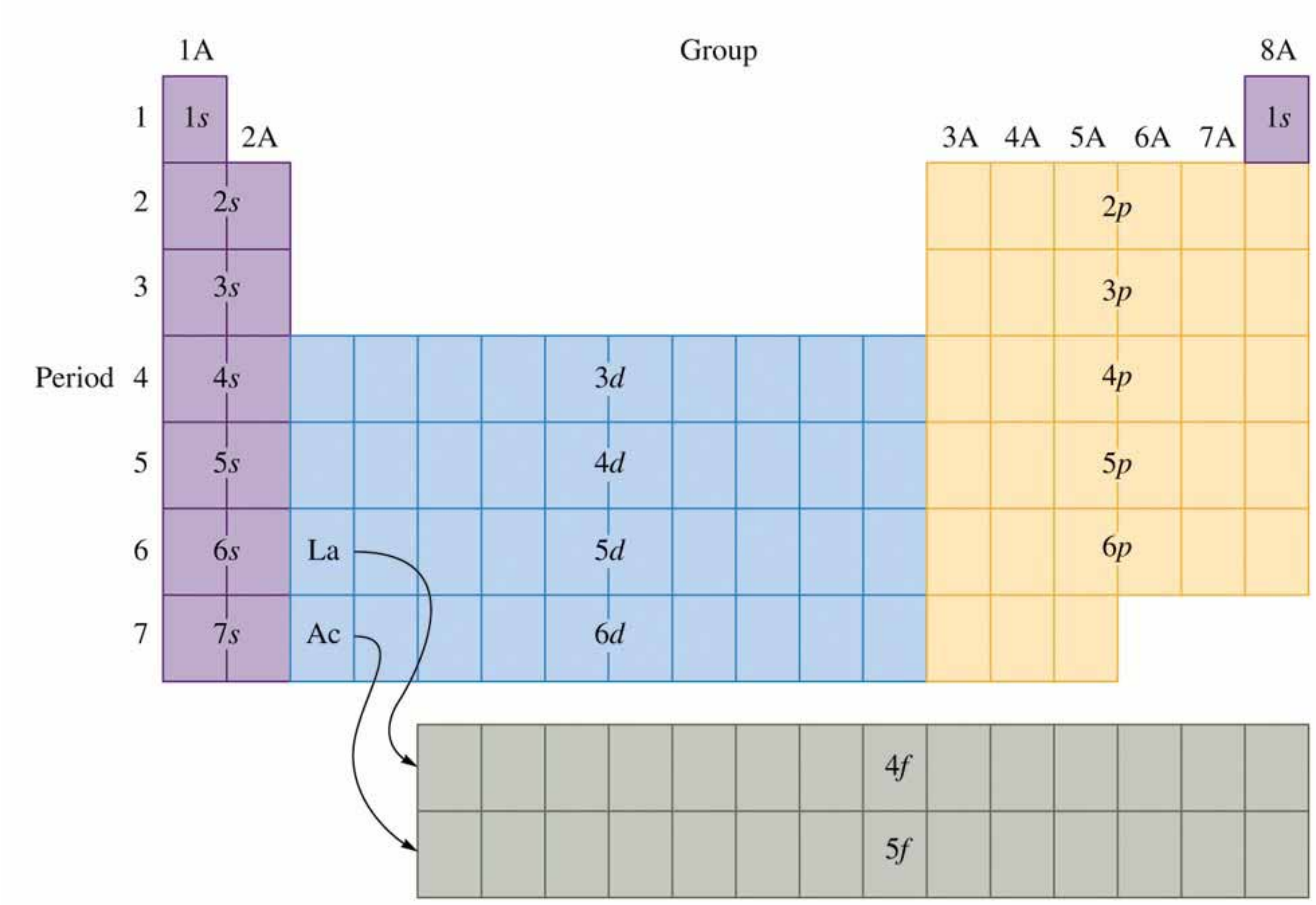

1A
Group
8A
1
1s
2A
3A
4A
5A
6A
7A
1s
2
2s
2p
3
3s
3p
Period 4
4s
3d
4p
5
5s
4d
5p
6
6s
La
5d
6p
7
7s
Ac
6d
4f
5f

Figure 7.27

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

filling of the *s* orbitals can be explained by the penetration effect. For example, the 4*s* orbital allows for so muh more penetration to the vicinity of the nucleus that it becomes lower in energy than the 3*d* orbital. Thus the 4*s* fill before the 3*d*. The same thing can be said about the 5*s* and 4*d*, the 6*s* and 5*d*, and the 7*s* and 6*d* orbitals.

2. After lanthanum, which has the configuration [Xe]$6s^2 5d^1$, a group of 14 elements called the

lanthanide series, or the **lanthanides**, occurs. This series of elements corresponds to the filling of the seven 4*f* orbitals. Note that sometimes an electron occupies a 5*d* orbital instead of a 4*f* orbital. This occurs because the energies of the 4*f* and 5*d* orbitals are very similar.

3. After actinium, which has the configuration [Rn] $7s^2 6d^1$, a group of 14 elements called the actinide series, or the actinides, occurs. This series corresponds

to the filling of the seven 5*f* orbitals. Note that sometimes one or two electrons occupy the 6*d* orbitals instead of the 5*f* orbitals, because these orbitals have very similar energies.

4. The group labels for Groups 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A indicate the total number of valence electrons for the atoms in these groups. For example, all the elements in Group 5A have the configuration ns^2np^3. (The d electrons fill one period late and are

usually nor counted as valence electrons.) The meaning of the group labels for the transition metals is not as clear as for the Group A elements, and these will not be used in this text.

5. The groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A are often called the **main-group**, or **representative**, **elements**. Every member of these groups has the same valence electron configuration.

- The International Union of Pure and Applied Chemistry (IUPAC), a body of scientists organized to standardize scientific conventions, has recommended a new form for the periodic table, which the American Chemical Society has adopted (see the blue numbers in Fig. 7.28).

