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CHAPTER 5

Atoms, Nuclear Decay, Electronic Structure, and Atomic Chemical Behavior

Read This Chapter to Learn About

- Atomic Nucleus
- Electronic Structure
- The Periodic Table: Classification of Elements into Groups by Electronic Structure
- The Periodic Table: Variations of Chemical Properties with Group and Row

ATOMIC NUCLEUS

The smallest building block, or unit, of all matter is the **atom**. All atoms consist of three basic particles: **protons**, **neutrons**, and **electrons**. The protons and neutrons are tightly packed in a positively charged nucleus situated at the center of the atom, and the electrons are in continual orbit around the nucleus. The protons and neutrons, collectively known as **nucleons**, account for the majority of the mass of the atom. The proton charge is identical in magnitude to that of the electron but is positive, whereas the electron is negatively charged. The neutron is neutrally charged (uncharged) and is slightly heavier than the proton.

Mass of the proton	$m_p = 1.67 \times 10^{-27}$ kg
Mass of the neutron	$m_n = 1.68 \times 10^{-27}$ kg
Mass of the electron	$m_e = 9.11 \times 10^{-31}$ kg

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Atomic Number and Atomic Weight

Elements are categorized according to the following properties based on the numbers of protons and neutrons:

Mass number $\boldsymbol{A}$ = number of protons and neutrons (collectively known as nucleons)

Atomic number $\boldsymbol{Z}$ = number of protons (which is equal to the number of electrons)

The mass number is representative of the weight of an atom and is often referred to as **atomic weight**.

Another symbol, N, is used to represent the number of neutrons in the nucleus and can be determined by:

$$N = A - Z$$

The quantities, A, Z, and N are related by the equation:

$$A = N + Z$$

In symbolic form, an atom is represented by:

$$^{A}_{Z}X$$

For example, consider the elements carbon $^{12}_{6}\text{C}$, sulfur $^{32}_{16}\text{S}$, and potassium $^{39}_{19}\text{K}$. Carbon has 12 protons and neutrons ($A = 12$), 6 protons ($Z = 6$), and 6 neutrons ($N = 12 - 6 = 6$). Sulfur has 32 protons and neutrons ($A = 32$), 16 protons ($Z = 16$), and 16 neutrons ($N = 32 - 16 = 16$). Potassium has 39 protons and neutrons ($A = 39$), 19 protons ($Z = 19$), and 20 neutrons ($N = 39 - 19 = 20$).

Isotopes

Isotopes represent a class of nuclei with the same number of protons (Z) but different number of neutrons (N) and thus of nucleons (A). They usually do not decay into different nuclei. As an example, the nuclides $^{1}_{1}\text{H}$, $^{2}_{1}\text{H}$ (deuterium), and $^{3}_{1}\text{H}$ (tritium) are all isotopes of hydrogen. The nuclides $^{10}_{6}\text{C}$, $^{11}_{6}\text{C}$, $^{12}_{6}\text{C}$, $^{13}_{6}\text{C}$, $^{14}_{6}\text{C}$, and $^{15}_{6}\text{C}$ are all isotopes of carbon.

Nuclear Binding Energy

Applied to the atomic nucleus, the conservation of mass implies that the mass of the nucleus is equal to the sum of the masses of protons and neutrons, the particles that are housed in the nucleus. However, this is not the case with the **rest mass** of a nucleus, which is less than the sum of the rest masses of the protons and neutrons. The reason for this difference in mass, referred to as the **mass defect**, is that negative energy is required to bind the individual proton and neutron particles within the nucleus. This energy, referred to as the **nuclear binding energy**, is given by Einstein's

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equation that describes the conversion between mass and energy, or

$$\text{Nuclear binding energy} = \left\{(Zm_p)c^2 + (Nm_n)c^2\right\} - M_{\text{nuc}}c^2$$

where $M_{\text{nuc}}c^2$ is the mass defect.

Radioactive Decay

Radioactive decay is a nuclear phenomenon exhibited by radioactive isotopes or elements with an atomic number Z greater than that of lead ($Z = 82$). In these elements, which contain generally more neutrons (N) than protons (Z), the repulsive electric forces in the nucleus become greater than the attractive nuclear forces, making the nuclei unstable. In nature, the radioactive element strives toward a stabilized state of existence and, in the process, spontaneously emits particles (photons and charged and uncharged particles), and in so doing transforms to a different nucleus and hence a different element. This process is referred to as radioactive decay and is dependent on the amount and identity of the radioactive element.

ALPHA, BETA, GAMMA DECAY

Radionuclides typically undergo radioactive decay of three common types.

- **Alpha decay**, caused by the repulsive electric forces between the protons, involves the emission of an alpha particle (or a helium nucleus that consists of two protons and two neutrons) by nuclei with many protons. In alpha decay, the radioactive nucleus **decreases** in A (mass number) by 4 and **decreases** in Z (number of protons) by 2.
- **Beta decay**, which occurs in nuclei that have too many neutrons, can occur by emission of a β particle. A β^- particle is an electron, and a β^+ particle is a positively charged electron, known as a **positron**. In β^- decay, the radioactive nucleus **remains unchanged** in A and **increases** in Z by 1. In β^+ decay, the radioactive nucleus **remains unchanged** in A and **decreases** in Z by 1.
- **Gamma decay** occurs by the emission of highly energetic photons. In gamma decay, the radioactive nucleus **remains unchanged** in A and **remains unchanged** in Z.

EXAMPLE: The isotope radium-226 decays according to the reaction ${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{A}_{Z}\text{X}$. What is the identity of the unknown element ${}^{A}_{Z}\text{X}$?

SOLUTION: By the conservation of mass, the mass number, A, and the atomic number, Z, must be equal on either side of the reaction. Thus,

$$226 = 222 + A_{\text{unk}} \quad \text{or} \quad A_{\text{unk}} = 226 - 222 = 4$$

$$88 = 86 + Z_{\text{unk}} \quad \text{or} \quad Z_{\text{unk}} = 88 - 86 = 2$$

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The unknown element has a mass number of $A = 4$ and an atomic number of $Z = 2$, which is a helium atom or ${}^{4}_{2}\text{He}$.

