Lecture 2
Atomic Structure

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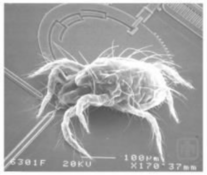
Materials scientists and engineers have developed a set of instruments in order to characterize the structure of materials at various length scales.

We can examine and describe the structure of materials at five different levels:

1. Atomic structure .
2. Short- and long-range atomic arrangements .
3. Nanostructure .
4. Microstructure .
5. Macrostructure .

The Scale of Things – Nanometers and More

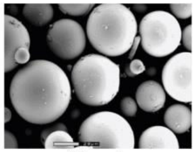
Things Natural



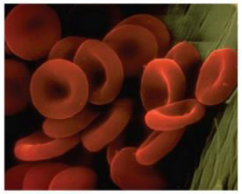
Dust mite
↔
200 µm

Ant
~ 5 mm

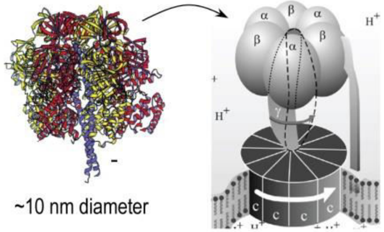
Human hair
~ 60-120 µm wide



Fly ash
~ 10-20 µm

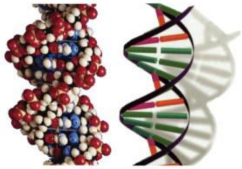


Red blood cells
(~7-8 µm)

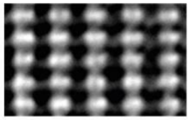


~10 nm diameter

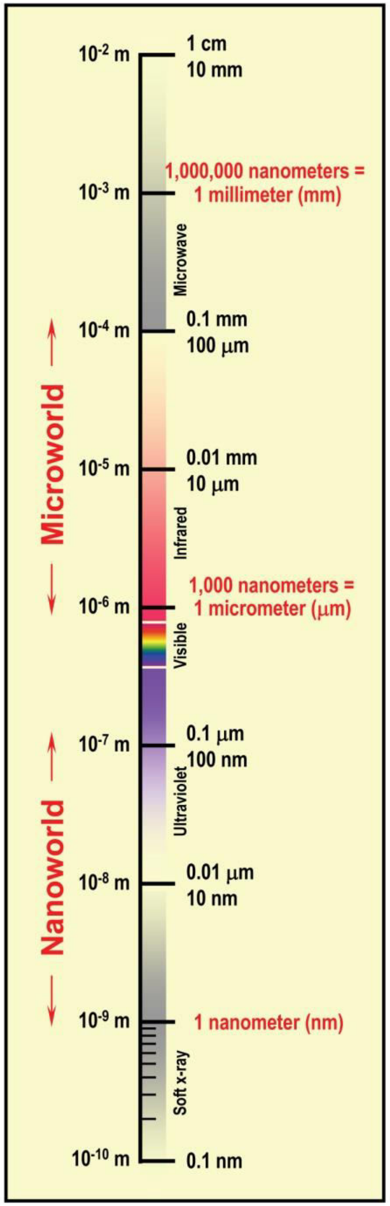
ATP synthase



DNA
~2-1/2 nm diameter



Atoms of silicon
spacing 0.078 nm



10^{-2} m — 1 cm, 10 mm

1,000,000 nanometers = 1 millimeter (mm)

10^{-3} m

Microwave

10^{-4} m — 0.1 mm, 100 µm

Microworld

10^{-5} m — 0.01 mm, 10 µm

Infrared

1,000 nanometers = 1 micrometer (µm)

10^{-6} m

Visible

10^{-7} m — 0.1 µm, 100 nm

Nanoworld

Ultraviolet

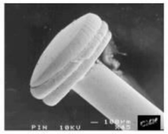
10^{-8} m — 0.01 µm, 10 nm

10^{-9} m — **1 nanometer (nm)**

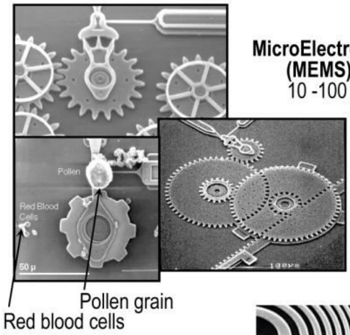
Soft x-ray

10^{-10} m — 0.1 nm

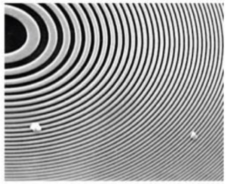
Things Manmade



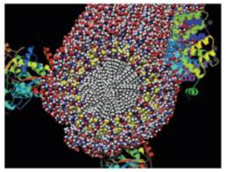
Head of a pin
1-2 mm



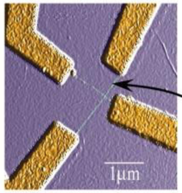
MicroElectroMechanical (MEMS) devices
10 -100 µm wide



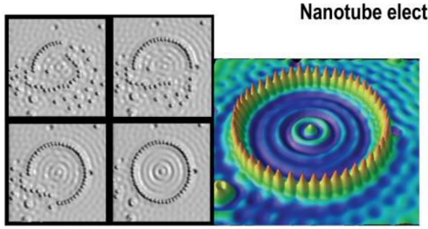
Zone plate x-ray "lens"
Outer ring spacing ~35 nm



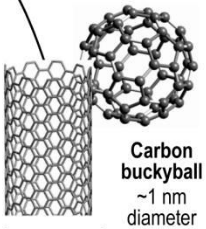
Self-assembled, Nature-inspired structure
Many 10s of nm



Nanotube electrode



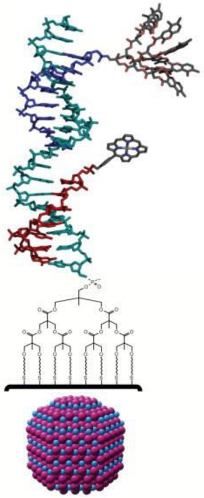
Quantum corral of 48 iron atoms on copper surface positioned one at a time with an STM tip
Corral diameter 14 nm



Carbon nanotube
~1.3 nm diameter

Carbon buckyball
~1 nm diameter

The Challenge



Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

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Office of Science, U.S. DOE
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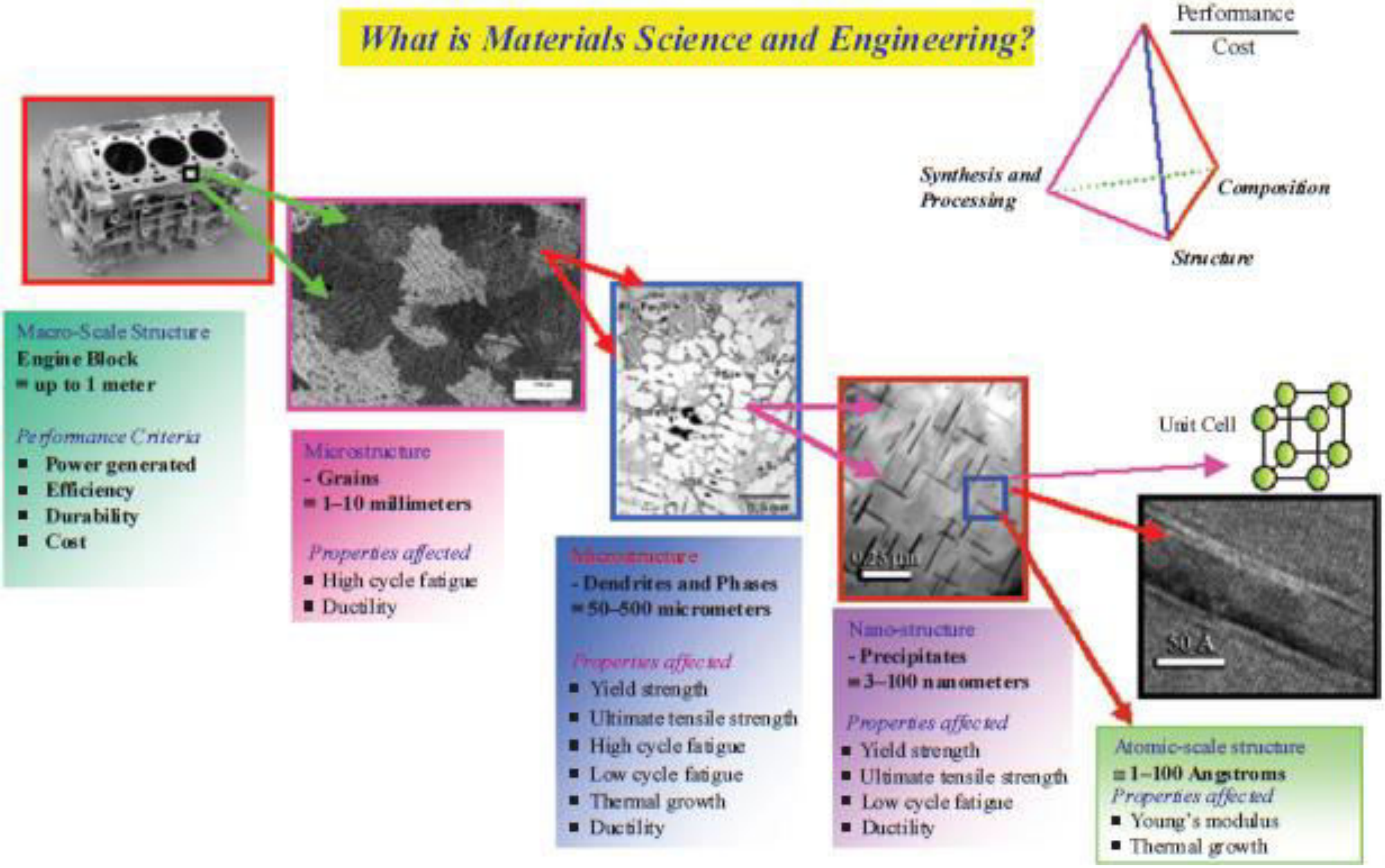
What is Materials Science and Engineering?



Macro-Scale Structure

Engine Block

≈ up to 1 meter

Performance Criteria

- **Power generated**
- **Efficiency**
- **Durability**
- **Cost**

Microstructure

- Grains

≈ 1–10 millimeters

Properties affected

- High cycle fatigue
- Ductility

Microstructure

- Dendrites and Phases

≈ 50–500 micrometers

Properties affected

- Yield strength
- Ultimate tensile strength
- High cycle fatigue
- Low cycle fatigue
- Thermal growth
- Ductility

Nano-structure

- Precipitates

≈ 3–100 nanometers

Properties affected

- Yield strength
- Ultimate tensile strength
- Low cycle fatigue
- Ductility

Atomic-scale structure

≅ 1–100 Angstroms

Properties affected

- Young's modulus
- Thermal growth

Atomic structure : (the nucleus consisting of protons and neutrons and the electrons surrounding the nucleus) in order to lay a foundation for understanding how atomic structure affects the properties, behavior, and resulting applications of engineering materials.

We will see that the structure of atoms affects the types of bonds that hold materials together. These different types of bonds directly affect the suitability of materials for real-world engineering applications. The diameter of atoms typically is measured using the angstrom unit (A° or 10^{-10} m)

Crystalline materials : **T**hat exhibit periodic geometrical arrangements of atoms or ions , have **short-** and **long-range atomic arrangements**. In the atoms or ions show a particular short-range atomic arrangements, order only over relatively short distances (1 to 10 A^o)For

crystalline materials, the long-range atomic order is in the form of atoms or ions arranged in a three-dimensional pattern that repeats over much larger distances (from 10 nm to cm)

Amorphous materials: have only short-range atomic arrangements.

Nanoscience : the study of materials at the nanometer length Scale.

Nanotechnology : is the manipulation and development of devices at the nanometer length scale.

Nanostructure: is the structure of a material at a length scale of 1 to 100 nm.

The **Microstructure : is the structure of materials at a length scale of 100 to** 100,000 nm or 0.1 to 100 micrometers (often written as µm and pronounced as "microns"). The microstructure typically refers to features such as the grain size of a crystalline material and others related to defects in materials. (A *grain is a single crystal* in a material composed of many crystals.)

Macrostructure: is the structure of a material at a macroscopic level where the length scale is >100 µm . Features that constitute macrostructure include porosity, surface coatings, and internal and external micro cracks.

allotropes of carbon: We will see that, although both diamond and graphite are made from pure carbon, they have different materials properties.

The key to understanding these differences is to understand how the atoms are arranged in each allotrope.

2: 1 The Structure of the Atom

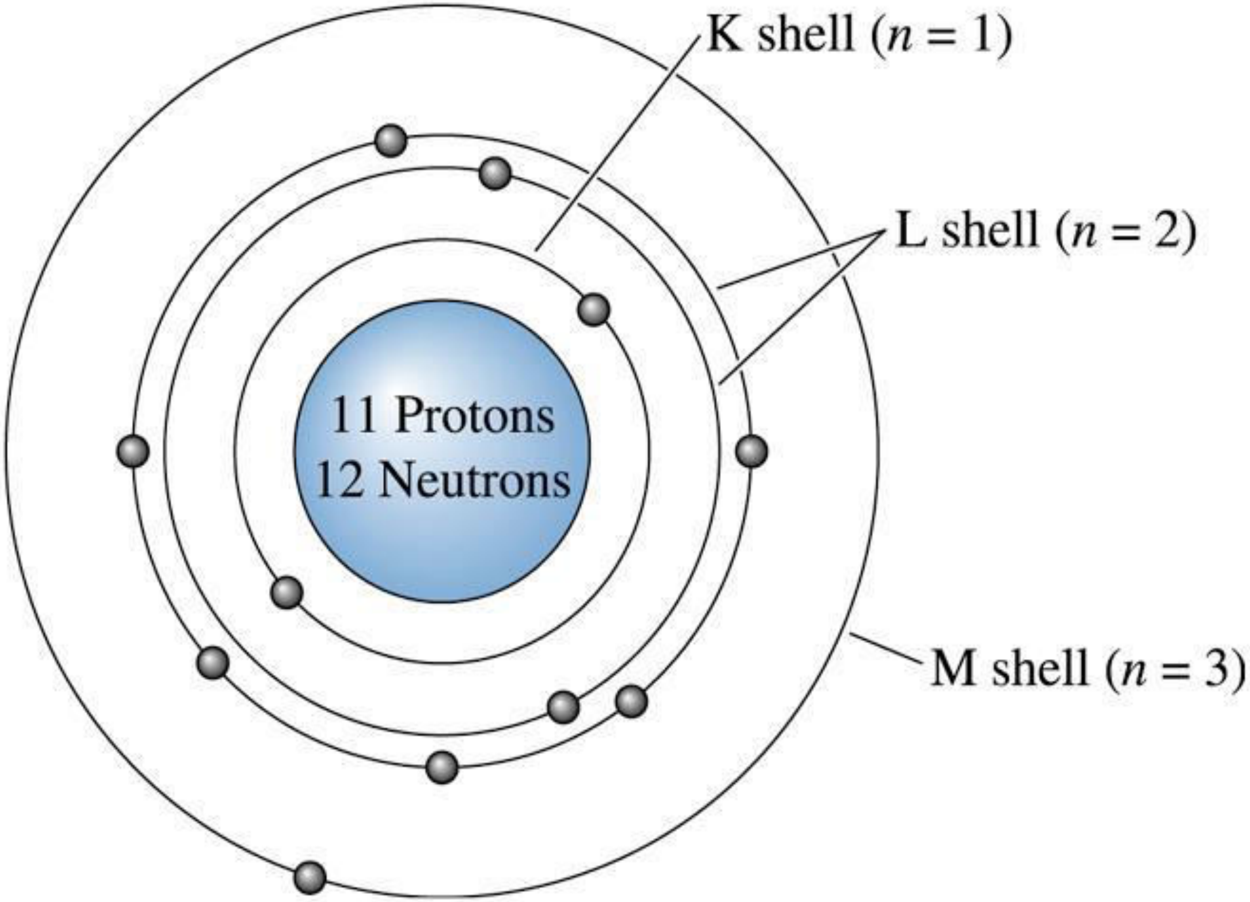


Figure 2.8 The atomic structure of sodium, atomic number 11, showing the electrons in the *K, L,* and *M* quantum shells

2: 1 The Structure of the Atom

An atom is composed of a nucleus surrounded by electrons. The nucleus contains neutrons and positively charged protons and carries a net positive charge. The negatively charged electrons are held to the nucleus by an electrostatic attraction. The electrical charge *q carried by each electron and proton* is $1.6 \ X\ 10^{-19}$ coulomb (C).