Figure 7.28

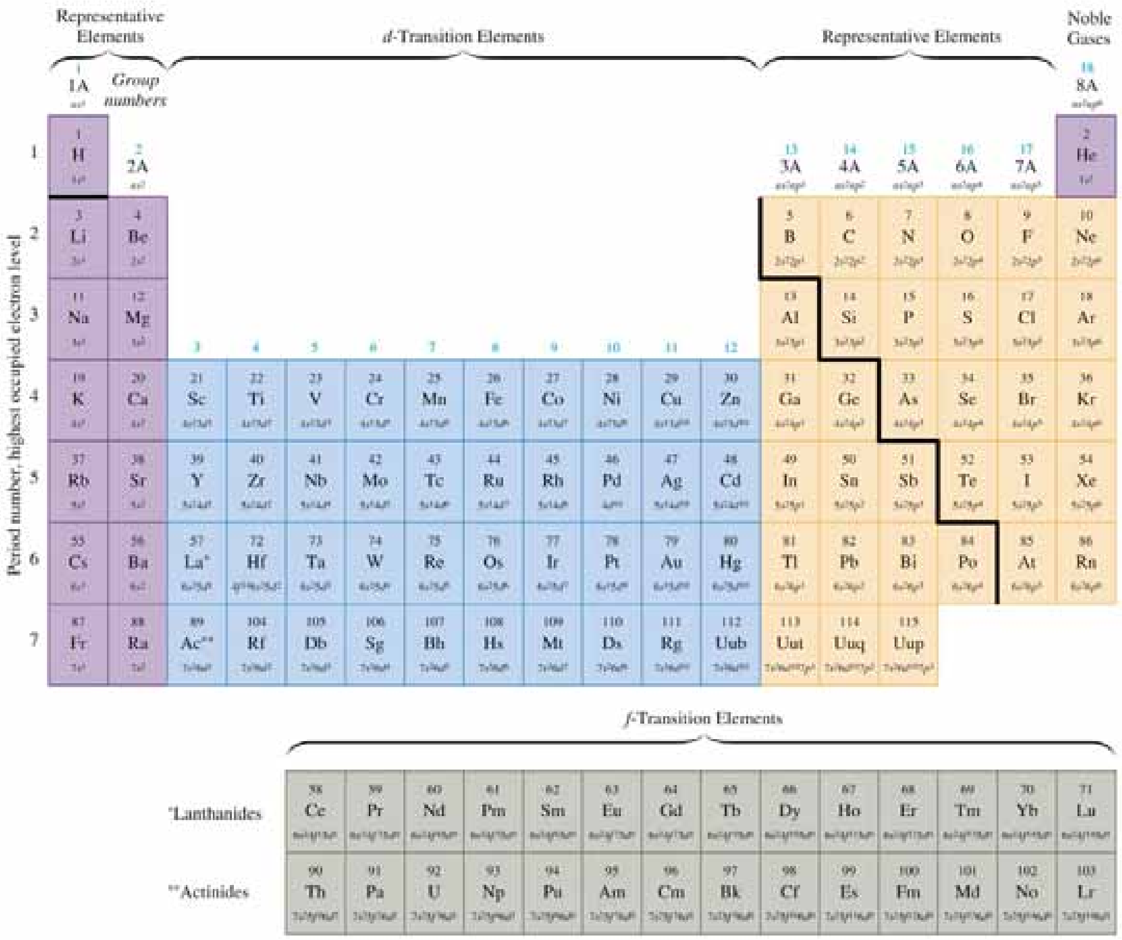

Representative Elements
d-Transition Elements
Representative Elements
Noble Gases
Group numbers
1A
2A
3A
4A
5A
6A
7A
8A
Period number, highest occupied electron level
f-Transition Elements
*Lanthanides
**Actinides

Figure 7.28

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

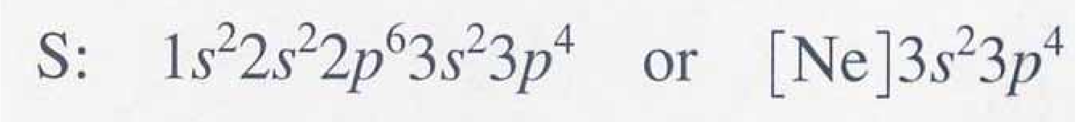
Sample Exercise 7.7

Electron configurations

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

Solution

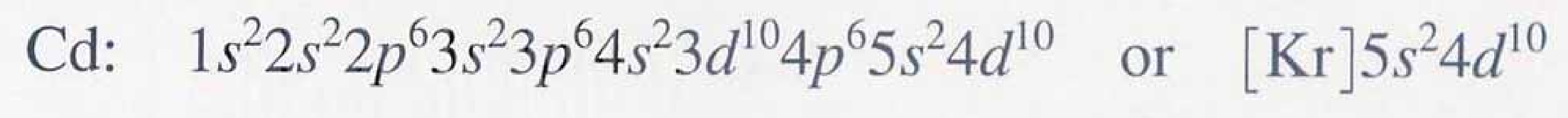
Sulfur is element 16 and resides in Period 3, where the 3*p* orbitals are being filled (see Fig. 7.29). Since sulfur is the fourth among the "3*p* elements," it must have four 3*p* electrons. Its configuration is



$$\text{S:} \quad 1s^2 2s^2 2p^6 3s^2 3p^4 \quad \text{or} \quad [\text{Ne}]3s^2 3p^4$$

Sample Exercise 7.7

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



$$\text{Cd:}\quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} \quad \text{or} \quad [\text{Kr}]5s^2 4d^{10}$$

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

Sample Exercise 7.7

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

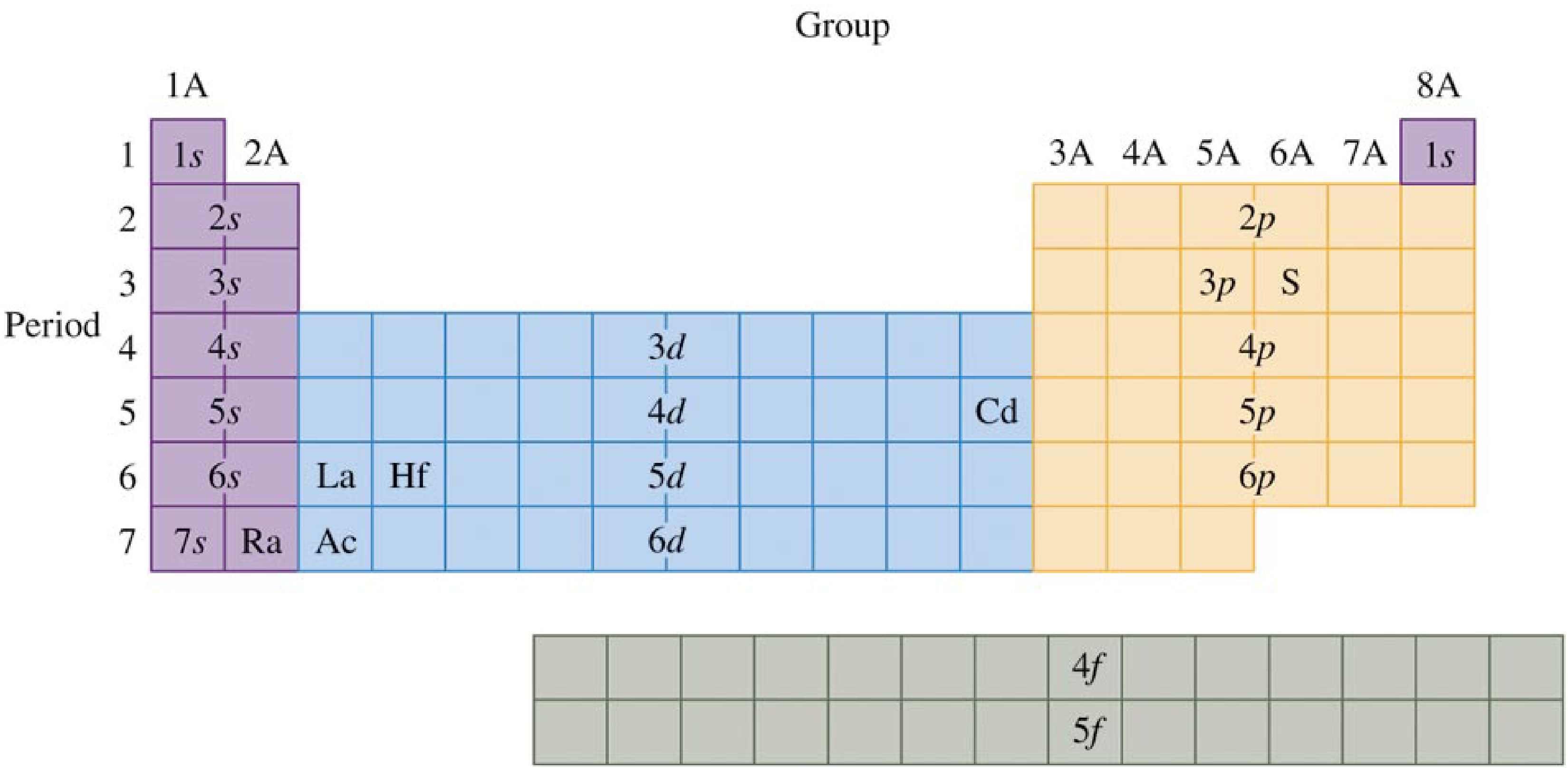
$$\text{Hf:}\quad 1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^2 \quad \text{or} \quad [\text{Xe}]6s^24f^{14}5d^2$$