HALF-LIFE AND EXPONENTIAL DECAY

Given a radioactive element originally with N_o number of atoms, the number of atoms present at any time t is:

$$N(t) = N_o e^{-\lambda t}$$

where λ is a decay constant, defined by:

$$\lambda = \frac{0.693}{T_{1/2}}$$

Here, $T_{1/2}$ is the **half-life** of the radioactive element and represents the time required for one-half of the radioactive atoms to remain unchanged. Half-lives for radioactive elements range from fractions of seconds (e.g., polonium-212 [^{212}Po], $T_{1/2} = 3\times10^{-7}$ s) to billions of years (e.g., uranium-238 [^{238}U], $T_{1/2} = 4.5 \times 10^{9}$ yr). Radioactive decay is an exponential curve and is illustrated in Figure 5-1.

EXAMPLE: Oxygen-15 is a radioisotope with a half-life of 2.1 min. What is the decay constant λ of oxygen-15?

SOLUTION: The decay constant is related to the half-life of a radioactive element by:

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{(2.1\text{ min}) \cdot \left(\frac{60\text{ s}}{1\text{ min}}\right)} = 5.5 \times 10^{-3}\text{ s}^{-1}$$

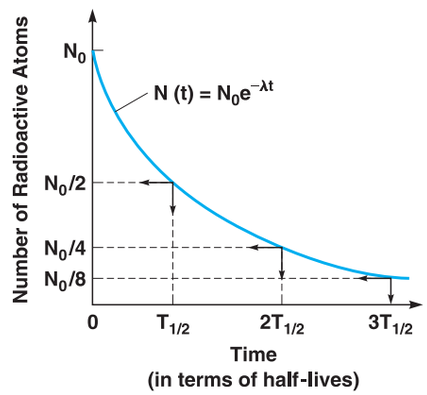

FIGURE 5-1 Radioactive decay. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

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Mass Spectrometry

Mass spectrometry is based on the principle of differentiating molecules by accelerating charged species through a strong magnetic field or across a voltage potential, in which behavior is dictated by the charge-to-mass ratio of the ions. In a common technique, a sample is bombarded with very high-energy electrons, which transfer energy into the molecules, much like photons of visible light induce the formation of an excited state. However, these excited species are so energetic that the only way to relax is by releasing an electron, thereby forming a **radical cation**, known as the **molecular ion**.

Once formed, these ions are accelerated through some differentiating field. The classic approach for differentiation is to pass the beam of charged particles through a magnetic field, which refracts the ions based on their charge-to-mass ratios and velocities. In a very broad sense, this is analogous to the refraction of white light into a spectrum of colors based on the differential interaction of variously energetic photons with the medium of the prism.

ELECTRONIC STRUCTURE

The electron of the hydrogen atom is known to have a wavelike nature. When hydrogen atoms are heated to glowing, they emit light in a quantized series of discrete lines. The wavelike nature of the hydrogen atom is described fully by the **Schrödinger wave equation**, which has four solutions called **wave functions**, represented by ψ.

When ψ is squared, a three-dimensional probability map for finding the electron around the nucleus results. This map shows where the likelihood of finding the electron is 95% or greater. This area is called an **orbital**.

There are four orbitals, one for each of the ψ^2 areas. The orbitals are called s, p, d, and f. These orbitals are described by four variables, which are called **quantum numbers**, contained in each wave function. A quantum number indicates the energy of the orbital.

Quantum Numbers

PRINCIPAL QUANTUM NUMBER, *n*

The **principal quantum number, *n***, is a positive integer that describes the size and energy level of the orbital. Orbitals are grouped according to their n value. All orbitals with the same n value are said to be in the ***n* shell**. The total number of orbitals per energy level is given by n^2.

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ANGULAR MOMENTUM QUANTUM NUMBER

The **quantum number *l*** is called the **angular momentum quantum number**. It describes the three-dimensional shape of an orbital. It can be any integer value from 0 up to $n-1$. A given n shell contains all the orbitals from $l=0$ up to $l=n-1$.

The $l=0$ orbital is called the ***s* orbital**. It is spherical with the nucleus at the center of the sphere. The s orbital can hold up to 2 electrons.

The $l=1$ orbital is called the ***p* orbital**. It is dumbbell shaped with 2 lobes and a node (0% probability) at the nucleus. The p orbital can hold up to 6 electrons.

The $l=2$ orbital is called the ***d* orbital** and it has various shapes, including 4 lobes. The d orbital can hold up to 10 electrons.

The $l=3$ orbital is called the ***f* orbital** and it also has various shapes, including 8 lobes. The f orbital can hold up to 14 electrons.

MAGNETIC QUANTUM NUMBER

The **quantum number m_l** is called the **magnetic quantum number**. It describes the orientation of the orbital about an x, y, z coordinate system. Each possible orientation can hold up to 2 electrons maximum. For each orbital, there are $2l+1$ different orientations. The quantum number m_l is all integer values from $-l$ up to $+l$.

For the ***s* orbital**, $l=0$ and $m_l=0$. There is one orientation; it is labeled $m_l=0$ and it can hold up to 2 electrons maximum.

For the ***p* orbital**, $l=1$ and $m_l=-1, 0, +1$. There are three orientations, one along the x axis, one along the y axis, and the third along the z axis. Each orientation has an m_l label, and each orientation can hold 2 electrons, for a total of 6 electrons.

For the ***d* orbital**, $l=2$ and $m_l=-2, -1, 0, +1, +2$. There are 5 orientations and each has an m_l label. The d orbital can hold a total of 10 electrons.