The **atomic number of an element :** is equal to the number of protons in each atom. Thus, an iron atom, which contains 26 protons, has an atomic number of 26 . The atom as a whole is electrically neutral because the number of protons and electrons are equal.

Most of the mass of the atom is contained within the nucleus.

The mass of each proton and neutron is $1.6\,7X\ 10^{-24}\ g$

But the mass of each electron is only 9.11×10^{-28} g.

The **atomic mass M, which is equal to the total mass of the average number of protons and neutrons** in the atom in atomic mass units, is also the mass in grams of the **Avogadro constant** N_A of atoms.

The quantity $N_A = 6.022 \times 10^{23}$ atoms/ mol is the number of atoms or molecules in a mole. Therefore, the atomic mass has units of g/mol. An alternative unit for atomic mass is the **atomic mass unit, or amu, which is 1/12 the mass of carbon 12 (i.e., the** carbon atom with twelve **nucleons—six protons and six neutrons).**

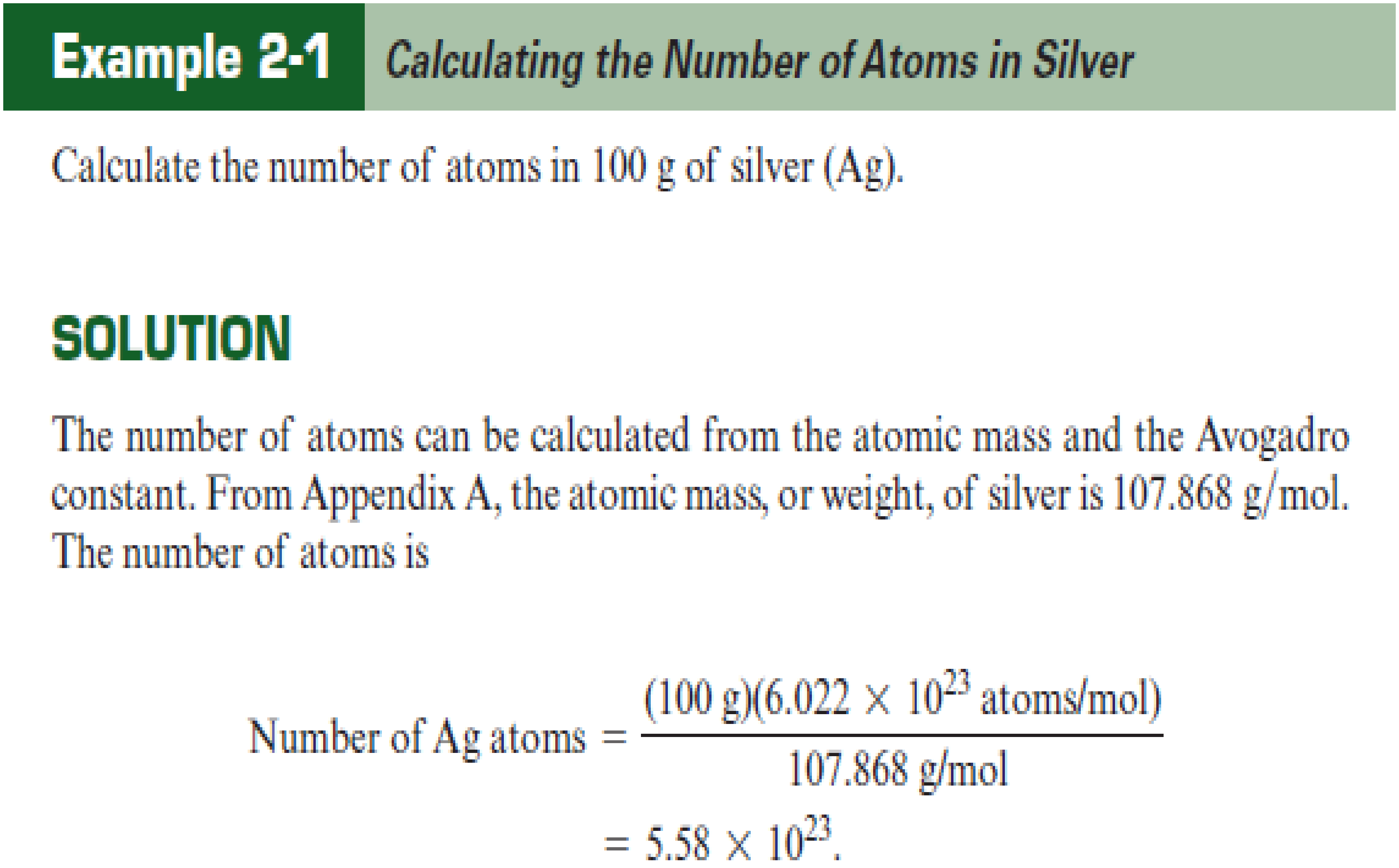
As an example, one mole of iron contains 6.022×10^{23} atoms and has a mass of 55.847 g, or 55.847 amu.

Calculations

Including a material’s atomic mass and the Avogadro constant are helpful to understanding more about the structure of a material.

Example 2-1 illustrates how to calculate the number of atoms for silver, a metal and a good electrical conductor.

Example 2-2 illustrates an application to magnetic materials.



Example 2-1 *Calculating the Number of Atoms in Silver*

Calculate the number of atoms in 100 g of silver (Ag).

SOLUTION

The number of atoms can be calculated from the atomic mass and the Avogadro constant. From Appendix A, the atomic mass, or weight, of silver is 107.868 g/mol. The number of atoms is

$$\text{Number of Ag atoms} = \frac{(100\text{ g})(6.022 \times 10^{23}\text{ atoms/mol})}{107.868\text{ g/mol}}$$
$$= 5.58 \times 10^{23}.$$

Example 2-2 *Iron-Platinum Nanoparticles for Information Storage*

Scientists are considering using nanoparticles of such magnetic materials as iron-platinum (Fe-Pt) as a medium for ultra-high density data storage. Arrays of such particles potentially can lead to storage of trillions of bits of data per square inch—a capacity that will be 10 to 100 times higher than any other devices such as computer hard disks. If these scientists considered iron (Fe) particles that are 3 nm in diameter, what will be the number of atoms in one such particle?

SOLUTION

You will learn in a later chapter on magnetic materials that such particles used in recording media tend to be acicular (needle like). For now, let us assume the magnetic particles are spherical in shape.

The radius of a particle is 1.5 nm.

$$\text{Volume of each iron magnetic nanoparticle} = (4/3)\pi(1.5 \times 10^{-7}\text{ cm})^3 = 1.4137 \times 10^{-20}\text{ cm}^3$$

Density of iron = 7.8 g/cm^3. Atomic mass of iron = 55.847 g/mol.

$$\text{Mass of each iron nanoparticle} = 7.8\text{ g/cm}^3 \times 1.4137 \times 10^{-20}\text{ cm}^3 = 1.1027 \times 10^{-19}\text{ g}$$

One mole or 55.847 g of Fe contains 6.022×10^{23} atoms, therefore, the number of atoms in one Fe nanoparticle will be 1189. This is a very small number of atoms. Compare this with the number of atoms in an iron particle that is 10 micrometers in diameter. Such larger iron particles often are used in breakfast cereals, vitamin tablets, and other applications.

The Electronic Structure of the Atom

Electrons occupy discrete energy levels within the atom. Each electron possesses a particular energy with no more than two electrons in each atom having the same energy. This also implies that there is a discrete energy difference between any two energy levels. Since each element possesses a different set of these energy levels, the differences between them also are unique. Both the energy levels and the differences between them are known with great precision for every element, forming the basis for many types of **spectroscopy**. Using a spectroscopic method, the identity of elements in a sample may be determined.

Quantum Numbers The energy level to which each electron belongs is identified by four **quantum numbers**. The four quantum numbers are the principal quantum number n, the azimuthal or secondary quantum number l, the magnetic quantum number m_l, and the spin quantum number m_s.

The principal quantum number reflects the grouping of electrons into sets of energy levels known as shells. Azimuthal quantum numbers describe the energy levels within each shell and reflect a further grouping of similar energy levels, usually called orbitals. The magnetic quantum number specifies the orbitals associated with a particular azimuthal quantum number within each shell. Finally, the **spin quantum number** (m_s) is assigned values of $+1/2$ and $-1/2$, which reflect the two possible values of "spin" of an electron.

According to the **Pauli Exclusion Principle**, within each atom, no two electrons may have the same four quantum numbers, and thus, each electron is designated by a unique set of four quantum numbers. The number of possible energy levels is determined by the first three quantum numbers.

1. The principal quantum number n is assigned integer values 1, 2, 3, 4, 5, . . . that refer to the quantum shell to which the electron belongs. A **quantum shell** is a *set* of fixed energy levels to which electrons belong.

   Quantum shells are also assigned a letter; the shell for $n = 1$ is designated K, for $n = 2$ is L, for $n = 3$ is M, and so on. These designations were carried over from the nomenclature used in optical spectroscopy, a set of techniques that predates the understanding of quantized electronic levels.
2. The *number* of energy levels in *each* quantum shell is determined by the **azimuthal quantum number** l and the magnetic quantum number m_l. The azimuthal quantum numbers are assigned $l = 0, 1, 2, \ldots, n - 1$. For example, when $n = 2$, there are two azimuthal quantum numbers, $l = 0$ and $l = 1$. When $n = 3$, there are three azimuthal quantum numbers, $l = 0$, $l = 1$, and $l = 2$. The azimuthal quantum numbers are designated by lowercase letters; one speaks, for instance, of the d orbitals:

$$s \text{ for } l = 0 \quad d \text{ for } l = 2$$

$$p \text{ for } l = 1 \quad f \text{ for } l = 3$$

3. The number of values for the magnetic quantum number m_l gives the number of energy levels, or orbitals, for each azimuthal quantum number. The total number of magnetic quantum numbers for each l is $2l + 1$. The values for m_l are given by whole numbers between $-l$ and $+l$. For example, if $l = 2$, there are $2(2) + 1 = 5$ magnetic quantum numbers with values $-2, -1, 0, +1$, and $+2$. The combination of l and m_l specifies a particular orbital in a shell.
4. No more than two electrons with opposing electronic spins ($m_s = +1/2$ and $-1/2$) may be present in each orbital.

By carefully considering the possible numerical values for n, l, and m_l, the range of *possible* quantum numbers may be determined. For instance, in the K shell (that is, $n = 1$), there is just a single s orbital (as the only allowable value of l is 0 and m_l is 0). As a result, a K shell may contain no more than two electrons. As another example, consider an M shell. In this case, $n = 3$, so l takes values of 0, 1, and 2, (there are s, p, and d orbitals present). The values of m_l reflect that there is a single s orbital ($m_l = 0$, a single value), three p orbitals ($m_l = -1, 0, +1$, or three values), and five d orbitals ($m_l = -2, -1, 0, +1, +2$, or five discrete values).

The shorthand notation frequently used to denote the electronic structure of an atom combines the numerical value of the principal quantum number, the lowercase letter notation for the azimuthal quantum number, and a superscript showing the number of electrons in each type of orbital. The shorthand notation for neon, which has an atomic number of ten, is

$$1s^2 2s^2 2p^6$$

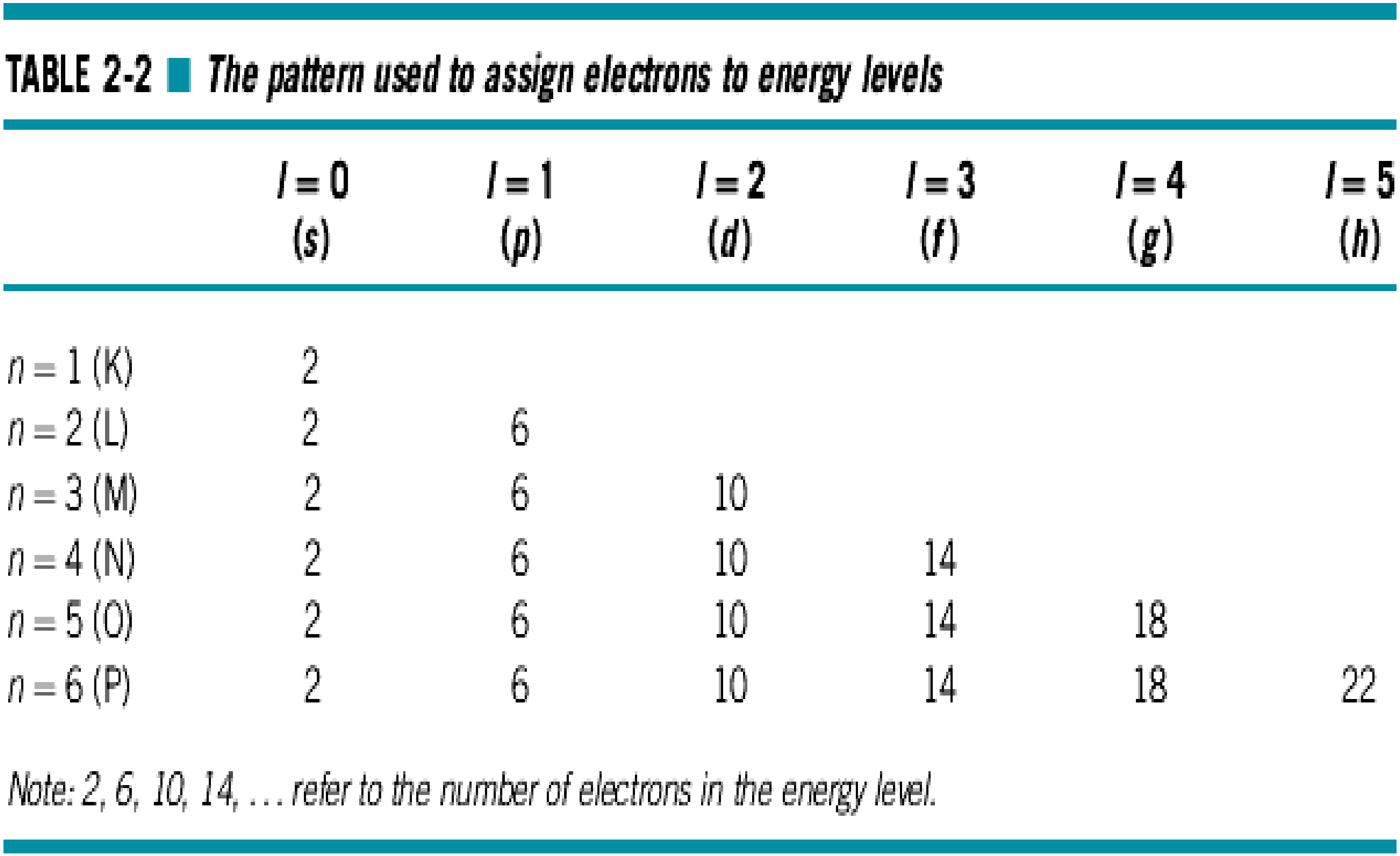
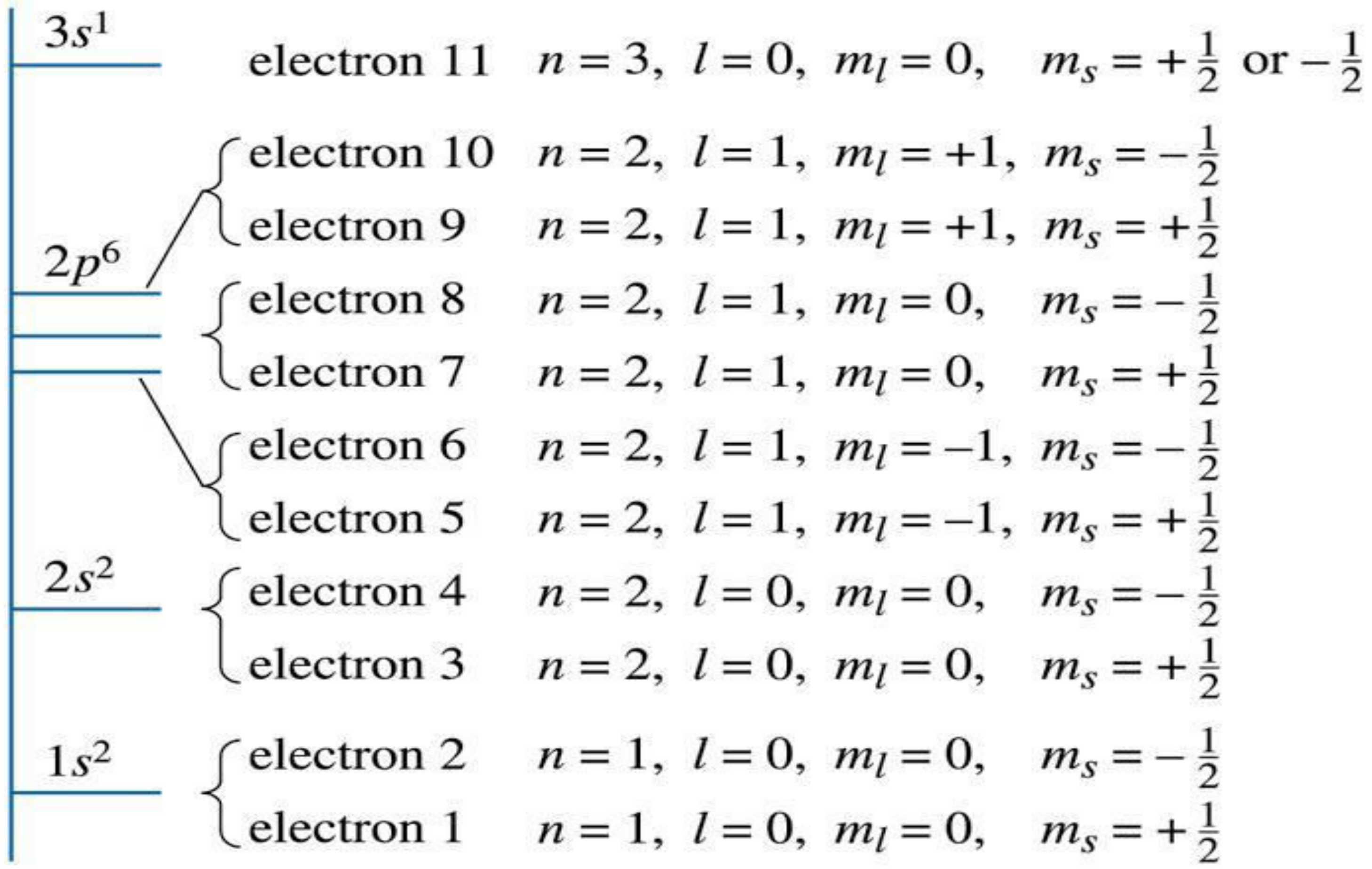