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

$$\text{Ra:}\quad 1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^2 \quad \text{or} \quad [\text{Rn}]7s^2$$

See Exercises 7.69 through 7.72

Figure 7.29



The positions of the elements considered in Sample Exercise 7.7.

7.12 Periodic Trends in Atomic Properties

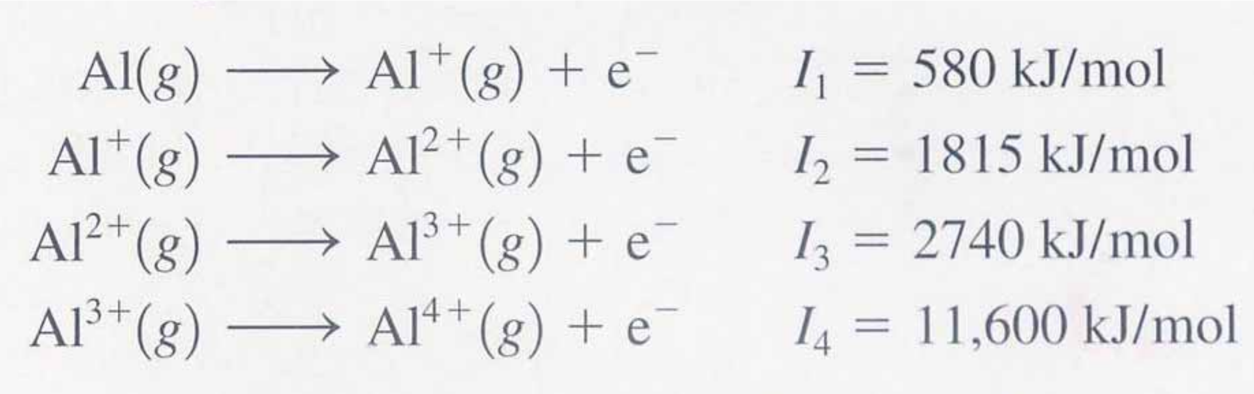
Ionization Energy

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

$$X(g) \longrightarrow X(g)^+ + e^-$$

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

- The ionization energies are

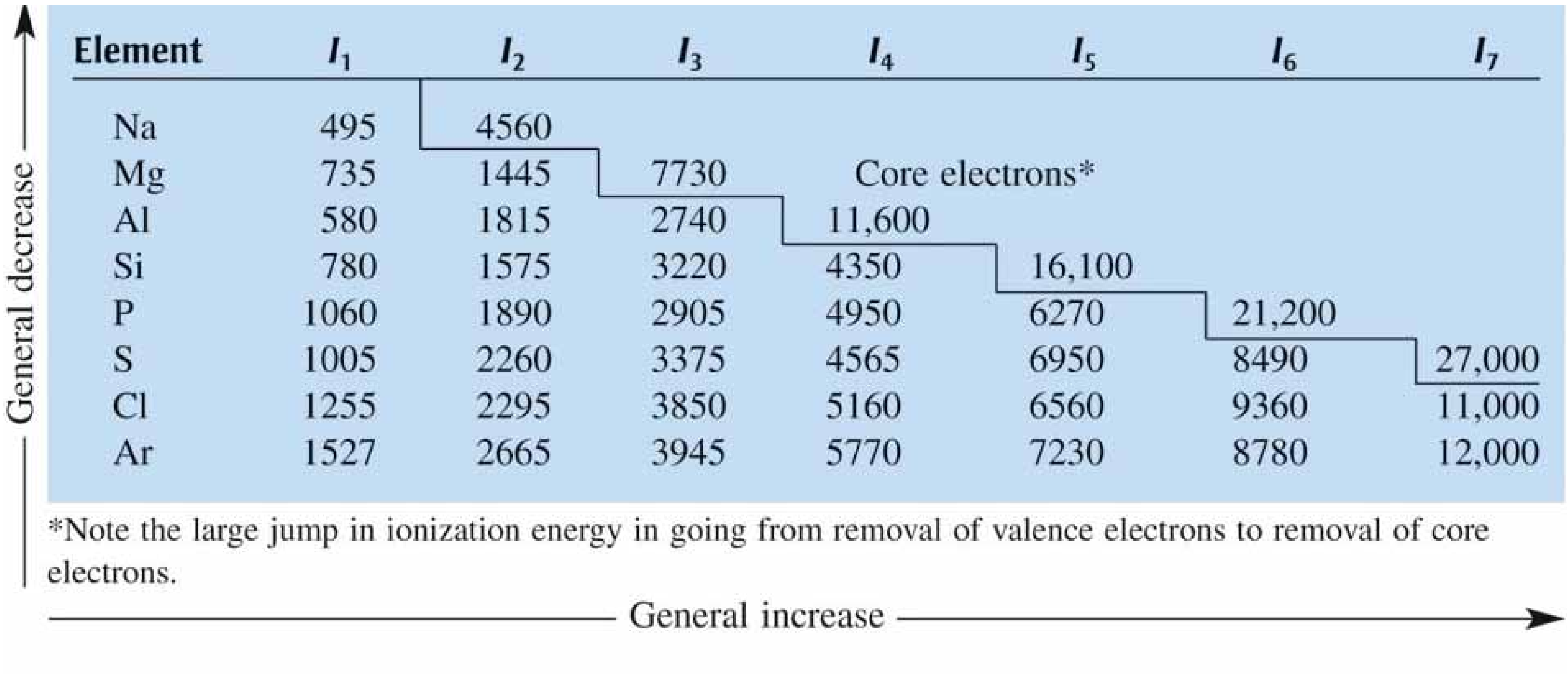


$$\begin{aligned}
\mathrm{Al}(g) &\longrightarrow \mathrm{Al}^{+}(g) + e^{-} & I_1 &= 580\ \mathrm{kJ/mol}\\
\mathrm{Al}^{+}(g) &\longrightarrow \mathrm{Al}^{2+}(g) + e^{-} & I_2 &= 1815\ \mathrm{kJ/mol}\\
\mathrm{Al}^{2+}(g) &\longrightarrow \mathrm{Al}^{3+}(g) + e^{-} & I_3 &= 2740\ \mathrm{kJ/mol}\\
\mathrm{Al}^{3+}(g) &\longrightarrow \mathrm{Al}^{4+}(g) + e^{-} & I_4 &= 11{,}600\ \mathrm{kJ/mol}
\end{aligned}$$

- The **first ionization energy** I_1 is the energy required to remove the highest-energy electron of an atom.