For the ***f* orbital**, $l=3$ and $m_l=-3, -2, -1, 0, +1, +2, +3$. There are 7 orientations and each has an m_l label. The f orbital can hold a total of 14 electrons.

SPIN QUANTUM NUMBER

Two electrons can occupy the individual orientations of each orbital. Both electrons in an orientation have a -1 charge. They do not repel each other, as might be expected, because of the spin quantum number.

When a charged particle spins, it acts like a bar magnet. When an electron spins in a clockwise manner, it acts like a magnet with, say, North up. If the other electrons spins in a counterclockwise manner, it has the opposite orientation—say, North down. So the 2 electrons pair up in a very stable manner. One of the electrons has spin $+1/2$, and the other has spin $-1/2$.

Electrons are often designated by an arrow, using $\uparrow$ for spin $+1/2$ and $\downarrow$ for spin $-1/2$ (although this is arbitrary).

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Thus for 2 electrons to occupy the same orbital orientation, they must have opposite spins.

Ground State, Excited States

Each orbital has a specific energy level associated with it. The energy levels of the orbitals are **quantized**—that is, only certain energy levels exist. If an electron that is in a low-energy orbital **(ground state)** absorbs light energy, it can use the energy to reach a higher-energy orbital, which is called an **excited state**. Which orbital it can reach depends on how much energy is absorbed.

Once in the excited state, the electron drops back to its original ground state. When it does this, it releases the energy as light energy. Figure 5-2 shows an electron in the 2-shell absorbing enough energy to reach the 5-shell, then dropping back down to the 2-shell. This process is called the **5 → 2 transition**.

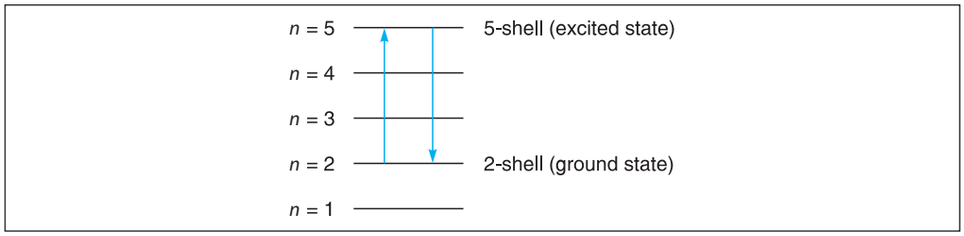

FIGURE 5-2 The 5 → 2 transition of the hydrogen atom.

When the 5 → 2 transition occurs, the electron emits light. It is a narrow band of blue light that can be seen in the visible spectrum of the light emitted by a glowing sample of hydrogen.

Absorption and Emission Line Spectra

Consider a hypothetical atom that has just three energy levels: 0 eV, 2 eV, and 5 eV. The 0 eV energy level is the ground state; the 2 eV energy level is the first excited state; and the 5 eV energy level is the second excited state. When this atom absorbs an energetic photon, the possible transitions that can occur are noted in Figure 5-3, depending on the atom's initial energy level and the energy of the photon. The emission of an energetic photon follows similar possible transitions in reverse to those reflecting the absorption of a photon as depicted in the energy-level diagram.

Photon energy is determined by the difference of the energy values of the two states involved in the transition. **Photon wavelength** can be calculated from the equation:

$$E = \frac{hc}{\lambda}$$

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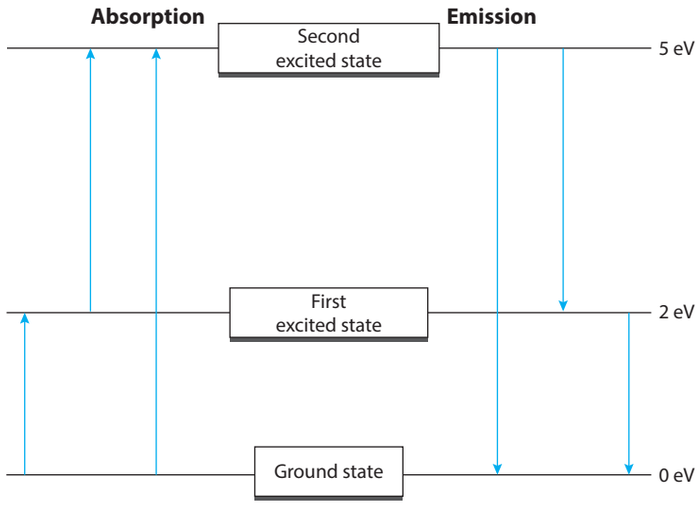

Absorption			Emission		
Energy level transition	**Photon energy**	**Photon wavelength**	**Energy level transition**	**Photon energy**	**Photon wavelength**
G⟶1	2 eV	6.21×10^{-7}m	2⟶G	5 eV	2.48×10^{-7}m
1⟶2	3 eV	4.13×10^{-7}m	2⟶1	3 eV	4.13×10^{-7}m
G⟶2	5 eV	2.48×10^{-7}m	1⟶G	2 eV	6.21×10^{-7}m

FIGURE 5-3 Energy level diagram.

or rearranging the equation to solve for λ yields:

$$\lambda = \frac{hc}{E}$$

If photon energy = 2 eV, then:

$$\lambda = \frac{hc}{E} = \frac{(4.135 \times 10^{-15}\ \text{eV} \cdot \text{s})\left(3.0 \times 10^{8}\ \frac{\text{m}}{\text{s}}\right)}{2\ \text{eV}} = 6.21 \times 10^{-7}\ \text{m}$$

If photon energy = 3 eV, then:

$$\lambda = \frac{hc}{E} = \frac{(4.135 \times 10^{-15}\ \text{eV} \cdot \text{s})\left(3.0 \times 10^{8}\ \frac{\text{m}}{\text{s}}\right)}{3\ \text{eV}} = 4.13 \times 10^{-7}\ \text{m}$$