TABLE 2-2 ■ *The pattern used to assign electrons to energy levels*

	$l = 0$ (s)	$l = 1$ (p)	$l = 2$ (d)	$l = 3$ (f)	$l = 4$ (g)	$l = 5$ (h)
$n = 1$ (K)	2					
$n = 2$ (L)	2	6				
$n = 3$ (M)	2	6	10			
$n = 4$ (N)	2	6	10	14		
$n = 5$ (O)	2	6	10	14	18	
$n = 6$ (P)	2	6	10	14	18	22

Note: 2, 6, 10, 14, . . . refer to the number of electrons in the energy level.



electron 11 $n = 3,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$ or $-\frac{1}{2}$

electron 10 $n = 2,\ l = 1,\ m_l = +1,\ m_s = -\frac{1}{2}$

electron 9 $n = 2,\ l = 1,\ m_l = +1,\ m_s = +\frac{1}{2}$

electron 8 $n = 2,\ l = 1,\ m_l = 0,\ m_s = -\frac{1}{2}$

electron 7 $n = 2,\ l = 1,\ m_l = 0,\ m_s = +\frac{1}{2}$

electron 6 $n = 2,\ l = 1,\ m_l = -1,\ m_s = -\frac{1}{2}$

electron 5 $n = 2,\ l = 1,\ m_l = -1,\ m_s = +\frac{1}{2}$

electron 4 $n = 2,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2}$

electron 3 $n = 2,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$

electron 2 $n = 1,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2}$

electron 1 $n = 1,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$

Figure 2.9 The complete set of quantum numbers for each of the 11 electrons in sodium

Deviations from Expected Electronic Structures The energy levels of the quantum shells do not fill in strict numerical order. The **Aufbau Principle** is a graphical device that predicts deviations from the expected ordering of the energy levels. The Aufbau principle is shown in Figure 2-7. To use the Aufbau Principle, write the possible combinations of the principal quantum number and azimuthal quantum number for each quantum shell. The combinations for each quantum shell should be written on a single line. As the principal quantum number increases by one, the number of combinations within each shell increases by one (i.e., each row is one entry longer than the prior row). Draw arrows through the rows on a diagonal from the upper right to the lower left as shown in Figure 2-7. By following the arrows, the order in which the energy levels of each quantum level are filled is predicted.

For example, according to the Aufbau Principle, the electronic structure of iron, atomic number 26, is

$$1s^22s^22p^63s^23p^64s^23d^6$$

Conventionally, the principal quantum numbers are arranged from lowest to highest when writing the electronic structure. Thus, the electronic structure of iron is written

$$1s^22s^22p^63s^23p^6 \qquad 3d^64s^2$$

The unfilled 3*d* level (there are five *d* orbitals, so in shorthand d^1, d^2, . . . , d^{10} are possible) causes the magnetic behavior of iron.

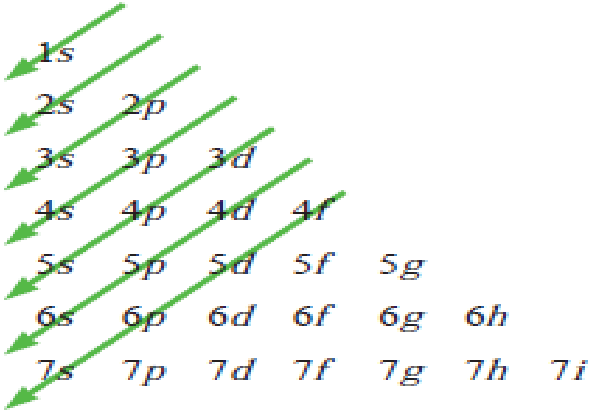


Figure 2-7
The Aufbau Principle. By following the arrows, the order in which the energy levels of each quantum level are filled is predicted: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, etc. Note that the letter designations for $l = 4, 5, 6$ are *g*, *h*, and *i*.

Note that not all elements follow the Aufbau principle. A few, such as copper, are exceptions. According to the Aufbau Principle, copper should have the electronic structure $1s^22s^22p^63s^23p^63d^94s^2$, but copper actually has the electronic structure

$$1s^22s^22p^63s^23p^63d^{10} \qquad 4s^1$$

Generally, electrons will occupy each orbital of a given energy level singly before the orbitals are doubly occupied. For example, nitrogen has the electronic structure

$$1s^2 \qquad 2s^22p^3$$

Each of the three *p* orbitals in the L shell contains one electron rather than one orbital containing two electrons, one containing one electron, and one containing zero electrons.

Valence

The **valence** of an atom is the number of electrons in an atom that participate in bonding or chemical reactions. Usually, the valence is the number of electrons in the outer *s* and *p* energy levels. The valence of an atom is related to the ability of the atom to enter into chemical combination with other elements. Examples of the valence are

$$\mathrm{Mg}: 1s^2\,2s^2\,2p^6 \qquad 3s^2 \qquad \text{valence} = 2$$

$$\mathrm{Al}: 1s^2\,2s^2\,2p^6 \qquad 3s^23p^1 \qquad \text{valence} = 3$$

$$\mathrm{Si}: 1s^2\,2s^2\,2p^6 \qquad 3s^2\,3p^2 \qquad \text{valence} = 4$$

Valence also depends on the immediate environment surrounding the atom or the neighboring atoms available for bonding. Phosphorus has a valence of five when it combines with oxygen, but the valence of phosphorus is only three—the electrons in the $3p$ level—when it reacts with hydrogen. Manganese may have a valence of 2, 3, 4, 6, or 7!

Atomic Stability and Electronegativity If an atom has a valence of zero, the element is inert (non-reactive). An example is argon, which has the electronic structure:

$$1s^2\,2s^2\,2p^6 \qquad 3s^2\,3p^6$$

Other atoms prefer to behave as if their outer *s* and *p* levels are either completely full, with eight electrons, or completely empty. Aluminum has three electrons in its outer *s* and *p* levels. An aluminum atom readily gives up its outer three electrons to empty the 3*s* and 3*p* levels. The atomic bonding and the chemical behavior of aluminum are determined by how these three electrons interact with surrounding atoms.

On the other hand, chlorine contains seven electrons in the outer 3*s* and 3*p* levels. The reactivity of chlorine is caused by its desire to fill its outer energy level by accepting an electron.

Electronegativity describes the tendency of an atom to gain an electron. Atoms with almost completely filled outer energy levels—such as chlorine—are strongly electronegative and readily accept electrons. Atoms with nearly empty outer levels—such as sodium—readily give up electrons and have low electronegativity. High atomic number elements also have low electronegativity because the outer electrons are at a greater distance from the positive nucleus, so that they are not as strongly attracted to the atom. Electronegativities for some elements are shown in Figure 2-8. Elements with low electronegativity (i.e., <2.0) are sometimes described as **electropositive**.

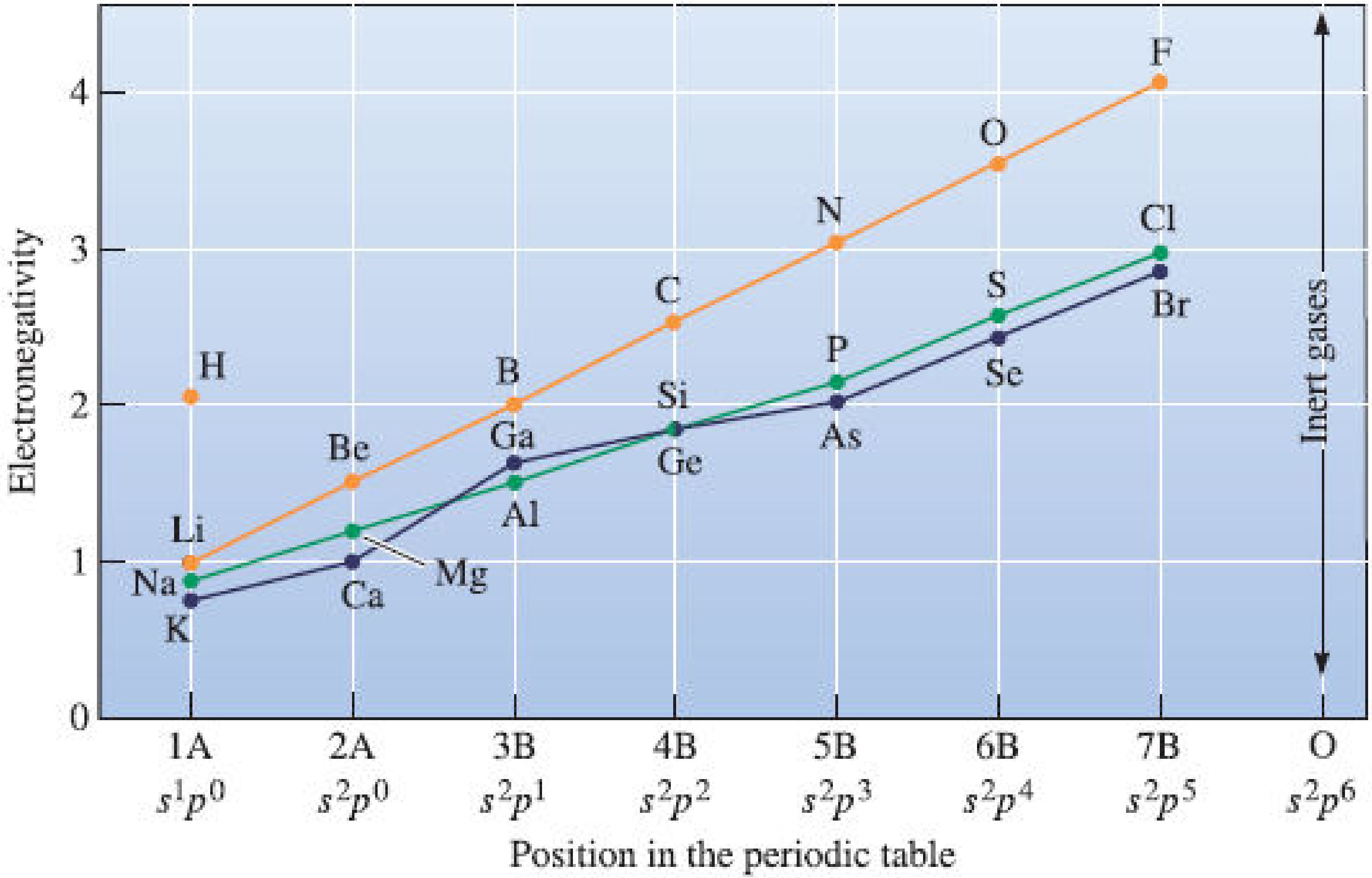
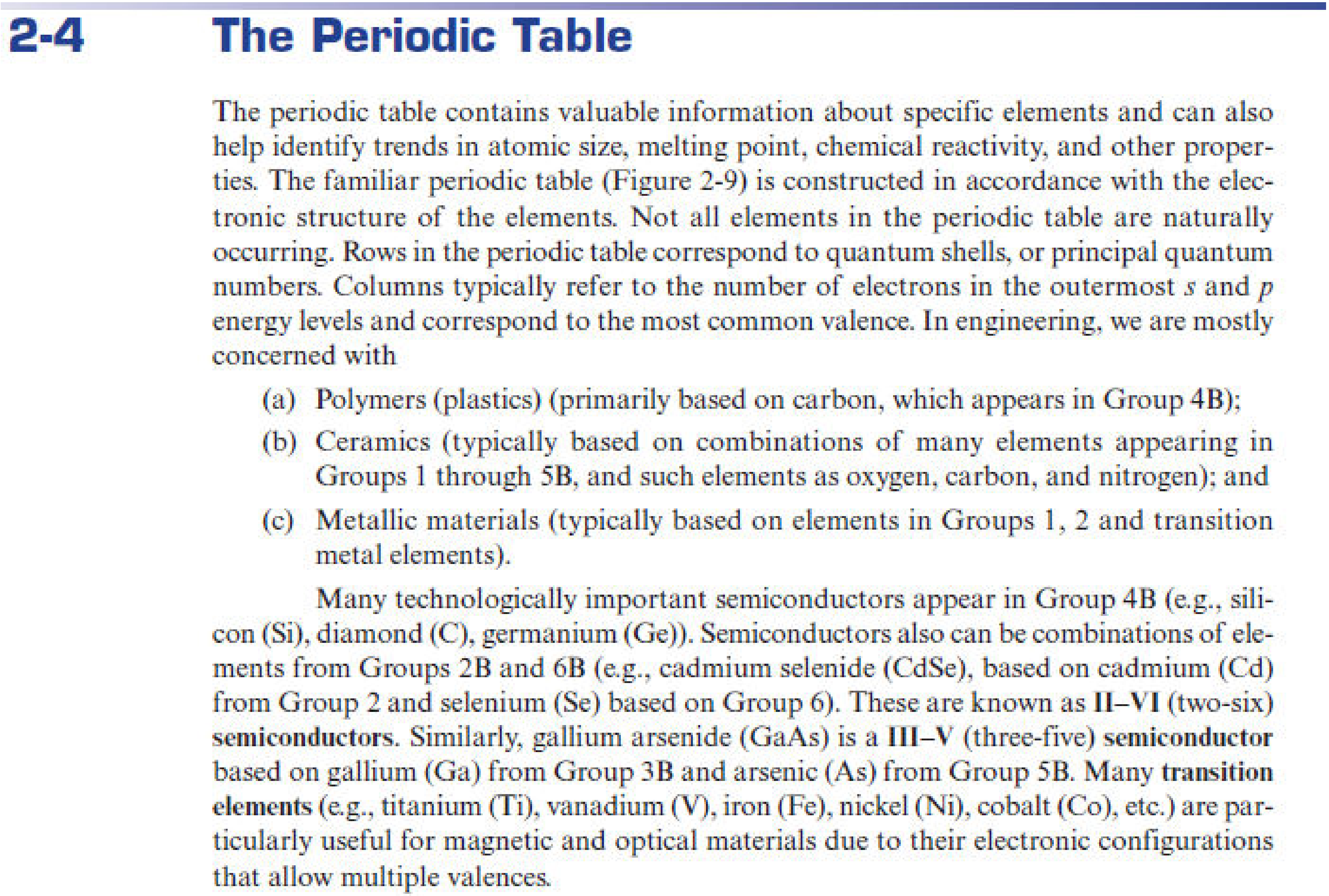