- The second electron comes from the 3*s* orbital (since Al^+ has the configuration [Ne]$3s^2$). Note that the value of I_1 is considerably smaller than the value of I_2, the **second ionization energy**.
- Table 7.5 gives the values of ionization energies for all the Period 3 elements. Note the large jump in energy in each case in going from removal of valence electrons to removal of core electrons.

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

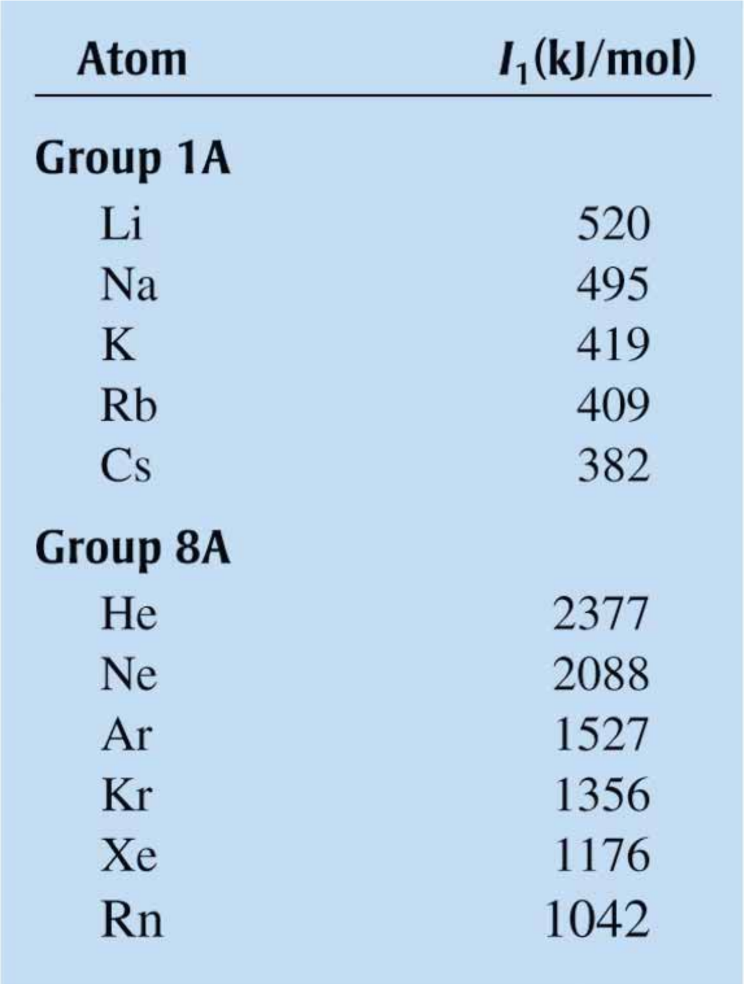


Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

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

- The values of the first ionization energies for the elements in the first six periods of the periodic table are graphed in Fig. 7.30.
- Note that in general as we go *across a period from left to right, the first ionization energy increase*.
- On the other hand, *first ionization energy decreases in going down a group*.
- This can be seen most clearly by focusing on the Group 1A elements (the alkali metals) and the Group 8A elements (the noble gases), as shown in Table 7.6.