If photon energy = 5 eV, then:

$$\lambda = \frac{hc}{E} = \frac{(4.135 \times 10^{-15}\ \text{eV} \cdot \text{s})\left(3.0 \times 10^{8}\ \frac{\text{m}}{\text{s}}\right)}{5\ \text{eV}} = 2.48 \times 10^{-7}\ \text{m}$$

The **visible emission spectrum** of the hydrogen atom consists of four distinct lines (collectively known as the **Balmer series**), with all transitions involving $n = 2$ as the ground state. The emitted photon wavelength for each of the four transitions within a hydrogen atom is noted in the following table:

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TABLE 5-1

Energy Level Transition	Wavelength of Emitted Photon (nm)	Color
$6 \rightarrow 2$	410.2	Violet
$5 \rightarrow 2$	434.1	Violet
$4 \rightarrow 2$	486.1	Cyan (Blue-green)
$3 \rightarrow 2$	656.3	Red

An expression for the energy of each of these transitions can be characterized by the following equation, expressed in terms of inverse wavelength:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

where R_H = Rydberg constant = $1.09 \times 10^7\ \text{m}^{-1}$, n_i = initial state, and n_f = final state.

Pauli Exclusion Principle

Every electron can be described by a unique set of quantum numbers n, l, m_l, and m_s.

EXAMPLE: Write all the possible quantum numbers for a $5p$ electron.

$$n = 5 \quad l = 1 \quad m_l = -1, 0, +1 \quad m_s = \pm 1/2$$

SOLUTION: A $5p$ electron can have one of six possible sets of quantum numbers, as shown in Figure 5-4.

If the $5p$ orbital is full, it will contain 6 electrons. Each electron has a different set of quantum numbers. This is called the **Pauli exclusion principle**—no two electrons in an atom can have the same set of quantum numbers.

Paramagnetism and Diamagnetism

Elements can exhibit magnetic behavior when placed in an external magnetic field. The magnetic behavior is based on the element's electronic configuration of orbital shells. Elements such as helium ($1s^2$), beryllium ($1s^2 2s^2$), and neon ($1s^2 2s^2 2p^6$) that have **filled orbital shells** are not affected by and do not respond to an external magnetic field. These elements are referred to as **diamagnetic elements**.

n	5	5	5	5	5	5
ℓ	1	1	1	1	1	1
m_ℓ	−1	0	+1	−1	0	+1
m_s	+1/2	+1/2	+1/2	−1/2	−1/2	−1/2

FIGURE 5-4 The six possible sets of quantum numbers for a $5p$ electron.

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Elements such as hydrogen ($1s^1$), lithium ($1s^2 2s^1$), and carbon ($1s^2 2s^2 2p^2$) that have **unfilled orbital shells** are strongly affected and thus do respond to an external magnetic field. These elements are referred to as **paramagnetic elements**.

Conventional Notation for Electronic Structure

THE SHELLS

The seven shells contain orbitals based on the quantum numbers. The **1-shell** contains the 1*s* orbital for a total of 2 electrons. The **2-shell** contains the 2*s* and the 2*p* orbitals for a total of 8 electrons. The **3-shell** contains the 3*s*, 3 *p*, and 3*d* orbitals, for a total of 18 electrons.

The **4-shell** contains the 4*s*, 4 *p*, 4*d*, and 4*f* orbitals. The **5-shell** contains the 5*s*, 5*p*, 5*d*, and 5*f* orbitals. There is room for a 5*g* orbital, but an element with this many electrons has not yet been discovered.

The **6-shell** contains the 6*s*, 6*p*, and 6*d* orbitals. The **7-shell** contains the 7*s* and 7*p* orbitals. Higher orbitals are also possible for these two shells, but elements with that many electrons are unknown.

The order of the orbitals from lowest to highest energy can be determined by using a mnemonic device made by listing the orbitals in each shell, then following the arrows as shown in Figure 5-5. This is called the **Aufbau principle**.

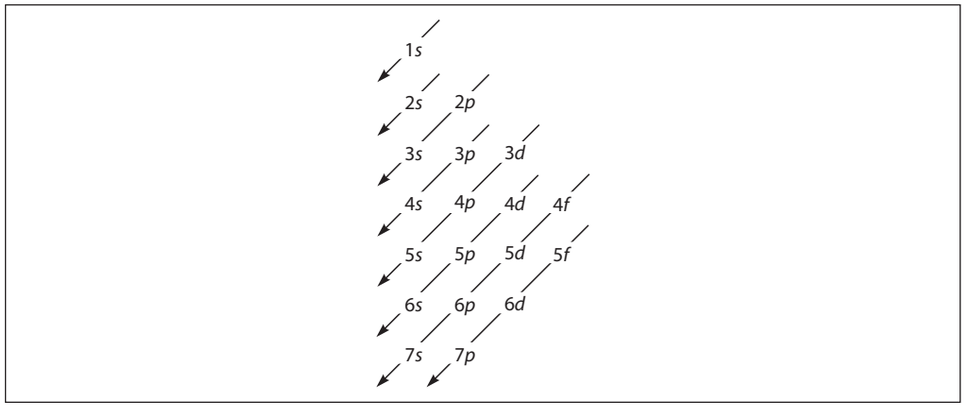

FIGURE 5-5 The order of the orbitals, in terms of increasing energy level.

ORBITAL DIAGRAMS OF MULTIELECTRON ATOMS

Going beyond hydrogen in the periodic table, an electron must be added for each subsequent element. Thus helium has two electrons, lithium has three, etc.

The first orbital is the lowest energy orbital, and the first electron always occupies this orbital. Because the first orbital is 1*s*, it holds two electrons. The second electron goes into the 1*s* orbital as well, but with an opposite spin to the first electron. The 1*s* orbital is now full. Figure 5-6 illustrates the filling of the 1*s* orbital.