Figure 2-8 The electronegativities of selected elements relative to the position of the elements in the periodic table.



2-4

The Periodic Table

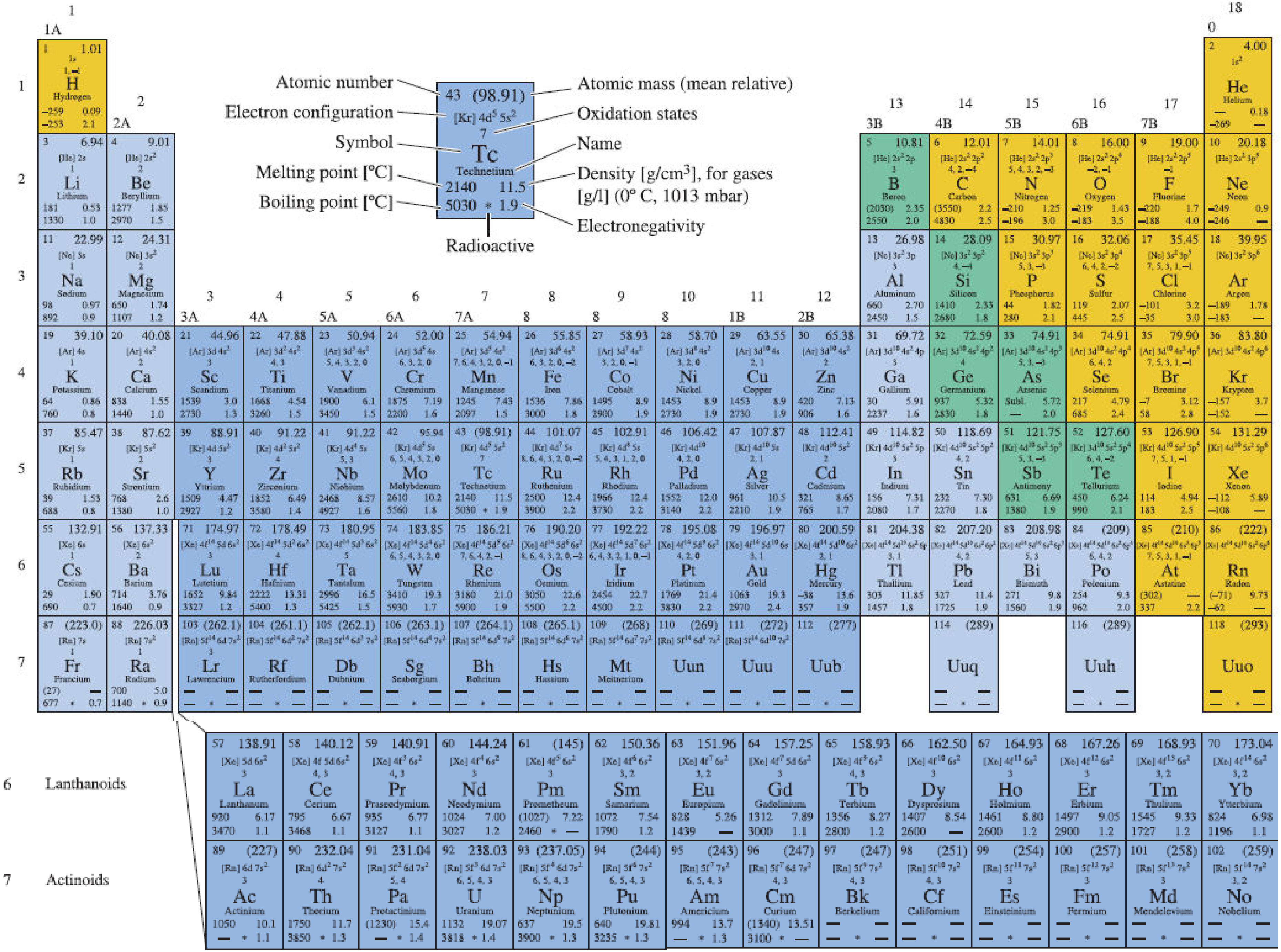
The periodic table contains valuable information about specific elements and can also help identify trends in atomic size, melting point, chemical reactivity, and other properties. The familiar periodic table (Figure 2-9) is constructed in accordance with the electronic structure of the elements. Not all elements in the periodic table are naturally occurring. Rows in the periodic table correspond to quantum shells, or principal quantum numbers. Columns typically refer to the number of electrons in the outermost *s* and *p* energy levels and correspond to the most common valence. In engineering, we are mostly concerned with

(a) Polymers (plastics) (primarily based on carbon, which appears in Group 4B);

(b) Ceramics (typically based on combinations of many elements appearing in Groups 1 through 5B, and such elements as oxygen, carbon, and nitrogen); and

(c) Metallic materials (typically based on elements in Groups 1, 2 and transition metal elements).

Many technologically important semiconductors appear in Group 4B (e.g., silicon (Si), diamond (C), germanium (Ge)). Semiconductors also can be combinations of elements from Groups 2B and 6B (e.g., cadmium selenide (CdSe), based on cadmium (Cd) from Group 2 and selenium (Se) based on Group 6). These are known as **II–VI** (two-six) **semiconductors**. Similarly, gallium arsenide (GaAs) is a **III–V** (three-five) **semiconductor** based on gallium (Ga) from Group 3B and arsenic (As) from Group 5B. Many **transition elements** (e.g., titanium (Ti), vanadium (V), iron (Fe), nickel (Ni), cobalt (Co), etc.) are particularly useful for magnetic and optical materials due to their electronic configurations that allow multiple valences.



Atomic number – 43
Electron configuration – [Kr] 4d^5 5s^2
Symbol – **Tc**
Melting point [°C] – 2140
Boiling point [°C] – 5030
Atomic mass (mean relative) – (98.91)
Oxidation states – 7
Name – Technetium
Density [g/cm^3], for gases [g/l] (0° C, 1013 mbar) – 11.5
Electronegativity – 1.9
Radioactive – *

	1 1A	2 2A	3 3A	4 4A	5 5A	6 6A	7 7A	8 8	9 8	10 8	11 1B	12 2B	13 3B	14 4B	15 5B	16 6B	17 7B	18 0
1	1 1.01 1s 1, –1 **H** Hydrogen –259 0.09 –253 2.1																	2 4.00 1s^2 **He** Helium — 0.18 –269 —
2	3 6.94 [He] 2s 1 **Li** Lithium 181 0.53 1330 1.0	4 9.01 [He] 2s^2 2 **Be** Beryllium 1277 1.85 2970 1.5											5 10.81 [He] 2s^2 2p 3 **B** Boron (2030) 2.35 2550 2.0	6 12.01 [He] 2s^2 2p^2 4, 2, –4 **C** Carbon (3550) 2.2 4830 2.5	7 14.01 [He] 2s^2 2p^3 5, 4, 3, 2, –3 **N** Nitrogen –210 1.25 –196 3.0	8 16.00 [He] 2s^2 2p^4 –2, –1 **O** Oxygen –219 1.43 –183 3.5	9 19.00 [He] 2s^2 2p^5 –1 **F** Fluorine –220 1.7 –188 4.0	10 20.18 [He] 2s^2 3p^5 **Ne** Neon –249 0.9 –246 —
3	11 22.99 [Ne] 3s 1 **Na** Sodium 98 0.97 892 0.9	12 24.31 [Ne] 3s^2 2 **Mg** Magnesium 650 1.74 1107 1.2											13 26.98 [Ne] 3s^2 3p 3 **Al** Aluminum 660 2.70 2450 1.5	14 28.09 [Ne] 3s^2 3p^2 4, –4 **Si** Silicon 1410 2.33 2680 1.8	15 30.97 [Ne] 3s^2 3p^3 5, 3, –3 **P** Phosphorus 44 1.82 280 2.1	16 32.06 [Ne] 3s^2 3p^4 6, 4, 2, –2 **S** Sulfur 119 2.07 445 2.5	17 35.45 [Ne] 3s^2 3p^5 7, 5, 3, 1, –1 **Cl** Chlorine –101 3.2 –35 3.0	18 39.95 [Ne] 3s^2 3p^6 **Ar** Argon –189 1.78 –183 —
4	19 39.10 [Ar] 4s 1 **K** Potassium 64 0.86 760 0.8	20 40.08 [Ar] 4s^2 2 **Ca** Calcium 838 1.55 1440 1.0	21 44.96 [Ar] 3d 4s^2 3 **Sc** Scandium 1539 3.0 2730 1.3	22 47.88 [Ar] 3d^2 4s^2 4, 3 **Ti** Titanium 1668 4.54 3260 1.5	23 50.94 [Ar] 3d^3 4s^2 5, 4, 3, 2, 0 **V** Vanadium 1900 6.1 3450 1.5	24 52.00 [Ar] 3d^5 4s 6, 3, 2, 0 **Cr** Chromium 1875 7.19 2200 1.6	25 54.94 [Ar] 3d^5 4s^2 7, 6, 4, 3, 2, 0, –1 **Mn** Manganese 1245 7.43 2097 1.5	26 55.85 [Ar] 3d^6 4s^2 6, 3, 2, 0, –2 **Fe** Iron 1536 7.86 3000 1.8	27 58.93 [Ar] 3d^7 4s^2 3, 2, 0, –1 **Co** Cobalt 1495 8.9 2900 1.9	28 58.70 [Ar] 3d^8 4s^2 3, 2, 0 **Ni** Nickel 1453 8.9 2730 1.9	29 63.55 [Ar] 3d^{10} 4s 2, 1 **Cu** Copper 1453 8.9 2730 1.9	30 65.38 [Ar] 3d^{10} 4s^2 2 **Zn** Zinc 420 7.13 906 1.6	31 69.72 [Ar] 3d^{10} 4s^2 4p 3 **Ga** Gallium 30 5.91 2237 1.6	32 72.59 [Ar] 3d^{10} 4s^2 4p^2 4 **Ge** Germanium 937 5.32 2830 1.8	33 74.91 [Ar] 3d^{10} 4s^2 4p^3 5, 3, –3 **As** Arsenic Subl. 5.72 — 2.0	34 74.91 [Ar] 3d^{10} 4s^2 4p^4 6, 4, 2 **Se** Selenium 217 4.79 685 2.4	35 79.90 [Ar] 3d^{10} 4s^2 4p^5 7, 5, 3, 1, –1 **Br** Bromine –7 3.12 58 2.8	36 83.80 [Ar] 3d^{10} 4s^2 4p^6 **Kr** Krypton –157 3.7 –152 —
5	37 85.47 [Kr] 5s 1 **Rb** Rubidium 39 1.53 688 0.8	38 87.62 [Kr] 5s^2 2 **Sr** Strontium 768 2.6 1380 1.0	39 88.91 [Kr] 4d 5s^2 3 **Y** Yttrium 1509 4.47 2927 1.2	40 91.22 [Kr] 4d^2 5s^2 4 **Zr** Zirconium 1852 6.49 3580 1.4	41 91.22 [Kr] 4d^4 5s 5, 3 **Nb** Niobium 2468 8.57 4927 1.6	42 95.94 [Kr] 4d^5 5s 6, 5, 4, 3, 2, 0 **Mo** Molybdenum 2610 10.2 5560 1.8	43 (98.91) [Kr] 4d^5 5s^2 7 **Tc** Technetium 2140 11.5 5030 * 1.9	44 101.07 [Kr] 4d^7 5s 8, 6, 4, 3, 2, 0, –2 **Ru** Ruthenium 2500 12.4 3900 2.2	45 102.91 [Kr] 4d^8 5s 5, 4, 3, 1, 2, 0 **Rh** Rhodium 1966 12.4 3730 2.2	46 106.42 [Kr] 4d^{10} 4, 2, 0 **Pd** Palladium 1552 12.0 3140 2.2	47 107.87 [Kr] 4d^{10} 5s 2, 1 **Ag** Silver 961 10.5 2210 1.9	48 112.41 [Kr] 4d^{10} 5s^2 2 **Cd** Cadmium 321 8.65 765 1.7	49 114.82 [Kr] 4d^{10} 5s^2 5p 3 **In** Indium 156 7.31 2080 1.7	50 118.69 [Kr] 4d^{10} 5s^2 5p^2 4, 2 **Sn** Tin 232 7.30 2270 1.8	51 121.75 [Kr] 4d^{10} 5s^2 5p^3 5, 3, –3 **Sb** Antimony 631 6.69 1380 1.9	52 127.60 [Kr] 3d^{10} 5s^2 5p^4 6, 4, –2 **Te** Tellurium 450 6.24 990 2.1	53 126.90 [Kr] 4d^{10} 5s^2 5p^5 7, 5, 1, –1 **I** Iodine 114 4.94 183 2.5	54 131.29 [Kr] 4d^{10} 5s^2 5p^6 **Xe** Xenon –112 5.89 –108 —
6	55 132.91 [Xe] 6s 1 **Cs** Cesium 29 1.90 690 0.7	56 137.33 [Xe] 6s^2 2 **Ba** Barium 714 3.76 1640 0.9	71 174.97 [Xe] 4f^{14} 5d 6s^2 3 **Lu** Lutetium 1652 9.84 3327 1.2	72 178.49 [Xe] 4f^{14} 5d^2 6s^2 4 **Hf** Hafnium 2222 13.31 5400 1.3	73 180.95 [Xe] 4f^{14} 5d^3 6s^2 5 **Ta** Tantalum 2996 16.5 5425 1.5	74 183.85 [Xe] 4f^{14} 5d^4 6s^2 6, 5, 4, 3, 2, 0 **W** Tungsten 3410 19.3 5930 1.7	75 186.21 [Xe] 4f^{14} 5d^5 6s^2 7, 6, 4, 2, –1 **Re** Rhenium 3180 21.0 5900 1.9	76 190.20 [Xe] 4f^{14} 5d^6 6s^2 8, 6, 4, 3, 2, 0, –2 **Os** Osmium 3050 22.6 5500 2.2	77 192.22 [Xe] 4f^{14} 5d^7 6s^2 6, 4, 3, 2, 1, 0, –1 **Ir** Iridium 2454 22.7 4500 2.2	78 195.08 [Xe] 4f^{14} 5d^9 6s 4, 2, 0 **Pt** Platinum 1769 21.4 3830 2.2	79 196.97 [Xe] 4f^{14} 5d^{10} 6s 3, 1 **Au** Gold 1063 19.3 2970 2.4	80 200.59 [Xe] 4f^{14} 5d^{10} 6s^2 2, 1 **Hg** Mercury –38 13.6 357 1.9	81 204.38 [Xe] 4f^{14} 5d^{10} 6s^2 6p 3, 1 **Tl** Thallium 303 11.85 1457 1.8	82 207.20 [Xe] 4f^{14} 5d^{10} 6s^2 6p^2 4, 2 **Pb** Lead 327 11.4 1725 1.9	83 208.98 [Xe] 4f^{14} 5d^{10} 6s^2 6p^3 5, 3 **Bi** Bismuth 271 9.8 1560 1.9	84 (209) [Xe] 4f^{14} 5d^{10} 6s^2 6p^4 6, 4, 2 **Po** Polonium 254 9.3 962 2.0	85 (210) [Xe] 4f^{14} 5d^{10} 6s^2 6p^5 7, 5, 3, 1, –1 **At** Astatine (302) — 337 2.2	86 (222) [Xe] 4f^{14} 5d^{10} 6s^2 6p^6 **Rn** Radon (–71) 9.73 –62 —
7	87 (223.0) [Rn] 7s 1 **Fr** Francium (27) — 677 * 0.7	88 226.03 [Rn] 7s^2 1 **Ra** Radium 700 5.0 1140 * 0.9	103 (262.1) [Rn] 5f^{14} 6d 7s^2 3 **Lr** Lawrencium — — — * —	104 (261.1) [Rn] 5f^{14} 6d^2 7s^2 **Rf** Rutherfordium — — — * —	105 (262.1) [Rn] 5f^{14} 6d^3 7s^2 **Db** Dubnium — — — * —	106 (263.1) [Rn] 5f^{14} 6d^4 7s^2 **Sg** Seaborgium — — — * —	107 (264.1) [Rn] 5f^{14} 6d^5 7s^2 **Bh** Bohrium — — — * —	108 (265.1) [Rn] 5f^{14} 6d^6 7s^2 **Hs** Hassium — — — * —	109 (268) [Rn] 5f^{14} 6d^7 7s^2 **Mt** Meitnerium — — — * —	110 (269) [Rn] 5f^{14} 6d^8 7s^2 **Uun** — — — * —	111 (272) [Rn] 5f^{14} 6d^{10} 7s^2 **Uuu** — — — * —	112 (277) **Uub** — — — * —		114 (289) **Uuq** — — — * —		116 (289) **Uuh** — — — * —		118 (293) **Uuo** — — — * —