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



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

Figure 7.30

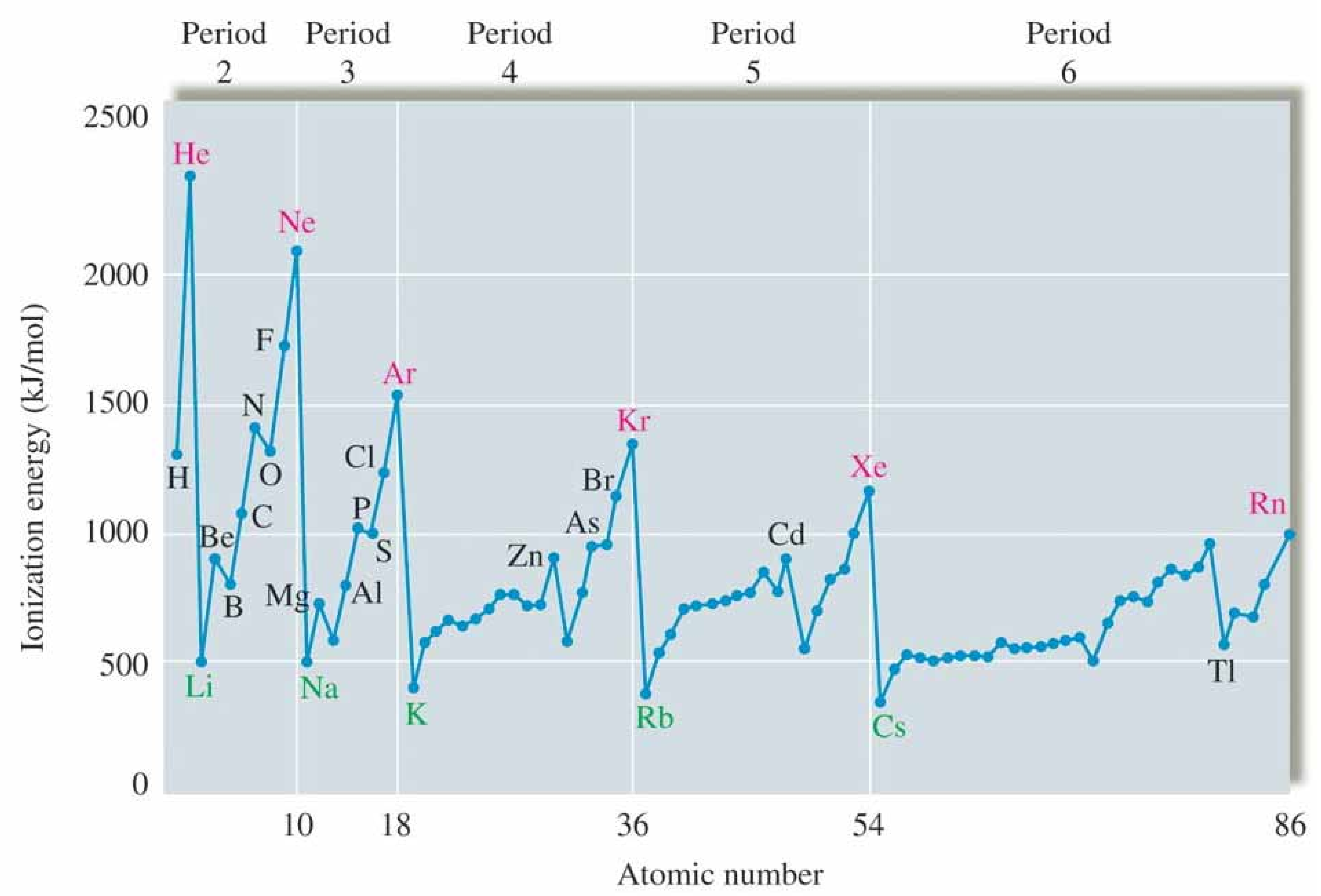
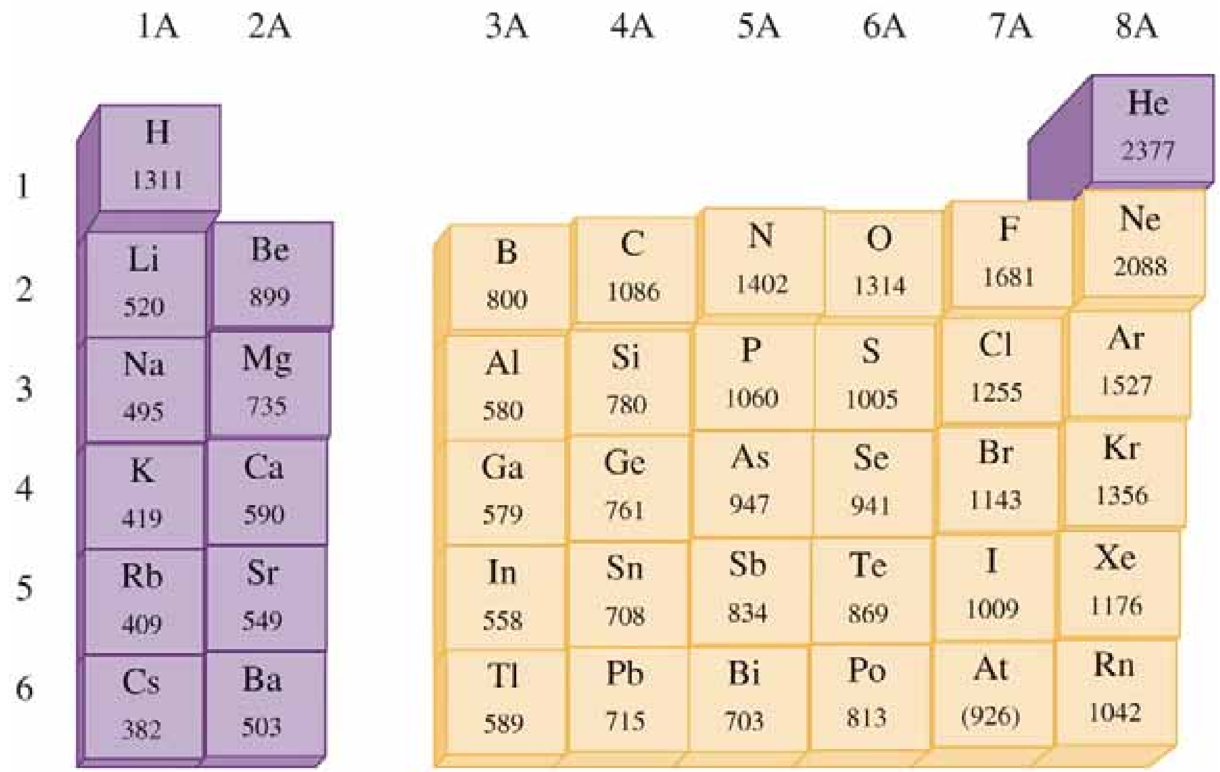

Period 2
Period 3
Period 4
Period 5
Period 6
Ionization energy (kJ/mol)
2500
2000
1500
1000
500
0
He
Ne
Ar
Kr
Xe
Rn
H
Li
Be
B
C
N
O
F
Na
Mg
Al
P
S
Cl
K
Zn
As
Br
Rb
Cd
Cs
Tl
10
18
36
54
86
Atomic number

Figure 7.30

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

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

Figure 7.31



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

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

Sample Exercise 7.9

Ionization Energies

Consider atoms with the following electron configurations:

$$1s^22s^22p^6$$

$$1s^22s^22p^63s^1$$

$$1s^22s^22p^63s^2$$

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

Solution

The atom with the largest value of I1 is the one with the configuration 1s22s22p6 (this is the neon atom), because

Sample Exercise 7.9

this element is found at the right end of Period 2. Since the 2p electrons do not shield each other very effectively, I_1 will be relatively large. The other configurations given include 3s electrons. These electrons are effectively shielded by the core electrons and are farther from the nucleus than the 2p electrons in neon. Thus I_1 for these atoms will be smaller than for neon.

The atom with the smallest value of I_2 is the one with the configuration $1s^22s^22p^63s^2$ (the magnesium atom). For magnesium, both I_1 and I_2 involve valence electrons. For

Sample Exercise 7.9

the atom with the configuration $1s^2 2s^2 2p^6 3s^1$ (sodium), the second electron lost (corresponding to I_2) is a core electron (from a 2*p* orbital).

See Exercises 7.121 and 7.123

Electron Affinity

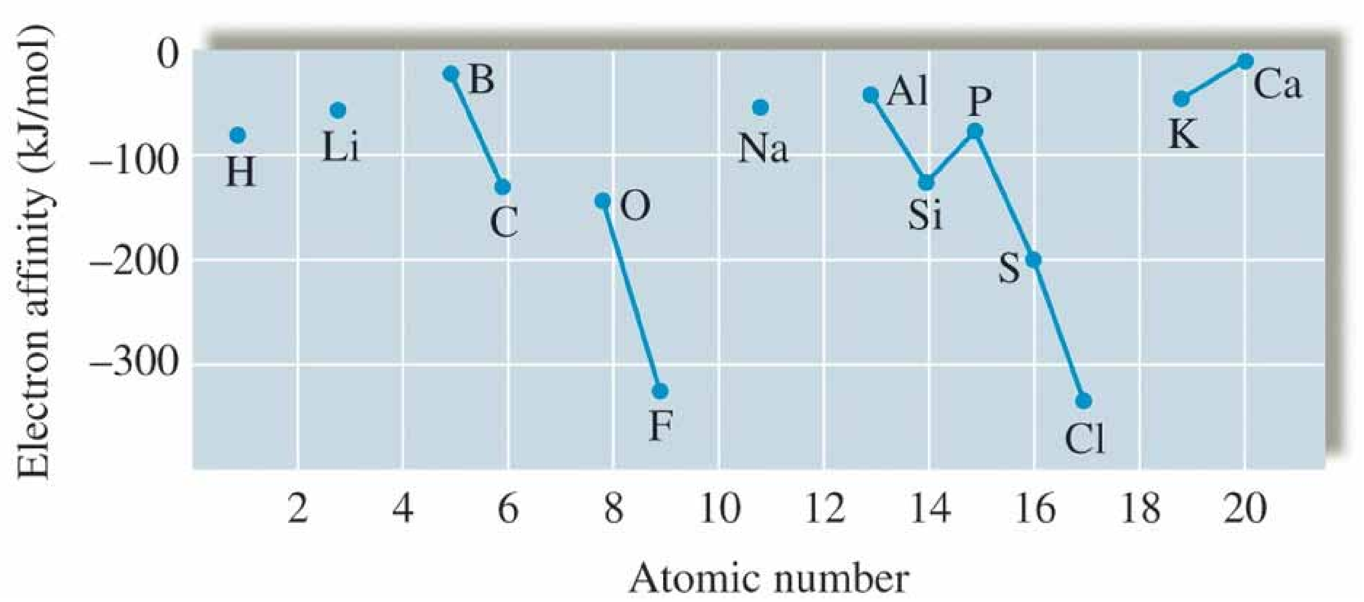
- **Electron affinity** *is the energy change associated with the addition of an electron to a gaseous atom*:

$$X(g) + e^{-} \longrightarrow X^{-}(g)$$

- Electron affinity has been defined in many textbooks as the energy *released* when an electron is added to a gaseous atom.

- Figure 7.32 shows the electron affinity values for the atoms among the first 20 elements that form stable, isolated negative ions-that is, the atoms that undergo the addition of an electron as shown above.
- Note that the *more negative* the energy, the greater the quantity of energy released.

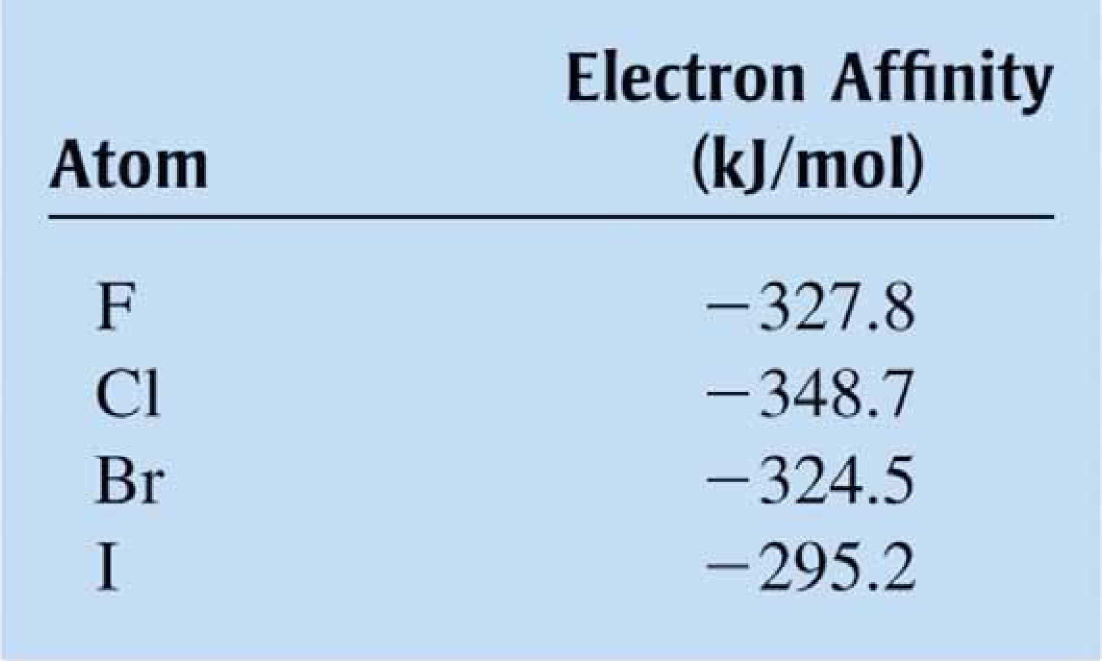
Figure 7.32



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

- When we go down a group, electron affinity should become more positive (less energy released), since the electron is added at increasing distances from the nucleus.
- Although this is generally the case, the changes in electron affinity in going down most groups are relatively small, and numerous exceptions occur.
- This behavior is demonstrated by the electron affinities of the Group 7A elements (the halogens) shown in Table 7.7.

TABLE 7.7 Electron Affinities of the Halogens

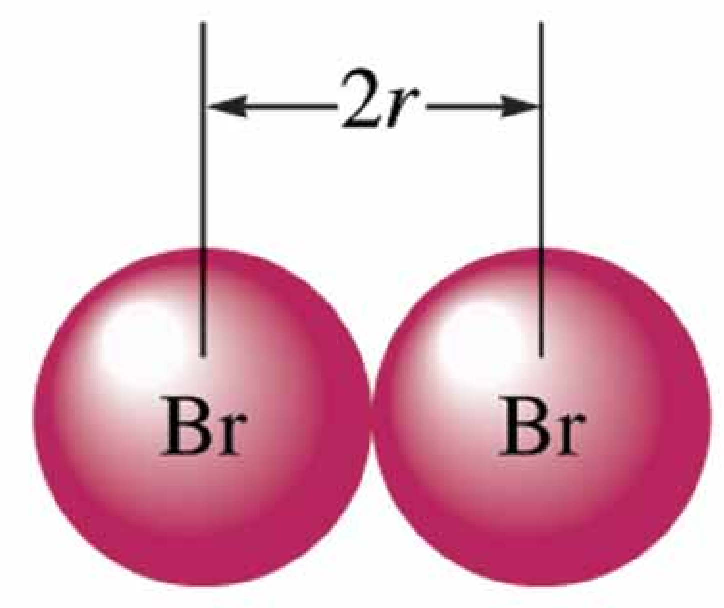


Atom	Electron Affinity (kJ/mol)
F	−327.8
Cl	−348.7
Br	−324.5
I	−295.2

Atomic Radius

- Just as the size of an orbital cannot be specified exactly, neither can the size of an atom. We must make some arbitrary choices to obtain values for atomic radii.
- In the bromine molecule, the distance between the two nuclei is known to be 228 pm.
- The bromine atomic radius is assumed to be half this distance, or 114 pm, as shown in Fig. 7.33.
- These radii are often called covalent atomic radii because of the way they are determined.

Figure 7.33



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

- The values of the atomic radii for the representative elements are shown in Fig. 7.34.
- Note that these values are significantly smaller than might be expected from the 90% electron density volumes of isolated atoms, because when atoms form bonds, their electron “clouds” interpenetrate.
- Note from Fig. 7.34 that the atomic radii decrease in going from left to right across a period.

- This decrease can be explained in terms of the increasing effective nuclear charge (decreasing shielding) in going from left to right.
- This means that the valence electrons are draw closer to the nucleus, decreasing the size of the atom.