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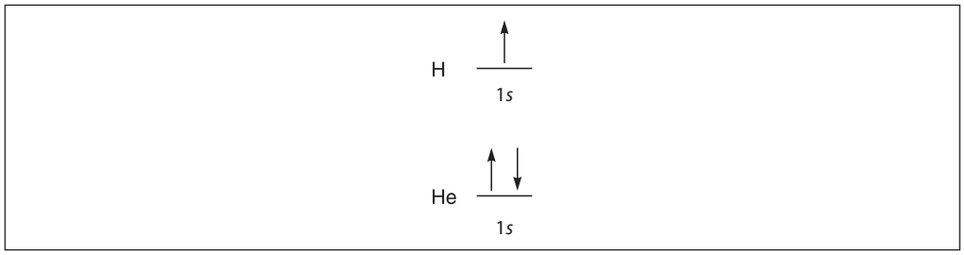

FIGURE 5-6 The orbital diagrams of hydrogen and helium.

The next higher energy orbital is the 2*s* orbital. Lithium's third electron must go into this orbital. Going on to boron, which has five electrons, the next orbital, 2*p*, is utilized. Figure 5-7 illustrates the orbital diagram of lithium and of boron.

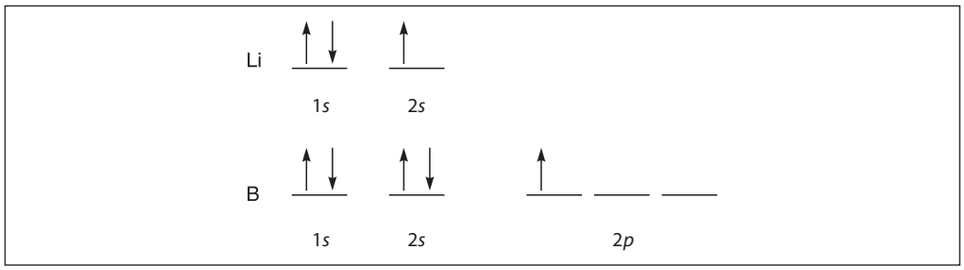

FIGURE 5-7 The orbital diagrams of lithium and boron.

With carbon, there are two electrons in the 2*p* orbital. The second electron goes into the second orientation, and it has the same spin as the first electron, as per **Hund's rule**, which states that each orientation must get one electron before any is filled. This maximizes the number of parallel spins, as shown in Figure 5-8.

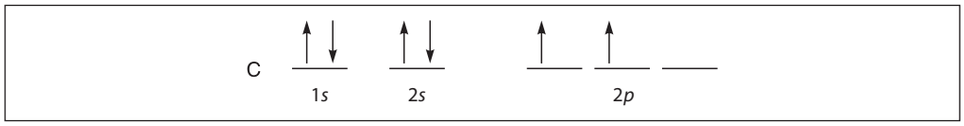

FIGURE 5-8 The orbital diagram of carbon.

Oxygen has four electrons in the 2*p* orbital. Each orientation gets a single electron, and then the first orientation gets the fourth, as shown in Figure 5-9.

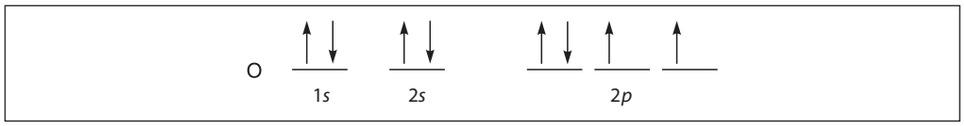

FIGURE 5-9 The orbital diagram of oxygen.

ELECTRON CONFIGURATIONS

The **electron configuration** of an element lists the orbitals in order of energy level and states how many electrons are in each orbital as a superscript. In most cases, all

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the orbitals are full until the last one, which is called the **valence orbital**. It may or may not be full. When the valence orbital is full or half-full, the element is particularly stable.

EXAMPLES

H is $1s^1$

He is $1s^2$

O is $1s^2 2s^2 2p^4$

Anomalous Electron Configurations. Very large orbitals, such as *d* and *f*, are especially stable when full or even when half-full. Some metals such as the **transition metals**, which have a higher *n* value *s* orbital preceding the valence orbital, can use the *s* electrons from that higher *n* value orbital in order to fill or half-fill the valence *d* orbital. This happens to Chromium (Cr), Copper (Cu), Niobium (Nb), Molybdenum (Mo), Lead (Pd), and Silver (Ag).

EXAMPLE: Copper looks like it would be $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$. But if one of the $4s$ electrons goes into the $3d$ orbital, the valence orbital will be full. So copper is actually $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$.

Bohr's Model of the Hydrogen Atom

In 1913, physicist Niels Bohr advanced a model of the hydrogen atom in which an electron moves in a circular orbit around the proton in the nucleus. It was explained that the attractive electric force between the positively charged proton and the negatively charged electron kept the electron in circular orbit. In Bohr's model of the atom, the electron could be found only in stable orbits or discrete energy states where no electromagnetic radiation was emitted by the atom. According to Bohr, radiation energy was emitted by the atom when the electron jumped between energy states. This model provided an explanation of atomic spectra.

In the Bohr atom, the lowest energy level, or **ground state** (characterized by the integer $n = 1$), required for the electron to maintain a circular orbit closest to the nucleus is -13.6 electron volts (eV). In order for an electron to orbit in excited energy states about the nucleus, energy must be given to the electron. Energy is provided in the form of electromagnetic radiation or light. When an electron absorbs electromagnetic radiation of a certain frequency, it jumps to the corresponding excited ground state with an energy equivalent to the frequency. When the electron returns to its ground state, the electron emits electromagnetic radiation of frequency equal to the energy difference between the two energy states. The relation for energy levels in a Bohr atom is given by:

$$E = -\left(13.6 \text{ eV}\right)\frac{Z^2}{n^2} \qquad n = 1, 2, 3, \ldots$$

and is depicted for the hydrogen atom ($Z = 1$) in Figure 5-10.