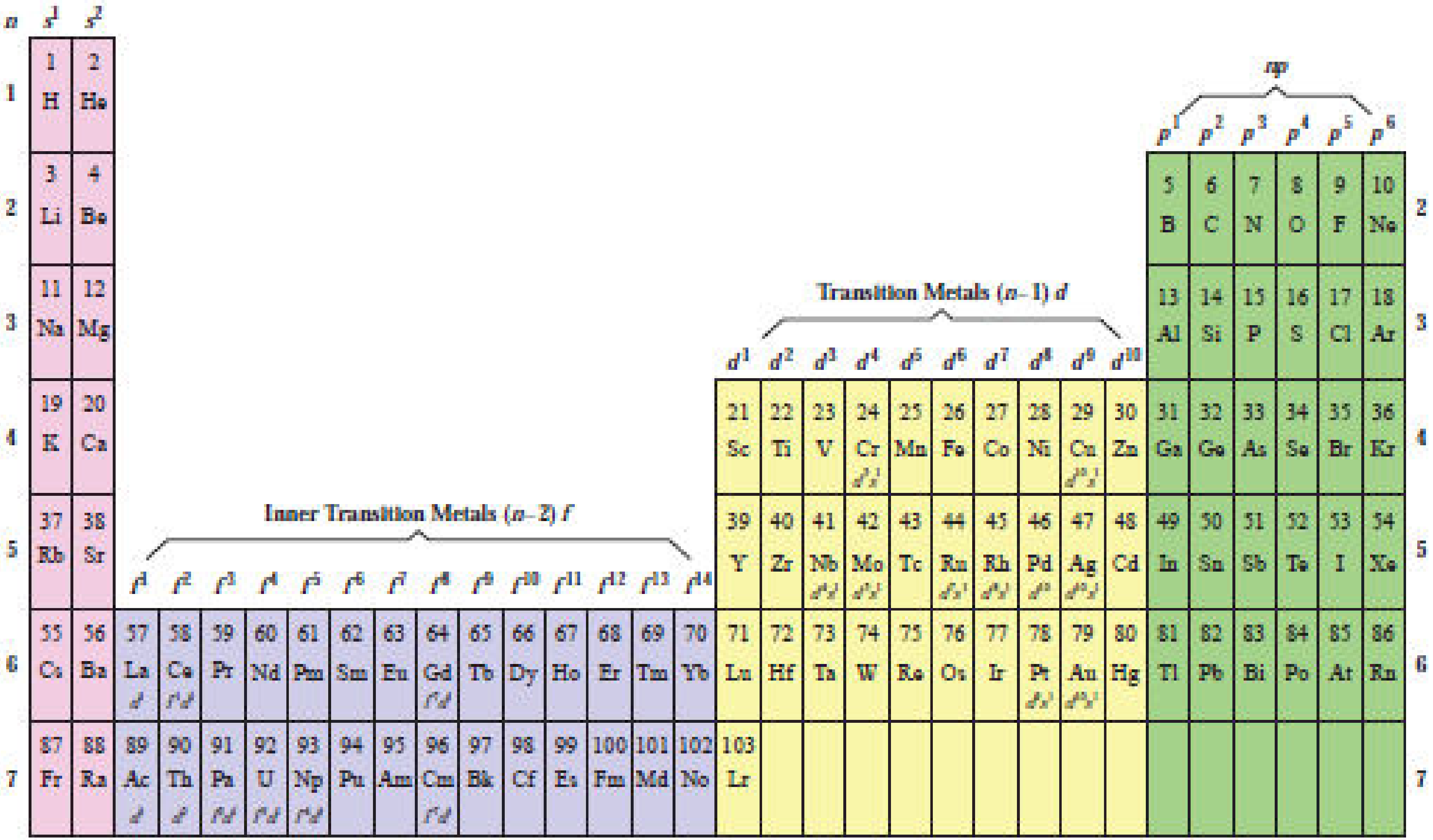
6 Lanthanoids	57 138.91 [Xe] 5d 6s^2 3 **La** Lanthanum 920 6.17 3470 1.1	58 140.12 [Xe] 4f 5d 6s^2 4, 3 **Ce** Cerium 795 6.67 3468 1.1	59 140.91 [Xe] 4f^3 6s^2 4, 3 **Pr** Praseodymium 935 6.77 3127 1.1	60 144.24 [Xe] 4f^4 6s^2 3 **Nd** Neodymium 1024 7.00 3027 1.2	61 (145) [Xe] 4f^5 6s^2 3 **Pm** Prometheum (1027) 7.22 2460 * —	62 150.36 [Xe] 4f^6 6s^2 3, 2 **Sm** Samarium 1072 7.54 1790 1.2	63 151.96 [Xe] 4f^7 6s^2 3, 2 **Eu** Europium 828 5.26 1439 —	64 157.25 [Xe] 4f^7 5d 6s^2 3 **Gd** Gadolinium 1312 7.89 3000 1.1	65 158.93 [Xe] 4f^9 6s^2 4, 3 **Tb** Terbium 1356 8.27 2800 1.2	66 162.50 [Xe] 4f^{10} 6s^2 3 **Dy** Dysprosium 1407 8.54 2600 —	67 164.93 [Xe] 4f^{11} 6s^2 3 **Ho** Holmium 1461 8.80 2600 1.2	68 167.26 [Xe] 4f^{12} 6s^2 3 **Er** Erbium 1497 9.05 2900 1.2	69 168.93 [Xe] 4f^{13} 6s^2 3, 2 **Tm** Thulium 1545 9.33 1727 1.2	70 173.04 [Xe] 4f^{14} 6s^2 3, 2 **Yb** Ytterbium 824 6.98 1196 1.1
7 Actinoids	89 (227) [Rn] 6d 7s^2 3 **Ac** Actinium 1050 10.1 — * 1.1	90 232.04 [Rn] 6d^2 7s^2 4 **Th** Thorium 1750 11.7 3850 * 1.3	91 231.04 [Rn] 5f^2 6d 7s^2 5, 4 **Pa** Protactinium (1230) 15.4 — * 1.4	92 238.03 [Rn] 5f^3 6d 7s^2 6, 5, 4, 3 **U** Uranium 1132 19.07 3818 * 1.4	93 (237.05) [Rn] 5f^4 6d 7s^2 6, 5, 4, 3 **Np** Neptunium 637 19.5 3900 * 1.3	94 (244) [Rn] 5f^6 7s^2 6, 5, 4, 3 **Pu** Plutonium 640 19.81 3235 * 1.3	95 (243) [Rn] 5f^7 7s^2 6, 5, 4, 3 **Am** Americium 994 13.7 — * 1.3	96 (247) [Rn] 5f^7 6d 7s^2 4, 3 **Cm** Curium (1340) 13.51 3100 * —	97 (247) [Rn] 5f^9 7s^2 4, 3 **Bk** Berkelium — — — * —	98 (251) [Rn] 5f^{10} 7s^2 4, 3 **Cf** Californium — — — * —	99 (254) [Rn] 5f^{11} 7s^2 3 **Es** Einsteinium — — — * —	100 (257) [Rn] 5f^{12} 7s^2 3 **Fm** Fermium — — — * —	101 (258) [Rn] 5f^{13} 7s^2 3 **Md** Mendelevium — — — * —	102 (259) [Rn] 5f^{14} 7s^2 3, 2 **No** Nobelium — — — * —

The ordering of the elements in the periodic table and the origin of the Aufbau Principle become even clearer when the rows for the Lathanoid and Actinoid series are inserted into their correct positions (see Figure 2-10) rather than being placed below the periodic table to conserve space. Figure 2-10 indicates the particular orbital being filled by each additional electron as the atomic number increases. Note that exceptions are indicated for those elements that do not follow the Aufbau Principle.

Trends in Properties The periodic table contains a wealth of useful information (e.g., atomic mass, atomic number of different elements, etc.). It also points to trends in atomic size, melting points, and chemical reactivity. For example, carbon (in its diamond form) has the highest melting point (3550°C). Melting points of the elements below carbon decrease (i.e., silicon (Si) (1410°C), germanium (Ge) (937°C), tin (Sn) (232°C), and lead (Pb) (327°C)). Note that the melting temperature of Pb is higher than that of Sn. The periodic table indicates trends and not exact variations in properties.

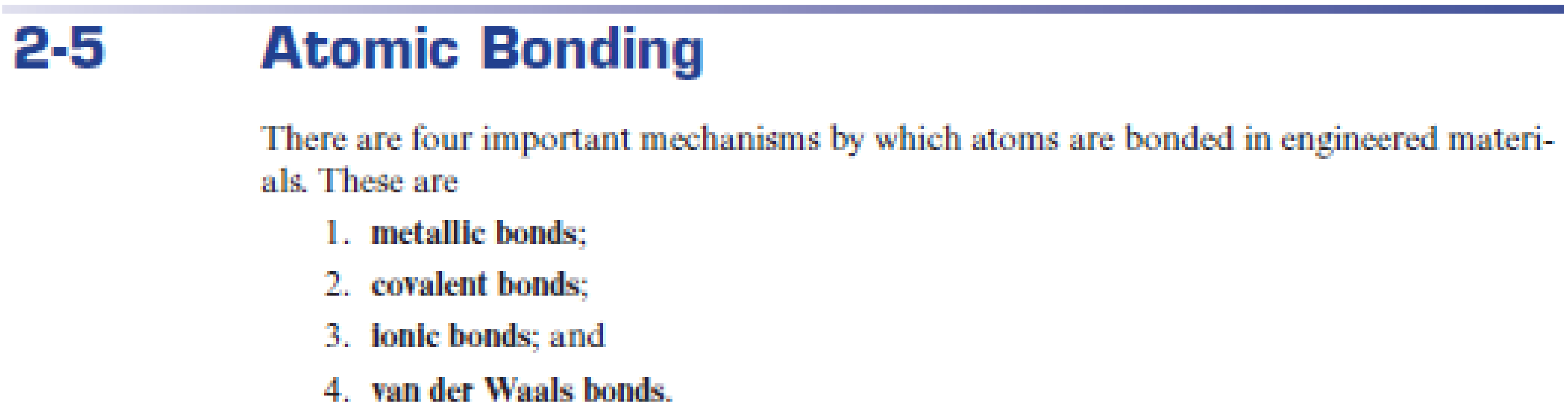
We can discern trends in other properties from the periodic table. Diamond is a material with a very large bandgap (i.e., it is not a very effective conductor of electricity). This is consistent with the fact that carbon (in diamond form) has the highest melting point among Group 4B elements, which suggests the interatomic forces are strong (see Section 2-6). As we move down the column, the bandgap decreases (the bandgaps of Si and Ge are 1.11 and 0.67 eV, respectively). Moving farther down, one form of tin is a semiconductor. Another form of tin is metallic. If we look at Group 1A, we see that lithium is highly electropositive (i.e., an element whose atoms want to participate in chemical interactions by donating electrons and are therefore highly reactive). Likewise, if we move down Column 1A, we can see that the chemical reactivity of elements decreases.

Thus, the periodic table gives us useful information about formulas, atomic numbers, and atomic masses of elements. It also helps us in predicting or rationalizing trends in properties of elements and compounds. This is why the periodic table is very useful to both scientists and engineers.



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

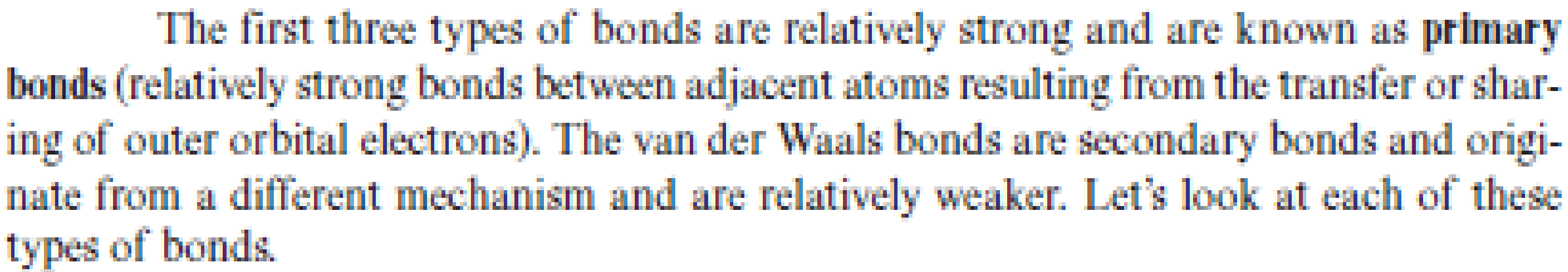
Figure 2-10 The periodic table for which the rows of the Lathanoid and Actinoid series are inserted into their correct positions. The column heading indicates the particular orbital being filled by each additional electron as the atomic number increases.