Figure 7.34

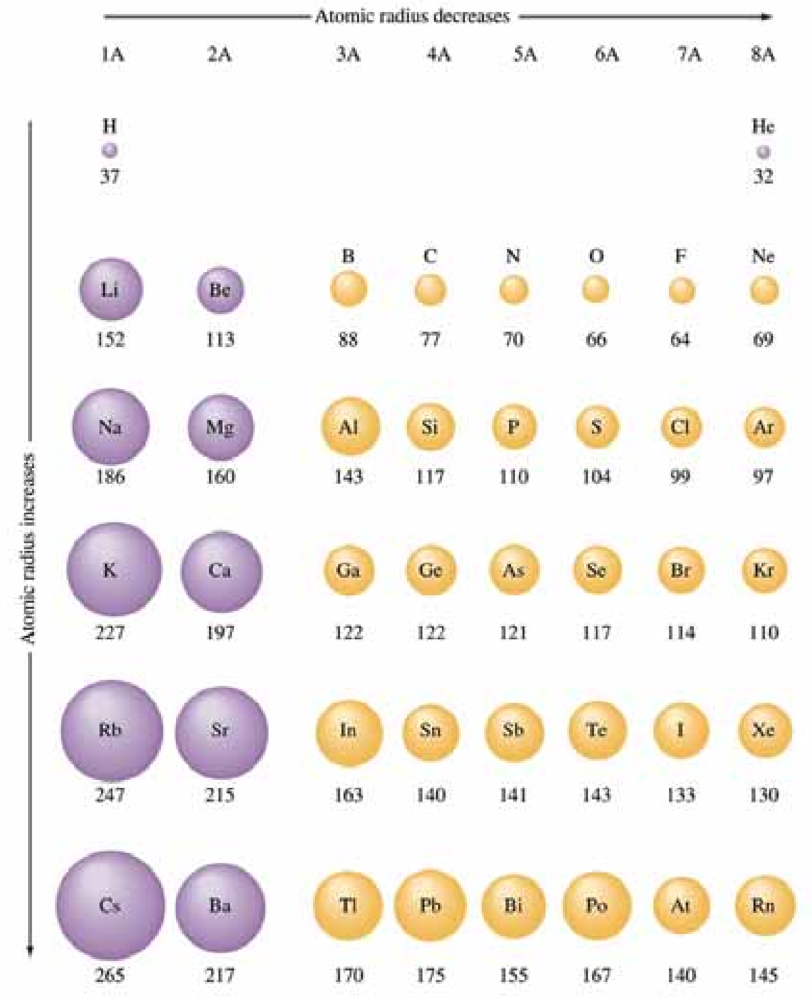

Atomic radius decreases
1A
2A
3A
4A
5A
6A
7A
8A
Atomic radius increases
H 37
He 32
Li 152
Be 113
B 88
C 77
N 70
O 66
F 64
Ne 69
Na 186
Mg 160
Al 143
Si 117
P 110
S 104
Cl 99
Ar 97
K 227
Ca 197
Ga 122
Ge 122
As 121
Se 117
Br 114
Kr 110
Rb 247
Sr 215
In 163
Sn 140
Sb 141
Te 143
I 133
Xe 130
Cs 265
Ba 217
Tl 170
Pb 175
Bi 155
Po 167
At 140
Rn 145

Figure 7.34

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

7.13 The Properties of Group: The Alkali Metals

Information Contained in the Periodic Table

1. The essence of the periodic table is that the groups of representative elements exhibit similar chemical properties that change in a regular way. The quantum mechanical model of the atom has allowed us to understand the basis for the similarity of properties in a group-that each group member has the same valence electron configuration. *It is the number and type of*

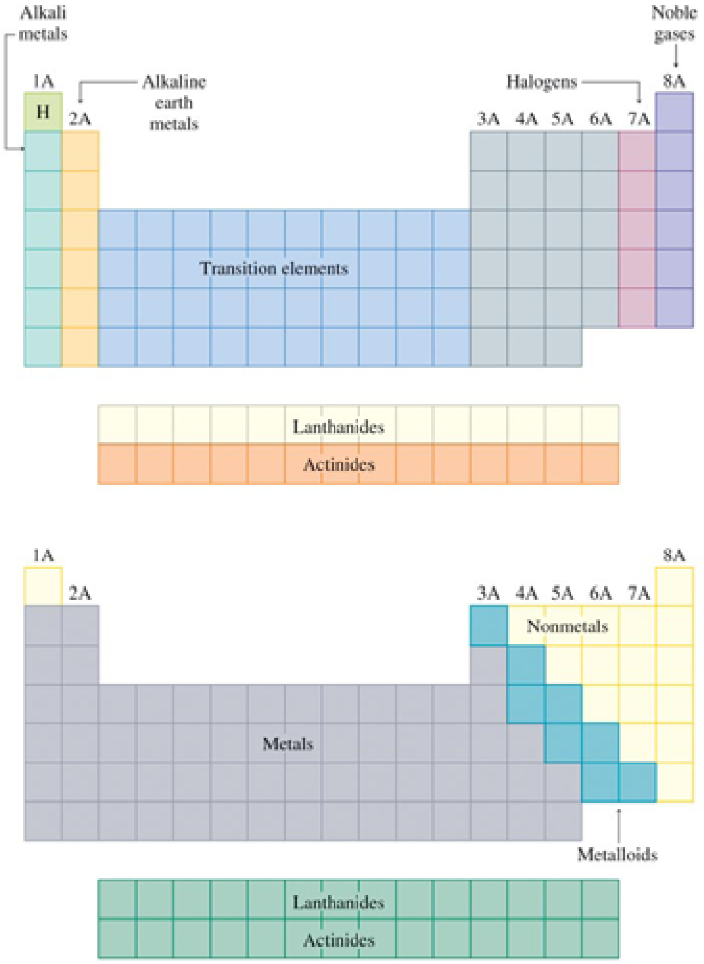
valence electrons that primarily determine an atom's chemistry.

2. One of the most valuable types of information available from the periodic table is the electron configuration of any representative element. If you understand the organization of the table, you will not need to memorize electron configurations for these elements. Although the predicted electron configurations for transition metals are sometimes incorrect, this is not a serious problem. You should,

however, memorize the configurations of two exceptions, chromium and copper, since these 3d transition elements are found in many important compounds.

3. As we mentioned in Chapter 2, certain groups in the periodic table have special names. These are summarized in Fig. 7.35. Groups are often referred to by these names, so you should learn them.

Figure 7.35



Special names for groups in the periodic table.