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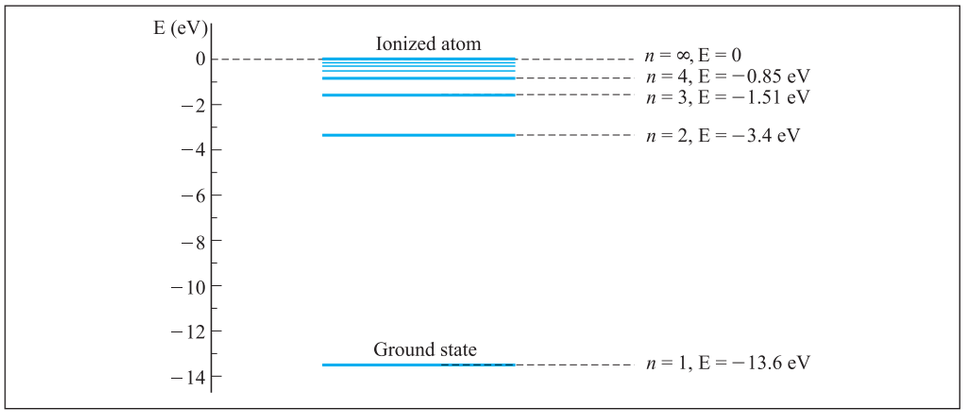

FIGURE 5-10 Energy levels in the Bohr atom. *Source:* From Frederick J. Bueche and Eugene Hecht, *Schaum's Outline of College Physics,* 10th ed., McGraw-Hill, 2006; reproduced with permission of The McGraw-Hill Companies.

Heisenberg Uncertainty Principle

The ability to accurately describe the energy level transitions of an atom depends on one's ability to quantify the motion of the orbiting atomic electron. The **Heisenberg uncertainty principle** states that it is not possible to simultaneously determine the position and momentum of the electron with a high degree of accuracy. This statement can be combined in equation form as the product of the uncertainties of measurement of position, Δx, and momentum, Δp, as:

$$\Delta x \Delta p > \frac{\hbar}{2}$$

where $\hbar = \dfrac{h}{2\pi}$ (h = Planck's constant). A similar statement can be made with regard to the product of the uncertainties of measurement of energy, ΔE, and time, Δt, as:

$$\Delta E \Delta t > \frac{\hbar}{2}$$

Effective Nuclear Charge

The **nuclear charge** of an atom would appear to be the same as its atomic number, or number of protons. However, the electrons in the innermost orbitals can have a shielding effect, so that the effective nuclear charge, Z_{eff}, is less than the atomic number Z, by the electron shielding effect. If this shielding were perfect, the maximum number of electrons in the innermost two shells would be 10. So any electrons in the third shell (such as a 3s electron) would be attracted to the nucleus by a charge equal to $Z - 10$ for an atom of atomic number Z.

Z_{eff} increases going across a row and up a column on the periodic table.

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Photoelectric Effect

Electrons are bound to the surface of a metal with an energy known as the work function. The **work function**, W_{min}, represents the minimum amount of work required to liberate the electron from the surface. When a beam of light strikes the surface of the metal, the energy of the photon is transferred to the electron. If the photon energy ($E = hf$) is greater than the work function of the bound electron, electrons (or photoelectrons) are ejected from the surface with a maximum kinetic energy, KE_{max}, given by

$$\text{KE}_{\text{max}} = hf - W_{\text{min}}$$

This is referred to as the **photoelectric effect**.

THE PERIODIC TABLE: CLASSIFICATION OF ELEMENTS INTO GROUPS BY ELECTRONIC STRUCTURE

Alkali Metals

The group IA metals are called the **alkali metals** and their valence shell electron configuration is ns^1. Hydrogen is in this group, but it has properties rather different from those of the other elements in the group. The other elements which include lithium, sodium, potassium, rubidium, and cesium are soft, low-melting, lustrous metals. They react violently with water, forming a +1 ion as a hydroxide salt and hydrogen gas. They become more reactive with increasing atomic number. Almost all of the compounds made with these metals are soluble in water.

Alkaline Earth Metals

The group IIA metals are called the **alkaline earth metals**. Their valence shell electron configuration is ns^2. Beryllium is in this group, but it has properties rather different than the others because it is a nonmetal. The other elements which include magnesium, calcium, strontium, barium, and radium are fairly soft with low density. They readily form oxides and hydroxides; they usually give up their valence electrons to form +2 ions. The oxides and hydroxides of this group are insoluble in water for the most part and do not decompose when heated. Barium hydroxide is soluble and is also a strong base.

Halogens

The group VIIA elements are called the **halogens**. This group includes fluorine, chlorine, bromine, iodine, and astatine. Their valence shell electron configuration is ns^2np^5. They have a tendency to gain one electron to form a −1 ion. They can make ionic bonds

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as a −1 ion, or they can share electrons in covalent bonds with other nonmetals. The elemental halogens exist as diatomic molecules, except for astatine. Most of the chemistry of the halogens involves oxidation–reduction reactions in water solution. Fluorine is the strongest oxidizing agent in the group and it is the most readily reduced.

Noble Gases

The elements in group VIIIA are called the **noble gases**. This group includes helium, neon, argon, krypton, xenon, and radon. Their valence shell electron configuration is ns^2np^6; in other words, their valence orbital is full.

Transition Metals

The **transition metals** have a *d* orbital as their valence orbital. Some of them use higher *n* value *s* orbital electrons in order to fill or half-fill their *d* orbital, thus stabilizing it.

The transition metals lose electrons easily and readily form ionic compounds. With the transition metals, it is the *d* orbital that gives the element its physical and chemical properties. They can form various different ionic states, ranging from +1 to +8. They tend to lose electrons from a higher *n* value shell first. Cations that have a half-full or full *d* orbital are especially stable.

Many transition metals form more than one stable oxide. Usually, the oxide that has a higher percentage of oxygen forms most easily.