2-5 Atomic Bonding

There are four important mechanisms by which atoms are bonded in engineered materials. These are

1. **metallic bonds;**
2. **covalent bonds;**
3. **ionic bonds;** and
4. **van der Waals bonds.**



The first three types of bonds are relatively strong and are known as **primary bonds** (relatively strong bonds between adjacent atoms resulting from the transfer or sharing of outer orbital electrons). The van der Waals bonds are secondary bonds and originate from a different mechanism and are relatively weaker. Let's look at each of these types of bonds.

The Metallic Bond The metallic elements have electropositive atoms that donate their valence electrons to form a "sea" of electrons surrounding the atoms (Figure 2-11). Aluminum, for example, gives up its three valence electrons, leaving behind a core consisting of the nucleus and inner electrons. Since three negatively charged electrons are missing from this core, it has a positive charge of three. The valence electrons move freely within the electron sea and become associated with several atom cores. The positively charged ion cores are held together by mutual attraction to the electrons, thus producing a strong metallic bond.

Because their valence electrons are not fixed in any one position, most pure metals are good electrical conductors of electricity at relatively low temperatures ($\sim T < 300$ K). Under the influence of an applied voltage, the valence electrons move, causing a current to flow if the circuit is complete.

Metals show good ductility since the metallic bonds are non-directional. There are other important reasons related to microstructure that can explain why metals actually exhibit *lower strengths* and *higher ductility* than what we may anticipate from their bonding. **Ductility** refers to the ability of materials to be stretched or bent permanently without breaking. We will discuss these concepts in greater detail in Chapter 6. In general, the melting points of metals are relatively high. From an optical properties viewpoint, metals make good reflectors of visible radiation. Owing to their electropositive character, many metals such as iron tend to undergo corrosion or oxidation. Many pure metals are good conductors of heat and are effectively used in many heat transfer applications. We emphasize that metallic bonding is *one of the factors* in our efforts to rationalize the trends observed with respect to the properties of metallic materials. As we will see in some of the following chapters, there are other factors related to microstructure that also play a crucial role in determining the properties of metallic materials.

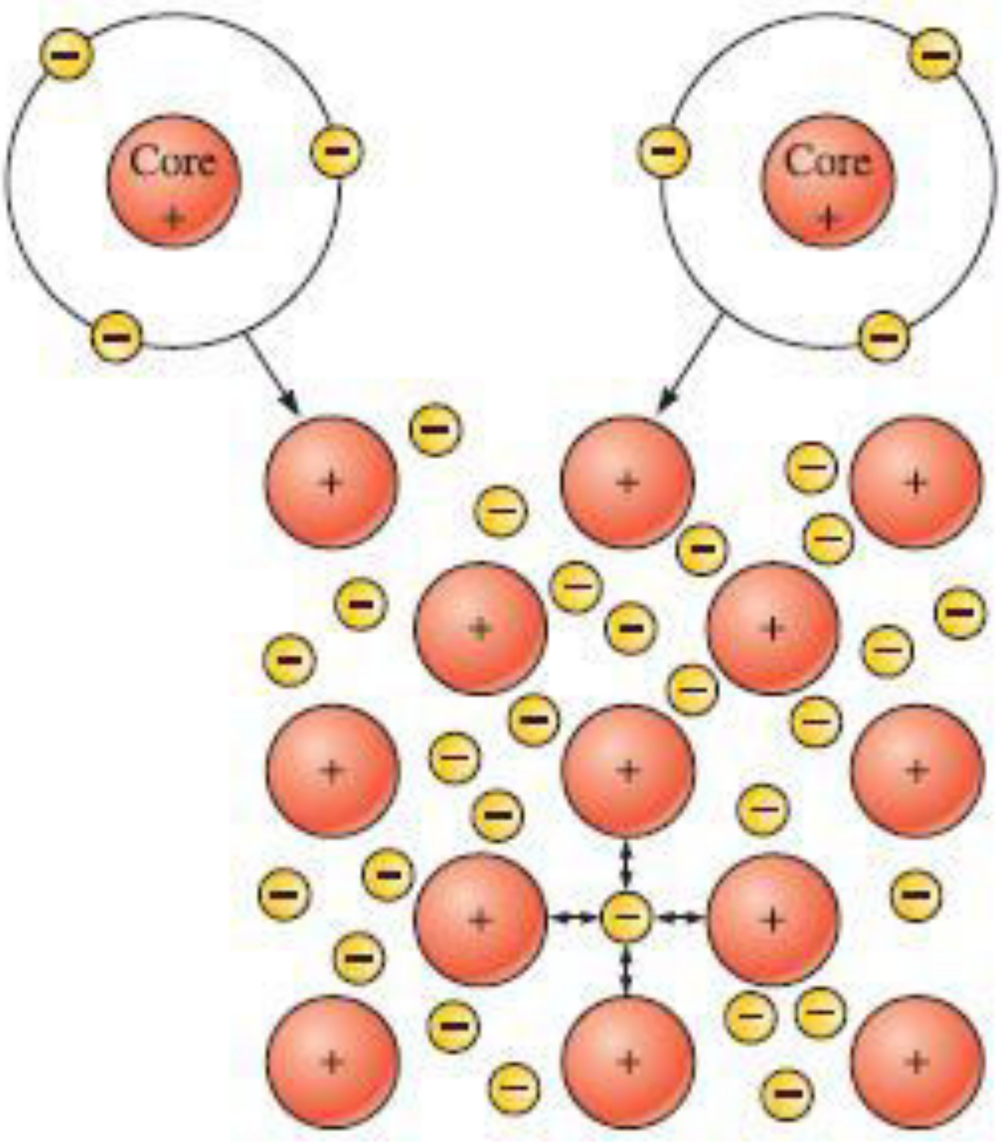


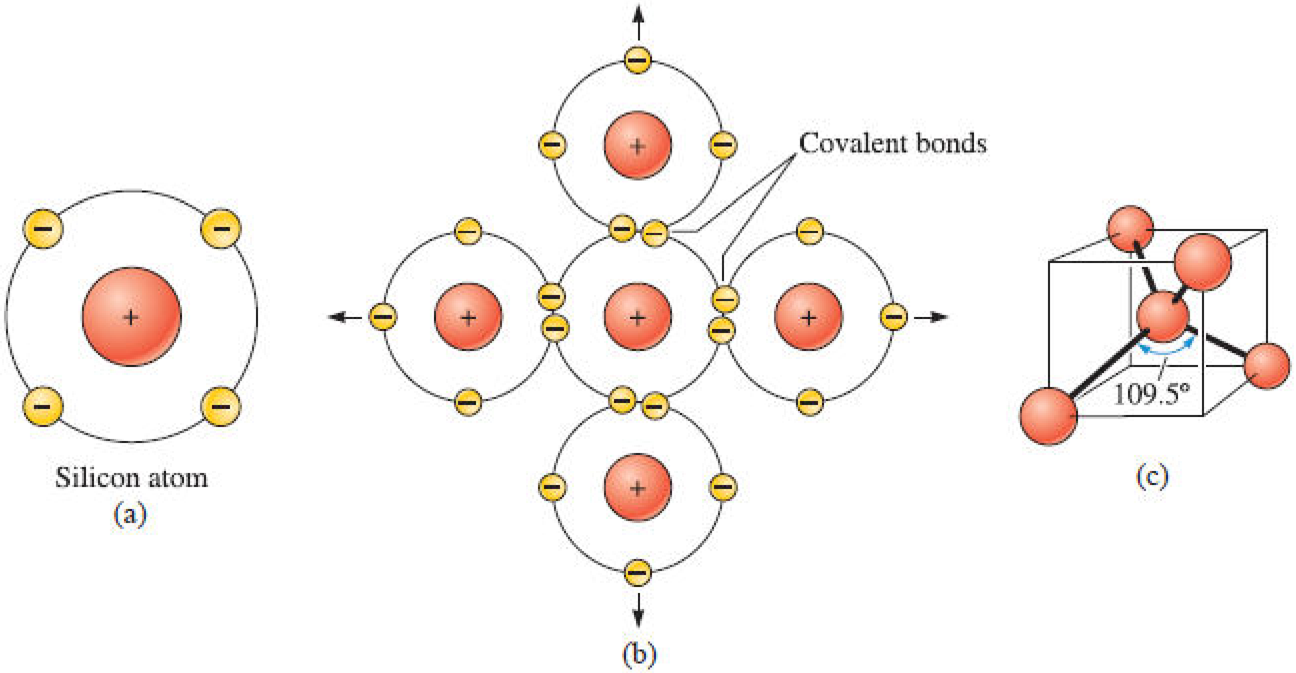
Figure 2-11
The metallic bond forms when atoms give up their valence electrons, which then form an electron sea. The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

The Covalent Bond

Materials with **covalent bonding** are characterized by bonds that are formed by sharing of valence electrons among two or more atoms. For example, a silicon atom, which has a valence of four, obtains eight electrons in its outer energy shell by sharing its valence electrons with four surrounding silicon atoms, as in Figure 2-12(a) and (b). Each instance of sharing represents one covalent bond; thus, each silicon atom is bonded to four neighboring atoms by four covalent bonds. In order for the covalent bonds to be formed, the silicon atoms must be arranged so the bonds have a fixed **directional relationship** with one another. A directional relationship is formed when the bonds between atoms in a covalently bonded material form specific angles, depending on the material. In the case of silicon, this arrangement produces a tetrahedron, with angles of 109.5° between the covalent bonds [Figure 2-12(c)].

Covalent bonds are very strong. As a result, covalently bonded materials are very strong and hard. For example, diamond (C), silicon carbide (SiC), silicon nitride (Si_3N_4), and boron nitride (BN) all have covalent bonds. These materials also exhibit very high melting points, which means they could be useful for high-temperature applications. On the other hand, the high temperature needed for processing presents a challenge. The materials bonded in this manner typically have limited ductility because the bonds tend to be directional. The electrical conductivity of many covalently bonded materials (i.e., silicon, diamond, and many ceramics) is not high since the valence electrons are locked in bonds between atoms and are not readily available for conduction. With some of these materials such as Si, we can get useful and controlled levels of electrical conductivity by deliberately introducing small levels of other elements known as dopants. Conductive polymers are also a good example of covalently bonded materials that can be turned into semiconducting materials. The development of conducting polymers that are lightweight has captured the attention of many scientists and engineers for developing flexible electronic components.

We cannot simply predict whether or not a material will be high or low strength, ductile or brittle, simply based on the nature of bonding! We need additional information on the atomic, microstructure, and macrostructure of the material; however, the nature of bonding does point to a trend for materials with certain types of bonding and chemical compositions. Example 2-3 explores how one such bond of oxygen and silicon join to form silica.



Silicon atom
(a)

(b)

(c)

Figure 2-12 (a) Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbitals filled. (b) In silicon, with a valence of four, four covalent bonds must be formed. (c) Covalent bonds are directional. In silicon, a tetrahedral structure is formed with angles of 109.5° required between each covalent bond.

Example 2-3 *How Do Oxygen and Silicon Atoms Join to Form Silica?*

Assuming that silica (SiO_2) has 100% covalent bonding, describe how oxygen and silicon atoms in silica (SiO_2) are joined.

SOLUTION

Silicon has a valence of four and shares electrons with four oxygen atoms, thus giving a total of eight electrons for each silicon atom. Oxygen has a valence of six and shares electrons with two silicon atoms, giving oxygen a total of eight electrons. Figure 2-13 illustrates one of the possible structures. Similar to silicon (Si), a tetrahedral structure is produced. We will discuss later in this chapter how to account for the ionic and covalent nature of bonding in silica.

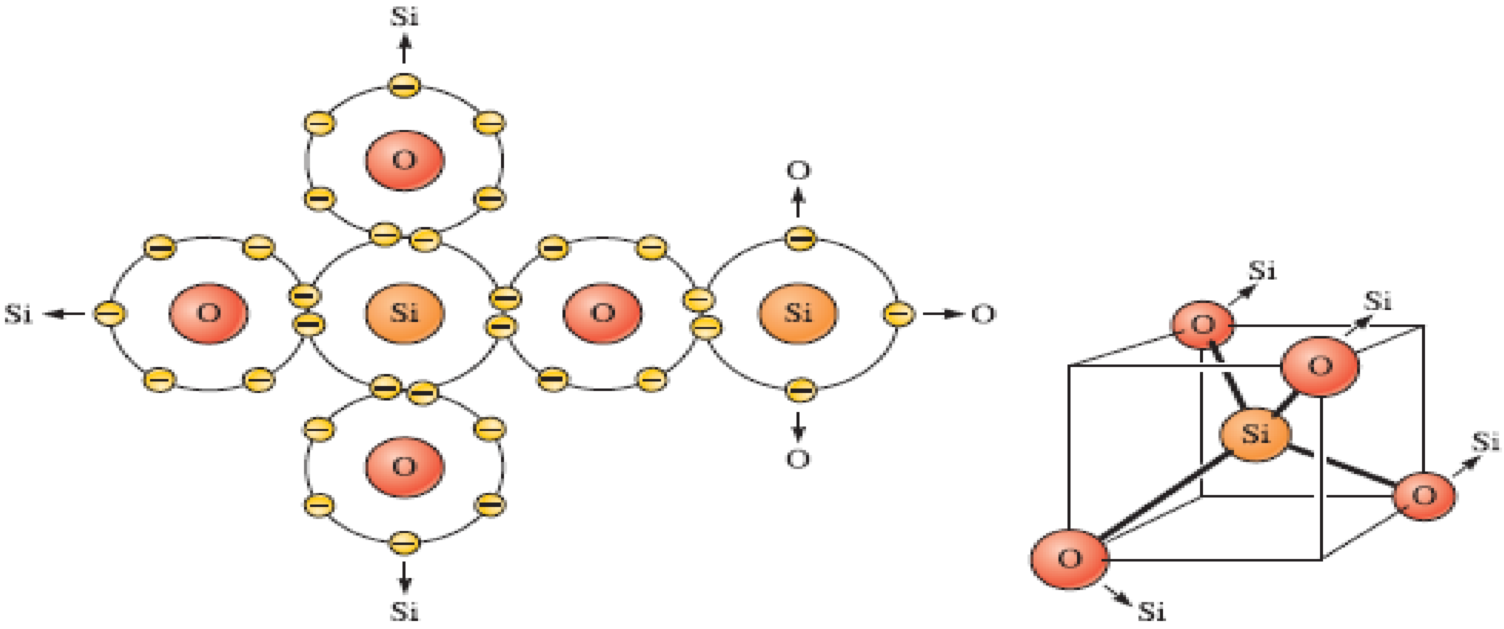


Figure 2-13 The tetrahedral structure of silica (SiO_2), which contains covalent bonds between silicon and oxygen atoms (for Example 2-3).

The Ionic Bond When more than one type of atom is present in a material, one atom may donate its valence electrons to a different atom, filling the outer energy shell of the second atom. Both atoms now have filled (or emptied) outer energy levels, but both have acquired an electrical charge and behave as ions. The atom that contributes the electrons is left with a net positive charge and is called a **cation**, while the atom that accepts the electrons acquires a net negative charge and is called an **anion**. The oppositely charged ions are then attracted to one another and produce the **ionic bond**. For example, the attraction between sodium and chloride ions (Figure 2-14) produces sodium chloride (NaCl), or table salt.