4. The most basic division of the elements in the periodic table is into metals and nonmetals. The most important chemical property of a metal atom is the tendency to give up one or more electrons to form a positive ion; metals tend to have low ionization energies. The metallic elements are found on the left side of the table, as shown in Fig. 7.35. The most chemically reactive metals are found on the lower left-hand portion of the table, where the ionization energies are smallest. The most distinctive chemical property of a nonmetal atom

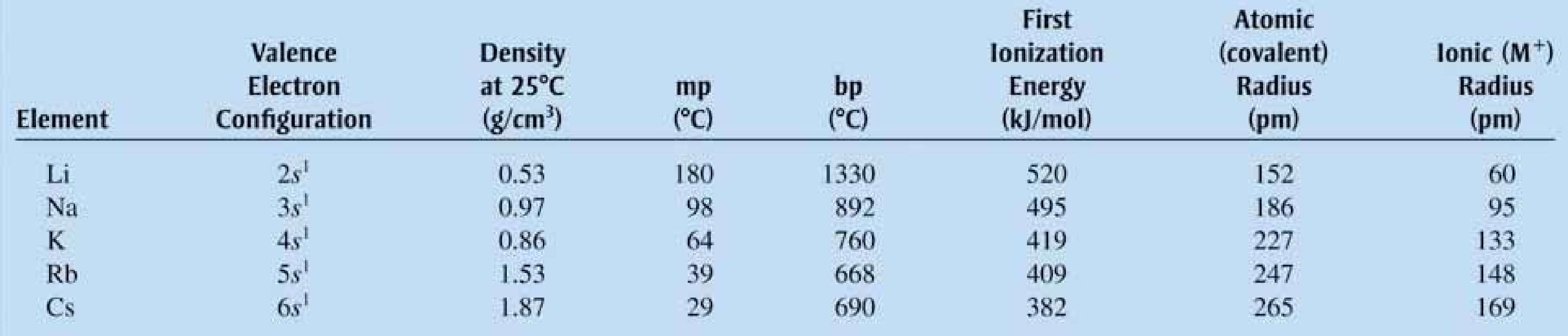
is the ability to gain one or more electrons to form an anion when reacting with a metal. Thus nonmetals are elements with large ionization energies and the most negative electron affinities. The nonmetals are found on the right side of the table, with the most reactive ones in the upper right-hand corner,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

The Alkali Metals

- The metals of groups 1A, the alkali metals, illustrate very well the relationships among the properties of the elements in a group.
- Lithium, sodium, potassium, rubidium, cesium, and francium are the most chemically reactive of the metals.
- Some important properties of the first five alkali metals are shown in Table 7.8.

- The data in Table 7.8 show that in going down the group, the first ionization energy decreases and the atomic radius increases.

TABLE 7.8 Properties of Five Alkali Metals

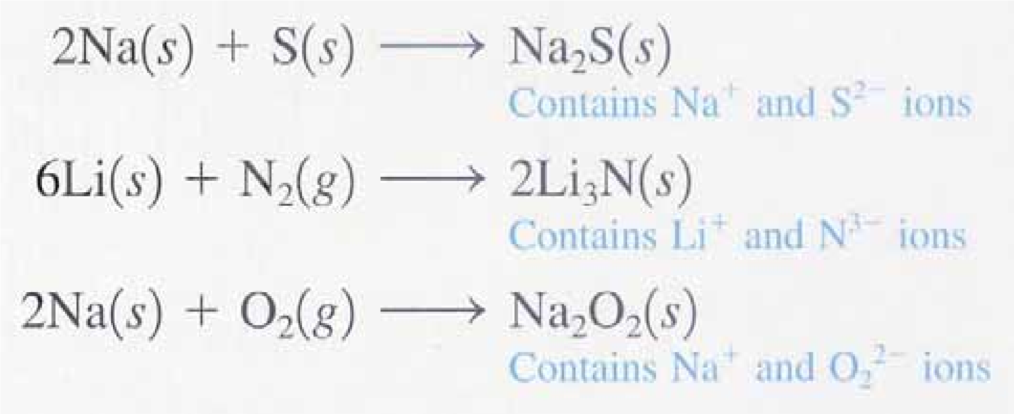


Element	Valence Electron Configuration	Density at 25°C (g/cm^3)	mp (°C)	bp (°C)	First Ionization Energy (kJ/mol)	Atomic (covalent) Radius (pm)	Ionic (M^+) Radius (pm)
Li	$2s^1$	0.53	180	1330	520	152	60
Na	$3s^1$	0.97	98	892	495	186	95
K	$4s^1$	0.86	64	760	419	227	133
Rb	$5s^1$	1.53	39	668	409	247	148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

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

$$2\text{Na}(s) + \text{Cl}2(g) \longrightarrow 2\text{NaCl}(s)$$

- where sodium chloride contains Na^+ and Cl^- ions.



$$2Na(s) + S(s) \longrightarrow Na_2S(s)$$

Contains Na^+ and S^{2-} ions

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

Contains Li^+ and N^{3-} ions

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

Contains Na^+ and O_2^{2-} ions

- The expected trend in reducing ability is

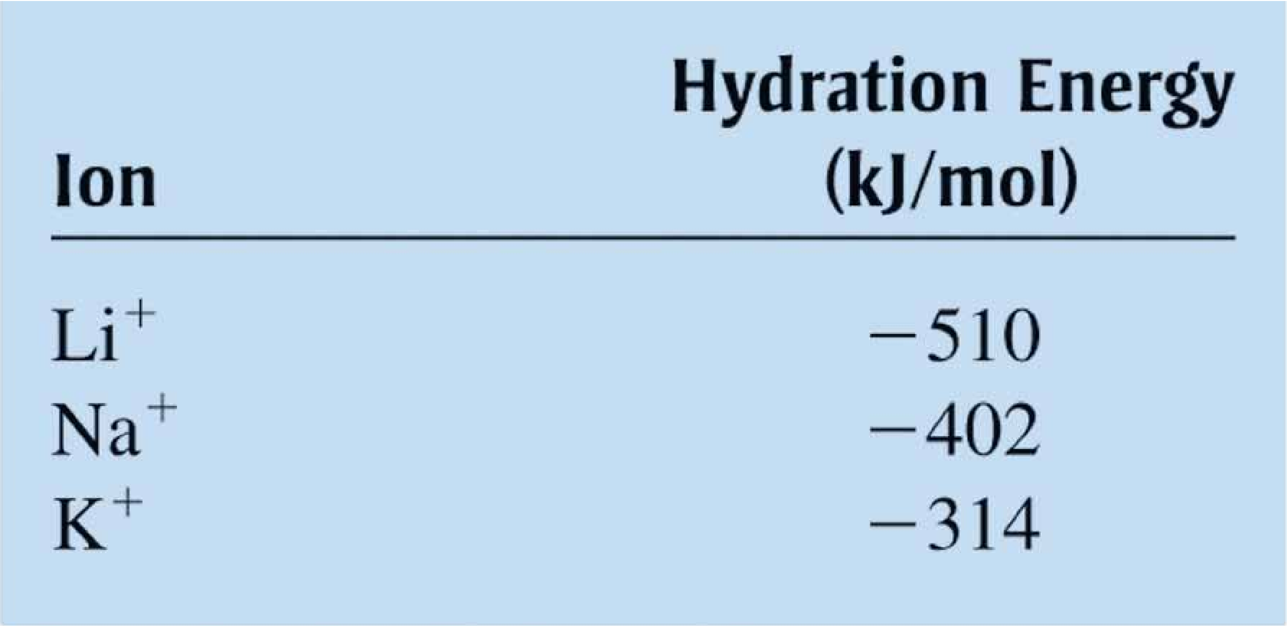
Cs > Rb > K > Na > Li

Li > K > Na

- lithium is the best reducing agent toward water.

- The hydration energy of an ion represents the change in energy that occurs when water molecules attach to the M^+ ion.
- The hydration energies for the Li^+, Na^+, and K^+ ions (shown in Table 7.9) indicate that the process is exothermic in each case.

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



Ion	Hydration Energy (kJ/mol)
Li^+	−510
Na^+	−402
K^+	−314