Representative Elements

The **representative**, or **main-group**, **elements** consist of all *p*-block elements except helium. This includes all nonmetals (except hydrogen and helium) and all metalloids.

Metals and Nonmetals

The elements can be divided into two major categories, the metals and the nonmetals. The dividing line between them is a stairline that starts at boron and goes down to astatine. The elements to the left of the stairline are metals; those to the right of it are the nonmetals.

Metals have certain properties in common. They have luster, are malleable, and can conduct electricity and heat. They lose electrons easily to form cations, and most of their bonding is ionic in nature.

The **nonmetals** have certain properties in common as well. The ones with lower molar masses tend to be gases in the elemental state. The elements from groups V, VI, and VII can gain electrons to form anions, although most of the bonding of nonmetals, including hydrogen, is covalent.

The **metalloids** are the compounds along the stairline that share properties of both metals and nonmetals. Silicon, for instance, has luster and malleability. Others in this

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group include germanium, arsenic, antimony, tellurium, polonium, and astatine. As one goes down a column, the main group elements of groups III through VII increase their metallic character. These elements are often used as **semiconductors**.

Oxygen Group

The group VIA elements are in the **oxygen group**. This group contains oxygen, sulfur, selenium, and tellurium. Their valence shell electron configuration is ns^2np^4. They tend to form −2 ions, and they often have a −2 oxidation state in covalent compounds. The number of oxidation states increases with atomic number. Oxygen reacts readily with most metals; this reactivity decreases going down the column. Selenium and tellurium are semiconductors, whereas sulfur is an electrical insulator.

THE PERIODIC TABLE: VARIATIONS OF CHEMICAL PROPERTIES WITH GROUP AND ROW

Electronic Structure

THE REPRESENTATIVE ELEMENTS

Groups IA through VIIIA are called the **representative**, or **main-group**, **elements**. They have either *s* or *p* orbitals for their valence orbital. The total number of electrons in the valence shell of each A group is equivalent to the group number. For instance, carbon in group IVA has the electron configuration $2s^2 2p^2$ and has 4 electrons in its 2-shell.

NOBLE GASES

Noble gases have complete valence orbitals, which make them very stable elements and, for the most part, they are nonreactive. They do not form ions. Xenon, krypton, and radon react with the very electronegative elements oxygen and fluorine to make a few covalent compounds. The noble gases are monatomic in the elemental form.

TRANSITION METALS

The B groups are called the **nonrepresentative elements**, or **the transition metals**. They are found in the middle of the periodic table. They have a *d* orbital for their valence orbital.

The **lanthanides** and the **actinides** are found at the bottom of the table. They have an *f* orbital for their valence orbital.

Valence Electrons

The chemical properties of elements are closely associated with the electron configuration of their outermost shells. The elements are arranged into groups (the columns)

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and periods (the rows). Within a group, every atom has the same number of electrons (valence electrons) in its valence orbital, and they share similar chemical properties. Within a period, electrons are added sequentially from left to right to fill the orbitals within the shells. The period number (1–7) corresponds exactly to the shell number for the *s* and *p* orbitals within that period (see Figure 5-11). The number of electrons in the valence orbital is what gives a group its characteristic chemical properties.

Ionization Energy

The **ionization energy**, ***I***, of an atom is the energy required to remove an electron from the valence shell, making it an ion.

VARIATION OF IONIZATION ENERGY WITH GROUP AND ROW

The ionization energy for the hydrogen atom is 1312 kJ/mole. Elements that have fewer electrons in their valence orbital have lower ionization energies. The elements in group I have the lowest first ionization energies in their respective periods; those in group VIII have the highest. It is more difficult to remove an electron from a full orbital than from one that is not full. If the removal of an electron results in a full valence orbital, the ionization energy is lower.

As shown in the following table, the ionization energy decreases as one goes down a group, because electrons that are held in higher *n* value shells are farther from the nucleus and held less tightly.

TABLE 5-2 The Ionization Energies (kJ/mol) of the First 20 Elements

Z	Element	First	Second	Third	Fourth	Fifth	Sixth
1	H	1,312.0					
2	He	2,373.0	5,251				
3	Li	520.0	7,300	11,815			
4	Be	899.0	1,757	14,850	21,005		
5	B	801.0	2,430	3,660	25,000	32,820	
6	C	1,086.0	2,350	4,620	6,220	38,000	47,261
7	N	1,400.0	2,860	4,580	7,500	9,400	53,000
8	O	1,314.0	3,390	5,300	7,470	11,000	13,000
9	F	1,680.0	3,370	6,050	8,400	11,000	15,200
10	Ne	2,080.0	3,950	6,120	9,370	12,200	15,000
11	Na	495.9	4,560	6,900	9,540	13,400	16,600
12	Mg	738.1	1,450	7,730	10,500	13,600	18,000
13	Al	577.9	1,820	2,750	11,600	14,800	18,400
14	Si	786.3	1,580	3,230	4,360	16,000	20,000
15	P	1,012.0	1,904	2,910	4,960	6,240	21,000
16	S	999.5	2,250	3,360	4,660	6,990	8,500
17	Cl	1,251.0	2,297	3,820	5,160	6,540	9,300
18	Ar	1,521.0	2,666	3,900	5,770	7,240	8,800
19	K	418.7	3,052	4,410	5,900	8,000	9,600
20	Ca	589.5	1,145	4,900	6,500	8,100	11,000

1 IA	2	3	4	5	6	7	8	9	10	11	12	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.0079	IIA																2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.989	12 Mg 24.305											13 Al 26.981	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 59.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.905	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.90	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 #Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)						

*Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
#Actinides	90 Th 232.03	91 Pa 231.03	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (257)	102 No (255)	103 Lr (256)

FIGURE 5-11 The periodic table.

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The first ionization energy is the lowest because subsequent electrons are more difficult to remove because of the positive charge produced. It is easiest to remove an electron from a partially-filled orbital, and more difficult from a filled valence orbital.