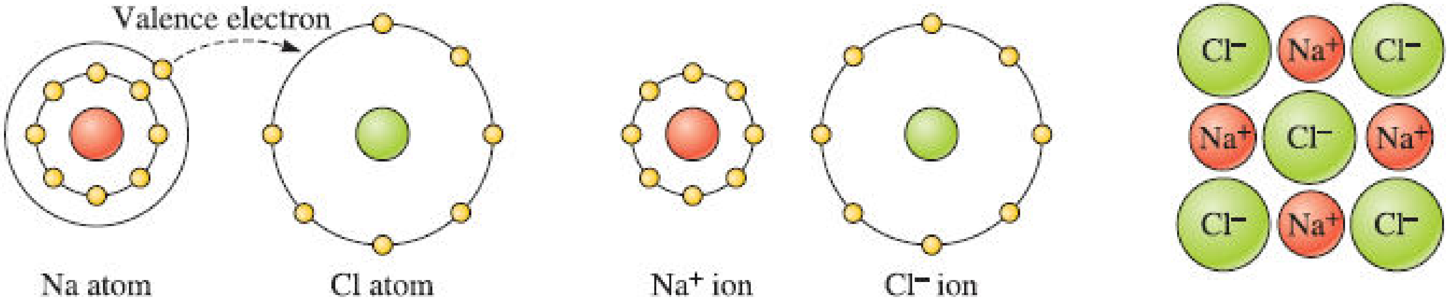
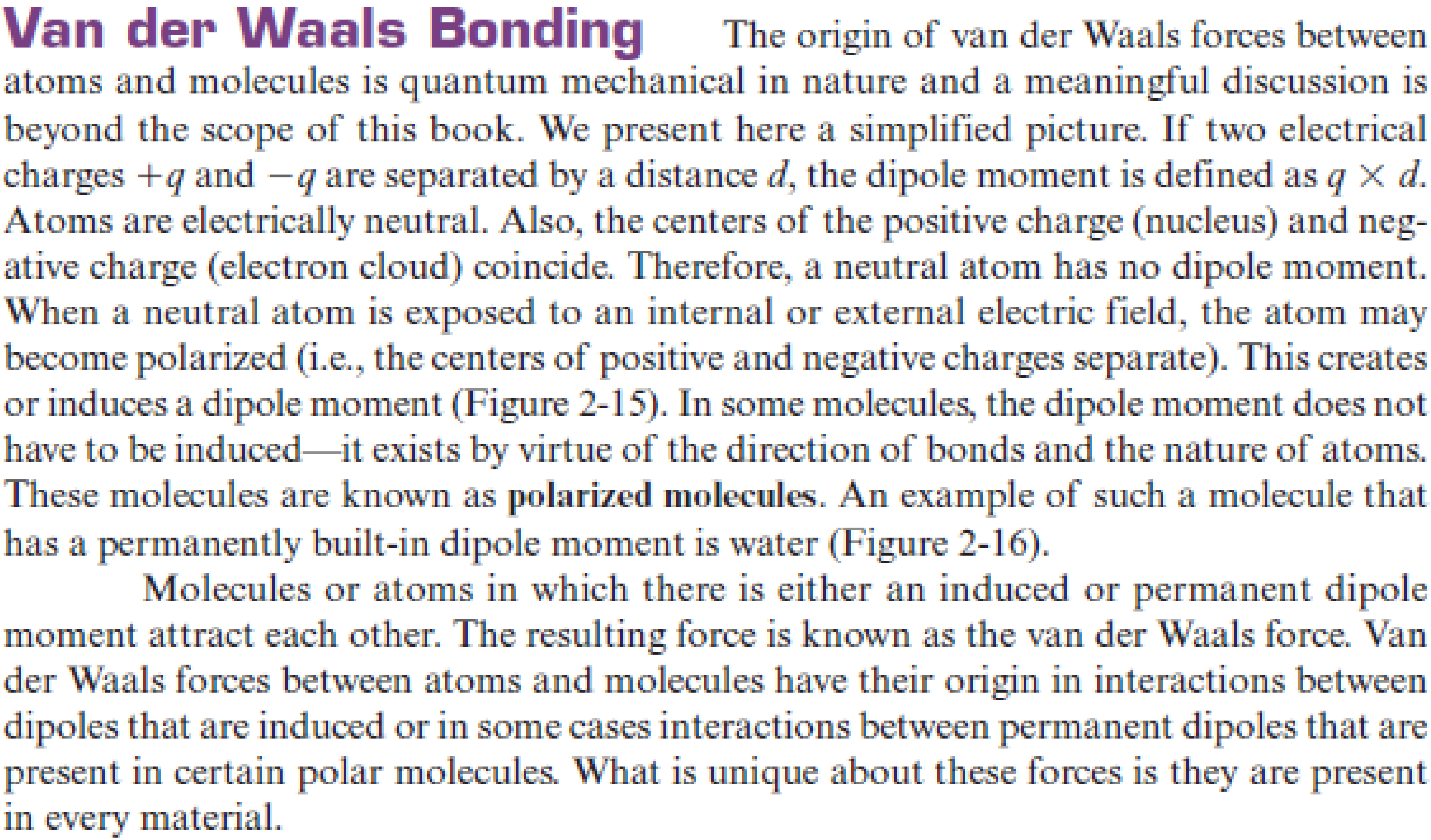


Figure 2-14 An ionic bond is created between two unlike atoms with different electronegativities. When sodium donates its valence electron to chlorine, each becomes an ion, attraction occurs, and the ionic bond is formed.



Van der Waals Bonding The origin of van der Waals forces between atoms and molecules is quantum mechanical in nature and a meaningful discussion is beyond the scope of this book. We present here a simplified picture. If two electrical charges $+q$ and $-q$ are separated by a distance d, the dipole moment is defined as $q \times d$. Atoms are electrically neutral. Also, the centers of the positive charge (nucleus) and negative charge (electron cloud) coincide. Therefore, a neutral atom has no dipole moment. When a neutral atom is exposed to an internal or external electric field, the atom may become polarized (i.e., the centers of positive and negative charges separate). This creates or induces a dipole moment (Figure 2-15). In some molecules, the dipole moment does not have to be induced—it exists by virtue of the direction of bonds and the nature of atoms. These molecules are known as **polarized molecules**. An example of such a molecule that has a permanently built-in dipole moment is water (Figure 2-16).

Molecules or atoms in which there is either an induced or permanent dipole moment attract each other. The resulting force is known as the van der Waals force. Van der Waals forces between atoms and molecules have their origin in interactions between dipoles that are induced or in some cases interactions between permanent dipoles that are present in certain polar molecules. What is unique about these forces is they are present in every material.

There are three types of **van der Waals** interactions, namely London forces, Keesom forces, and Debye forces. If the interactions are between two dipoles that are induced in atoms or molecules, we refer to them as **London forces** (e.g., carbon tetrachloride) (Figure 2-15). When an induced dipole (that is, a dipole that is induced in what is otherwise a non-polar atom or molecule) interacts with a molecule that has a permanent dipole moment, we refer to this interaction as a **Debye interaction**. An example of Debye interaction would be forces between water molecules and those of carbon tetrachloride.

If the interactions are between molecules that are permanently polarized (e.g., water molecules attracting other water molecules or other polar molecules), we refer to these as **Keesom interactions**. The attraction between the positively charged regions of one

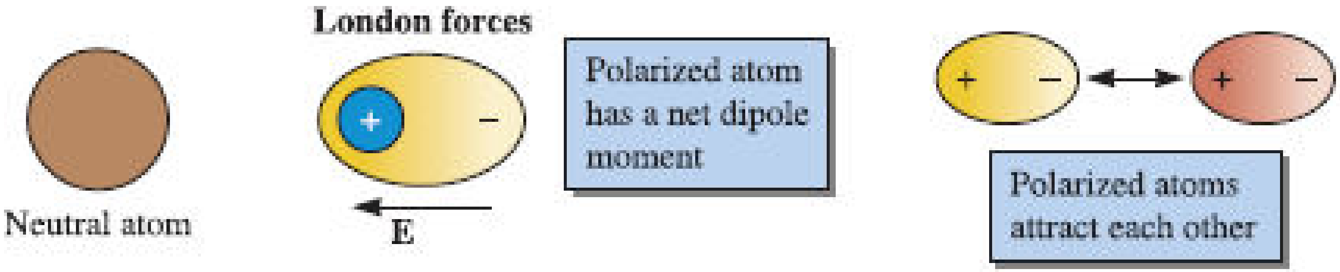


Figure 2-15 Illustration of London forces, a type of a van der Waals force, between atoms.

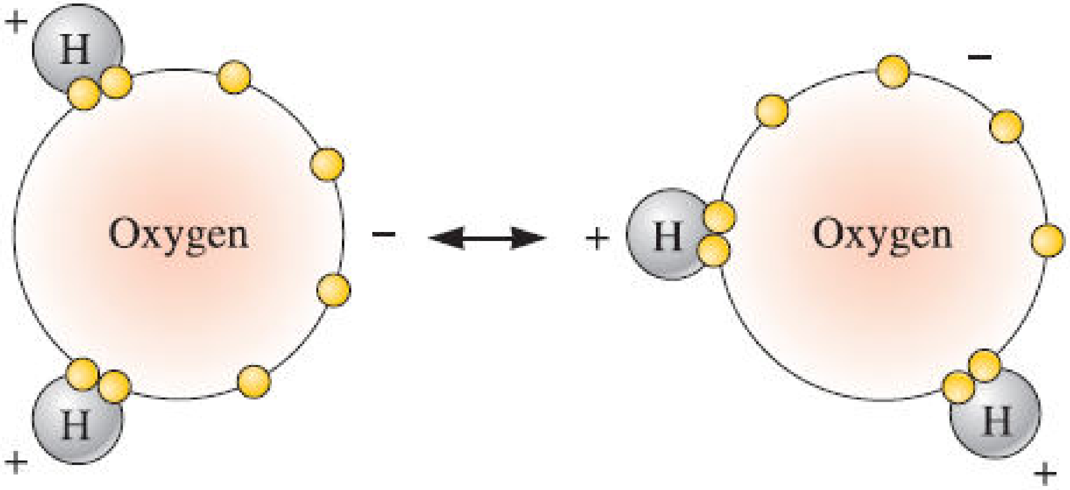


Figure 2-16
The Keesom interactions are formed as a result of polarization of molecules or groups of atoms. In water, electrons in the oxygen tend to concentrate away from the hydrogen. The resulting charge difference permits the molecule to be weakly bonded to other water molecules.

water molecule and the negatively charged regions of a second water molecule provides an attractive bond between the two water molecules (Figure 2-16).

The bonding between molecules that have a permanent dipole moment, known as the Keesom force, is often referred to as a **hydrogen bond**, where hydrogen atoms represent one of the polarized regions. Thus, hydrogen bonding is essentially a Keesom force and is a type of van der Waals force. The relatively strong Keesom force between water molecules is the reason why surface tension (72 mJ/m^2 or dyne/cm at room temperature) and the boiling point of water (100°C) are much higher than those of many organic liquids of comparable molecular weight (surface tension ~20 to 25 dyne/cm, boiling points up to 80°C).

Note that van der Waals bonds are **secondary bonds**, but the atoms within the molecule or group of atoms are joined by strong covalent or ionic bonds. Heating water to the boiling point breaks the van der Waals bonds and changes water to steam, but much higher temperatures are required to break the covalent bonds joining oxygen and hydrogen atoms.

Although termed "secondary," based on the bond energies, van der Waals forces play a very important role in many areas of engineering. Van der Waals forces between atoms and molecules play a vital role in determining the surface tension and boiling points of liquids. In materials science and engineering, the surface tension of liquids and the surface energy of solids come into play in different situations. For example, when we want to process ceramic or metal powders into dense solid parts, the powders often have to be dispersed in water or organic liquids. Whether we can achieve this dispersion effectively depends upon the surface tension of the liquid and the surface energy of the solid material. Surface tension of liquids also assumes importance when we are dealing with processing of molten metals and alloys (e.g., casting) and glasses.

Van der Waals bonds can dramatically change the properties of certain materials. For example, graphite and diamond have very different mechanical properties. In many plastic materials, molecules contain polar parts or side groups (e.g., cotton or cellulose, PVC, Teflon). Van der Waals forces provide an extra binding force between the chains of these polymers (Figure 2-17).

Polymers in which van der Waals forces are stronger tend to be relatively stiffer and exhibit relatively higher glass transition temperatures (T_g). The glass transition temperature is a temperature below which some polymers tend to behave as brittle materials (i.e., they show poor ductility). As a result, polymers with van der Waals bonding (in addition to the covalent bonds in the chains and side groups) are relatively brittle at room temperature (e.g., PVC). In processing such polymers, they need to be "plasticized" by adding other smaller polar molecules that interact with the polar parts of the long polymer chains, thereby lowering the T_g and enhancing flexibility.

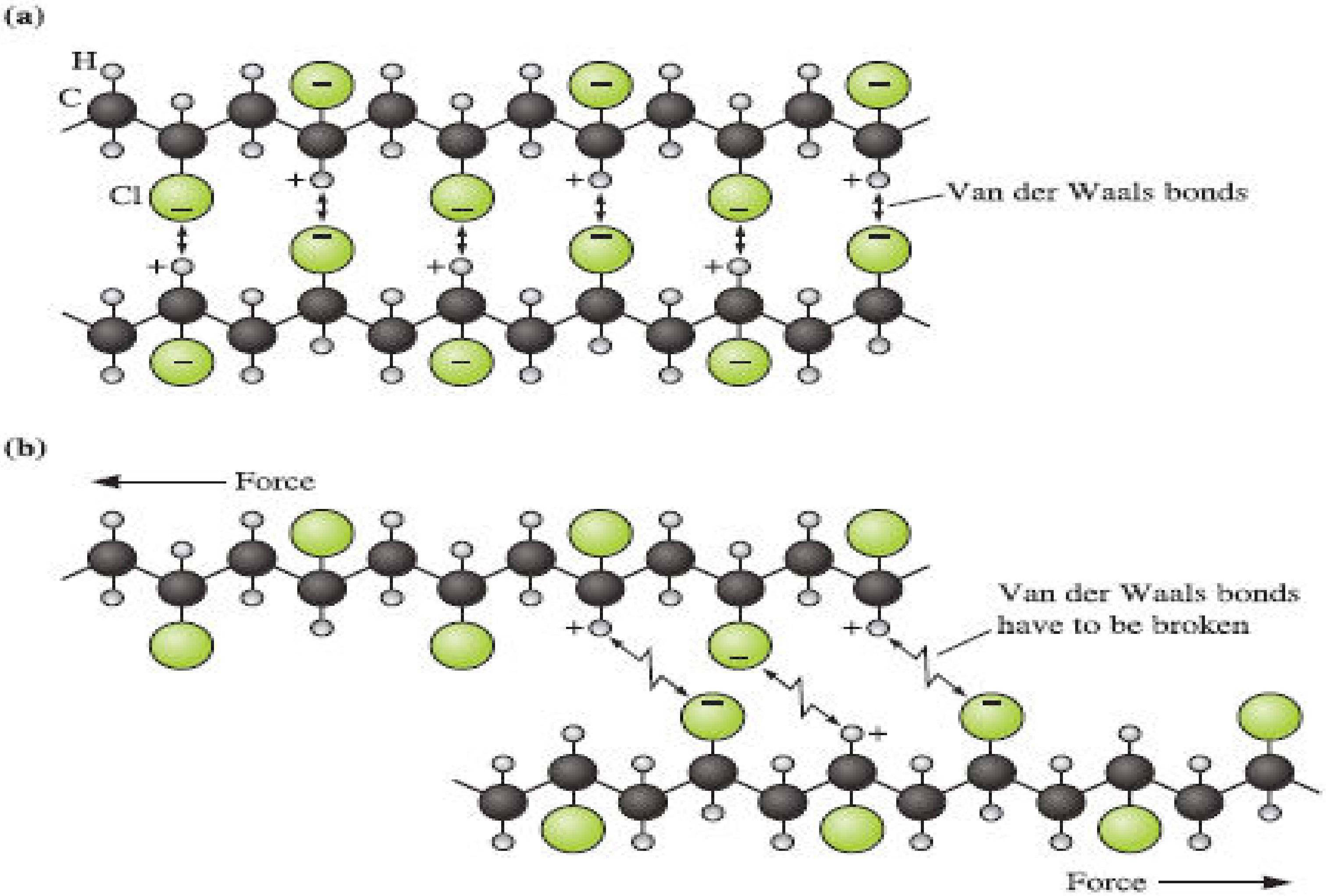


Figure 2-17 (a) In polyvinyl chloride (PVC), the chlorine atoms attached to the polymer chain have a negative charge and the hydrogen atoms are positively charged. The chains are weakly bonded by van der Waals bonds. This additional bonding makes PVC stiffer. (b) When a force is applied to the polymer, the van der Waals bonds are broken and the chains slide past one another.