Electron Affinity

Ionization energy is the energy required to form a cation. **Electron affinity** is the energy change that occurs when electrons are added to the valence orbital, producing an anion.

VARIATION OF ELECTRON AFFINITY WITH GROUP AND ROW

Energy is given off when anions are formed; thus, a negative sign accompanies the energy difference to indicate its direction of flow. The greater the electron affinity of an atom, the more stable the anion that is formed. It would be expected that group VII elements would have the largest (most negative) electron affinity, because only 1 electron is required to fill the valence orbital.

Generally, the electron affinity increases going across a period to group VII. It then drops, and then increases again going across the next period. Within a group, the electron affinities are approximately equal. Electron affinity is lower to produce a half-full or a full valence orbital, and it is higher if one is adding an electron to an already half-full or full orbital.

Electronegativity

Electronegativity is the ability of an atom in a molecule to pull electron density of a bond toward itself. It is used most often with covalently-bonded atoms.

VARIATION OF ELECTRONEGATIVITY WITH GROUP AND ROW

Electronegativity generally increases going across a period and decreases going down a group. Fluorine has the highest electonegativity, at 4.0 on the **Pauling scale**, followed by oxygen at 3.5, then chlorine and nitrogen at 3.0. These numbers are averages of the absolute values for the ionization energy for an atom.

Atomic Radius

The size of atoms is related to the number of electrons and shells that it has. Generally, the size decreases going across a period, because as the electron number increases, the attraction to the nucleus increases (Z_{eff} increases), thus the atomic radius decreases.

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Going down a group, the shell number increases and Z_{eff} decreases, thus the atomic radius increases (see Figure 5-12).

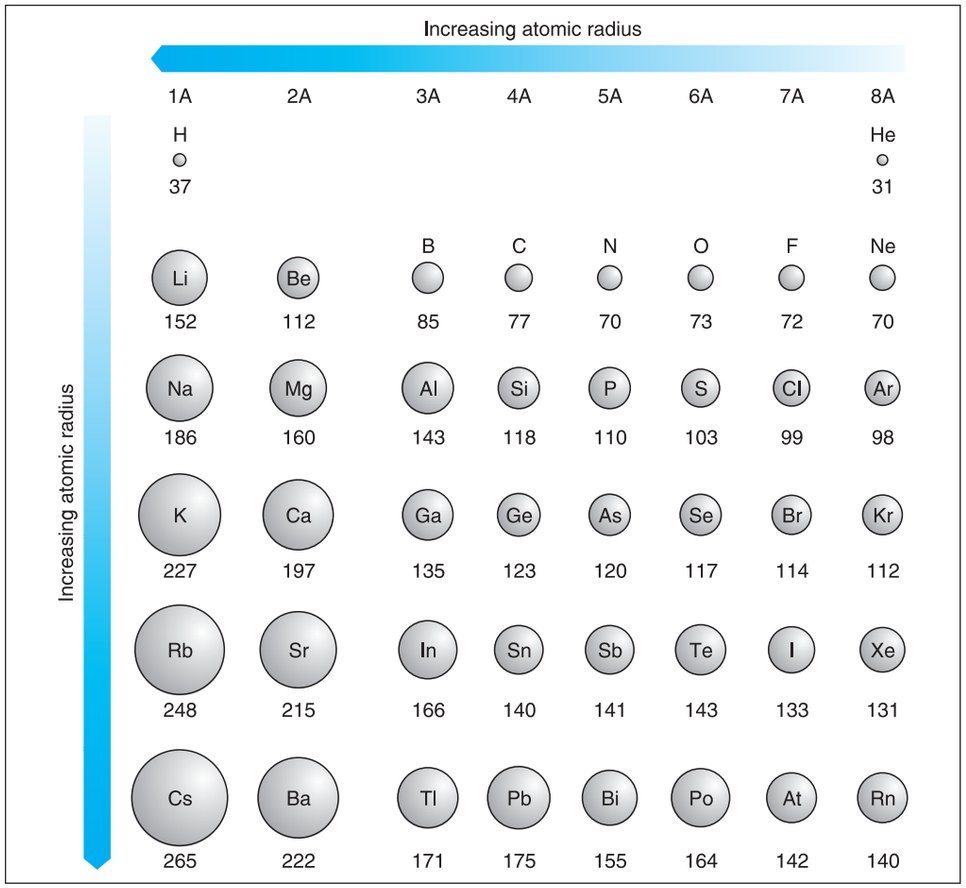

FIGURE 5-12 Atomic radii (in picometers) of the main group elements.

Ionic Radius

The sizes of ions depend on whether they have lost or gained electrons. The more electrons an ion has, the larger its radius. Thus Fe^{+2} is larger than Fe^{+3}, but both are smaller than an Fe atom. If two ions are **isoelectronic** (have the same number of electrons), then the radius decreases across a row and increases down a column, as do neutral atoms.

BONDING BETWEEN IONS

Bonds between atoms that have an electronegativity difference of more than 2 are ionic. An **ionic bond** consists of an electrostatic attraction between a positive ion and a negative ion. It occurs when an element with a low ionization energy encounters an

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element with a high electron affinity, such as when sodium encounters chlorine:

$$2Na + Cl_2 \rightarrow 2NaCl$$

Ions arrange themselves into a lattice network, where no two like ions are neighbors. The energy required to break up the lattice into individual ions is called the **lattice energy**, ***U***. The energy given off when a lattice is created is $-U$, where $U = kz_1z_2/d$.

In this equation, k is a proportionality constant, z_1 is the charge on the cation, z_2 is the charge on the anion, and d is the average distance between their nuclei. The lattice energy is greatest when the charges are large and the diameters are small. Thus LiF has a greater lattice energy than LiI, because F is smaller than I. By the same reasoning, AlI_3 has a greater lattice energy than NaI because the charges are greater.

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