Mixed Bonding In most materials, bonding between atoms is a mixture of two or more types. Iron, for example, is bonded by a combination of metallic and covalent bonding that prevents atoms from packing as efficiently as we might expect.

Compounds formed from two or more metals (**intermetallic compounds**) may be bonded by a mixture of metallic and ionic bonds, particularly when there is a large difference in electronegativity between the elements. Because lithium has an electronegativity of 1.0 and aluminum has an electronegativity of 1.5, we would expect AlLi to have a combination of metallic and ionic bonding. On the other hand, because both aluminum and vanadium have electronegativities of 1.5, we would expect Al_3V to be bonded primarily by metallic bonds.

Many ceramic and semiconducting compounds, which are combinations of metallic and nonmetallic elements, have a mixture of covalent and ionic bonding. As the electronegativity difference between the atoms increases, the bonding becomes more ionic. The fraction of bonding that is covalent can be estimated from the following equation:

$$\text{Fraction covalent} = \exp(-0.25\Delta E^2) \tag{2-1}$$

where ΔE is the difference in electronegativities. Example 2-4 explores the nature of the bonds found in silica.

Example 2-4 *Determining if Silica is Ionically or Covalently Bonded*

In a previous example, we used silica (SiO_2) as an example of a covalently bonded material. In reality, silica exhibits ionic and covalent bonding. What fraction of the bonding is covalent? Give examples of applications in which silica is used.

SOLUTION

From Figure 2-9, the electronegativity of silicon is 1.8 and that of oxygen is 3.5. The fraction of the bonding that is covalent is

$$\text{Fraction covalent} = \exp[-0.25(3.5 - 1.8)^2] = 0.486$$

Although the covalent bonding represents only about half of the bonding, the directional nature of these bonds still plays an important role in the eventual structure of SiO_2.

Silica has many applications. Silica is used for making glasses and optical fibers. We add nanoparticles of silica to tires to enhance the stiffness of the rubber. High-purity silicon (Si) crystals are made by reducing silica to silicon.

Binding Energy and Interatomic Spacing

Interatomic Spacing The equilibrium distance between atoms is caused by a balance between repulsive and attractive forces. In the metallic bond, for example, the attraction between the electrons and the ion cores is balanced by the repulsion between ion cores. Equilibrium separation occurs when the total interatomic energy (IAE) of the pair of atoms is at a minimum, or when no net force is acting to either attract or repel the atoms (Figure 2-18).

The **interatomic spacing** in a solid metal is *approximately* equal to the atomic diameter, or twice the atomic radius r. We cannot use this approach for ionically bonded materials, however, since the spacing is the sum of the two different ionic radii. Atomic and ionic radii for the elements are listed in Appendix B and will be used in the next chapter.

The minimum energy in Figure 2-18 is the **binding energy**, or the energy required to create or break the bond. Consequently, materials having a high binding energy also have a high strength and a high melting temperature. Ionically bonded materials have a particularly large binding energy (Table 2-2) because of the large difference in electronegativities between the ions. Metals have lower binding energies because the electronegativities of the atoms are similar.

Other properties can be related to the force-distance and energy-distance expressions in Figure 2-19. For example, the **modulus of elasticity** of a material (the slope (E) of the stress-strain curve in the elastic region, also known as Young's modulus) is related to the slope of the force-distance curve (Figure 2-19). A steep slope, which correlates with a higher binding energy and a higher melting point, means that a greater force is required to stretch the bond; thus, the material has a high modulus of elasticity.

An interesting point that needs to be made is that not all properties of engineered materials are microstructure sensitive. Modulus of elasticity is one such property. If we have two aluminum samples that have essentially the same chemical composition but different grain size, we expect that the modulus of elasticity of these samples will be about the same; however, **yield strengths**, the level of stress at which the material begins

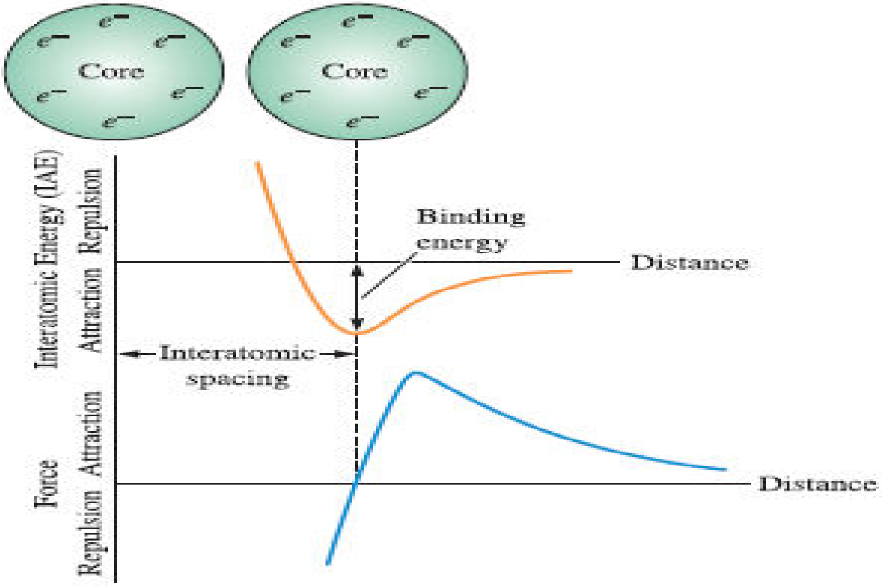


Figure 2-18
Atoms or ions are separated by an equilibrium spacing that corresponds to the minimum interatomic energy for a pair of atoms or ions (or when zero force is acting to repel or attract the atoms or ions).

TABLE 2-2 ■ ***Binding energies for the four bonding mechanisms***

Bond	**Binding Energy (kcal/mol)**
Ionic	150–370
Covalent	125–300
Metallic	25–200
Van der Waals	<10

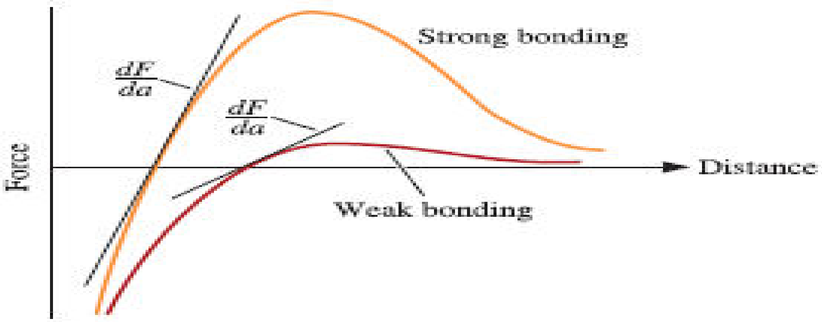
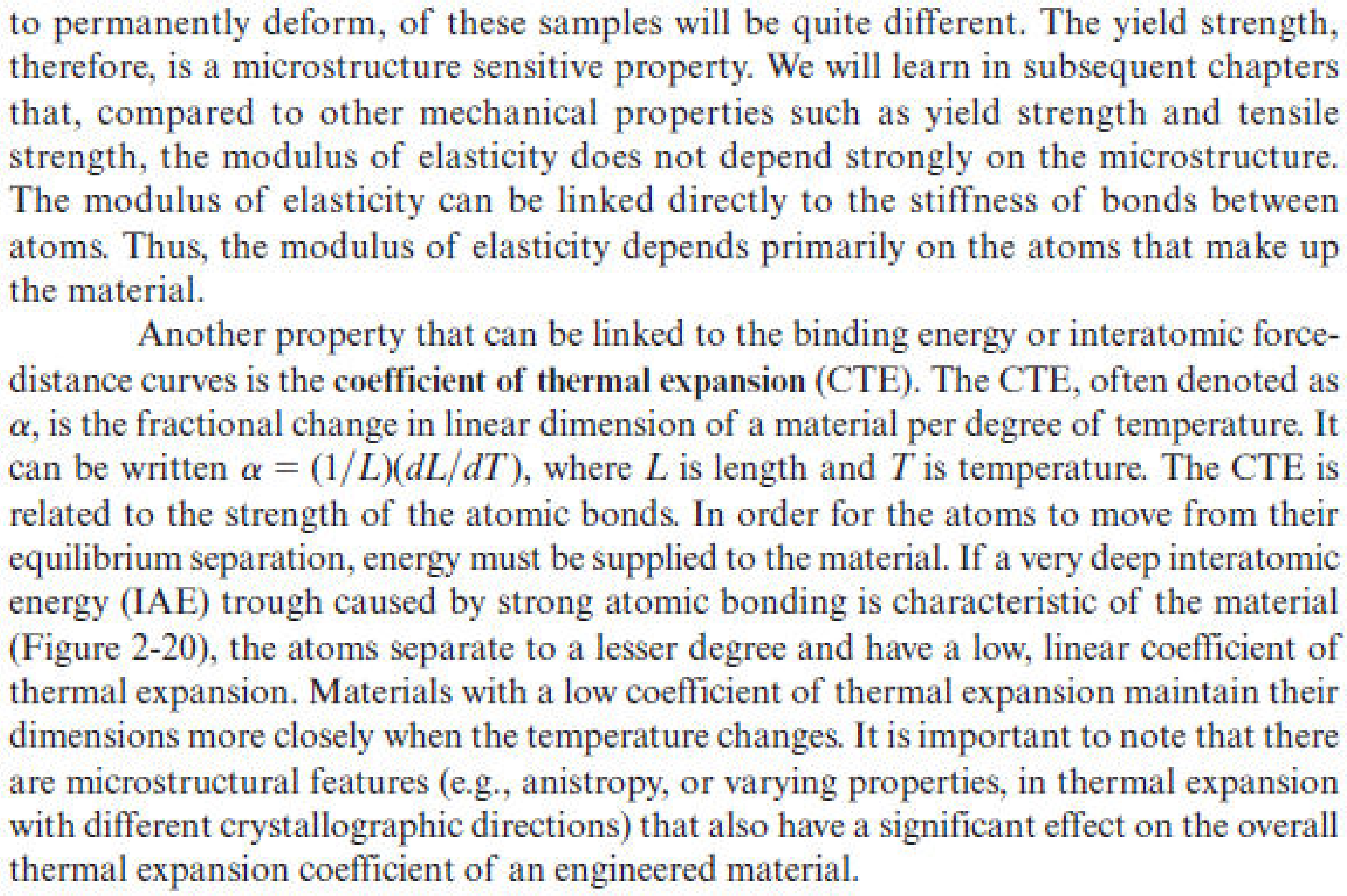


Figure 2-19
The force-distance (*F*–*a*) curve for two materials, showing the relationship between atomic bonding and the modulus of elasticity. A steep *dF/da* slope gives a high modulus.



to permanently deform, of these samples will be quite different. The yield strength, therefore, is a microstructure sensitive property. We will learn in subsequent chapters that, compared to other mechanical properties such as yield strength and tensile strength, the modulus of elasticity does not depend strongly on the microstructure. The modulus of elasticity can be linked directly to the stiffness of bonds between atoms. Thus, the modulus of elasticity depends primarily on the atoms that make up the material.

Another property that can be linked to the binding energy or interatomic force-distance curves is the **coefficient of thermal expansion** (CTE). The CTE, often denoted as α, is the fractional change in linear dimension of a material per degree of temperature. It can be written $\alpha = (1/L)(dL/dT)$, where L is length and T is temperature. The CTE is related to the strength of the atomic bonds. In order for the atoms to move from their equilibrium separation, energy must be supplied to the material. If a very deep interatomic energy (IAE) trough caused by strong atomic bonding is characteristic of the material (Figure 2-20), the atoms separate to a lesser degree and have a low, linear coefficient of thermal expansion. Materials with a low coefficient of thermal expansion maintain their dimensions more closely when the temperature changes. It is important to note that there are microstructural features (e.g., anistropy, or varying properties, in thermal expansion with different crystallographic directions) that also have a significant effect on the overall thermal expansion coefficient of an engineered material.

Materials that have very low expansion are useful in many applications where the components are expected to repeatedly undergo relatively rapid heating and cooling. For example, cordierite ceramics (used as catalyst support in catalytic converters in cars), ultra-low expansion (ULE) glasses, Visionware™, and other glass-ceramics developed by Corning, have very low thermal expansion coefficients. In the case of thin films or coatings on substrates, we are not only concerned about the actual values of thermal expansion coefficients but also the difference between thermal expansion coefficients between the substrate and the film or coating. Too much difference between these causes development of stresses that can lead to delamination or warping of the film or coating.

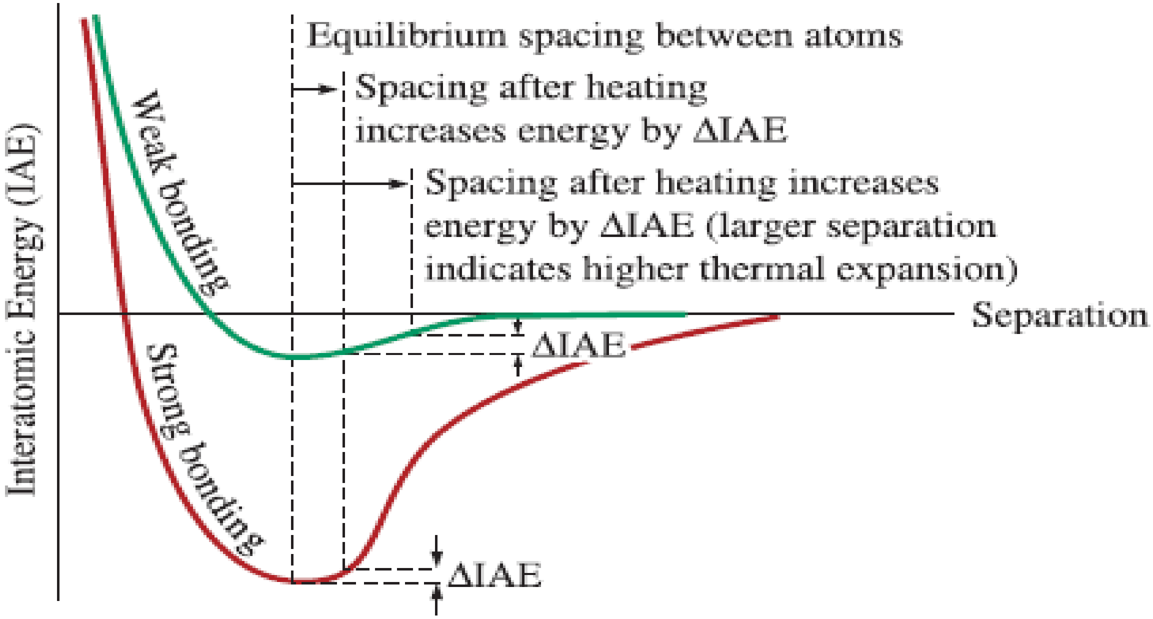


Figure 2-20 The interatomic energy (IAE)—separation curve for two atoms. Materials that display a steep curve with a deep trough have low linear coefficients of thermal expansion.