Chapter 8 – Solids

Introduction

Solids are characterized by an orderly arrangement of their particles. If the order is over short distances only (local order), the solid is an **amorphous solid**. Charcoal and glass are amorphous solids. If the order exists throughout the entire solid (long range order), the solid is said to be a **crystalline solid**. Table salt and sugar are two common examples of crystalline solids. This chapter is devoted to the study of crystalline solids. Even a small crystal contains millions and millions of particles. Thus, studying the solid state could be a formidable task.

8.1 Unit Cells
Introduction

However, the long range order that characterizes crystalline solids means that there is a small repeat unit, called the unit cell, that can be used to generate the entire crystal. Our study is simplified because, instead of studying the positions of the enormous number of particles that constitute the entire crystal, we need study only the small number of particles that comprise a unit cell. In this section, we define the unit cell and discuss how it is packed with atoms.
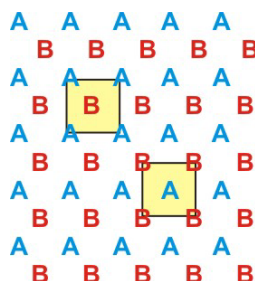
Objectives
- Define *unit cell* and *lattice*.

8.1-1. Definition

The unit cell is the smallest repeat unit of the crystalline lattice that generates the entire lattice with translation.

Crystalline solids are orderly, repeating, 3-D arrays of particles, which can be atoms, ions, or groups of atoms, such as polyatomic ions or molecules. The pattern of the array is called the crystal **lattice**, and the individual positions are called **lattice sites**. The simplest portion of the lattice that makes up the repeating unit is called the **unit cell**. When the unit cell is repeated in all three directions, it generates the entire crystalline lattice.

The figure shows two different but equivalent unit cells in a two-dimensional array. One unit cell consists of four A's on the corners and a B in the face center, while the other has B's on the corners with an A in the center. Translation by the length of one of the cell edges of either cell in any of the four directions produces an adjacent cell. Continued operations of translation generate the complete crystalline lattice. A three-dimensional lattice is formed by translation of a three-dimensional unit cell in three directions.

Figure 8.1: Definitions of Lattice and Unit Cell The unit cell is the smallest repeat unit of the crystalline lattice that generates the entire lattice with translation. The figure shows two different but equivalent unit cells highlighted in yellow.

8.1-2. Unit Cell Parameters

All unit cells can be uniquely characterized by their three edge lengths, (a, b, and c) and the angles (α, β, and γ) defined in Figure 8.2. They must be six-sided polygons that completely fill space; that is, no holes are present when the unit cell polygons are packed in three dimensions. As a result, there are only seven different types of unit cells. We limit our discussion to the simplest type of unit cell, the cubic unit cell. The cubic unit cell is one in which

$a = b = c$ and $\alpha = \beta = \gamma = 90°$. There are three types of cubic unit cells that differ only in the manner in which the particles fill the cell.

- simple cubic (sc)
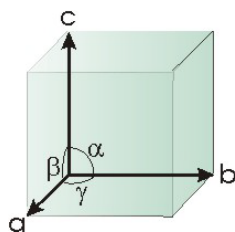- body-centered cubic (bcc)
- face-centered cubic (fcc)

Figure 8.2: Parameters that Define the Unit Cell Type

8.2 Cubic Unit Cells and Metallic Radii

Introduction

Unit cells must be six-sided polygons that completely fill space (no space between unit cells), and there are only seven types of unit cells that fulfill this requirement. However, our discussion is limited to only one type, the cubic unit cell.

Objectives
- Distinguish between simple, body-centered, face-centered cubic unit cells.
- Determine atomic radii from the unit cell edge length or the edge length from the atomic radii.

8.2-1. The Cubic Unit Cells

There are three cubic unit cells that differ in how the particles fill the cube. In each cubic unit cell, the same atom-type occupies each of the eight corners of the cube. The unit cell type is then dictated by where else in the unit cell that atom-type is found. Note that in the images below, all spheres represent the same atom type—the color differences are used only to distinguish different positions in the cell. There are three different types of cubic unit cells.

Type of Cubic Unit Cell	Location of Identical Particles	Image
simple cubic (sc)	on the corners but nowhere else in the cell	
body-centered cubic (bcc)	on the corners and in the center of the cell	
face-centered cubic (fcc)	on the corners and in the centers of the six faces of the cell	

Table 8.1: Cubic Unit Cells

8.2-2. Metallic or Atomic Radii

Atoms are not hard spheres with distinct boundaries, so their sizes are not determined directly. However, the positions of the atoms in a solid can be determined by x-ray diffraction, and the sizes of the atoms are inferred from those distances. In this method, the radius of an atom is determined from the unit cell edge length (a), which is determined from the location of the atoms, and the assumption that the atoms touch as shown in Figures 8.3a, 8.3b, and 8.3c.
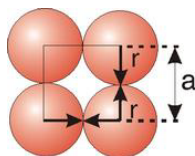

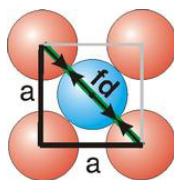**Figure 8.3a: Atom Contact in Simple Cubic Unit Cells**

$$2r = a \qquad \textbf{sc}$$

Figure 8.3b: Atom Contact in Face-Centered Cubic Unit Cells

$$
\begin{aligned}
fd &= 4r \\
fd^2 &= a^2 + a^2 \qquad \textbf{fcc} \\
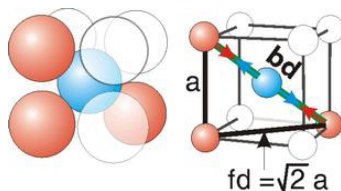(4r)^2 &= 2a^2
\end{aligned}
$$

Figure 8.3c: Atom Contact in Body-Centered Cubic Unit Cells

$$
\begin{aligned}
bd &= 4r \\
bd^2 &= fd^2 + a^2 \qquad \textbf{bcc} \\
(4r)^2 &= 2a^2 + a^2 = 3a^2
\end{aligned}
$$

Setting the edge length equal to $2r$ in the sc unit cell, and applying the Pythagorean theorem to the triangles shown in Figures 8.3a, 8.3b, 8.3c, we obtain the relationships between the atomic radius (r) of the atom and the edge length of the unit cell (a) given in Equation 8.1.

$$r = \frac{a}{2} \ \ (\text{sc})$$

$$r = \frac{\sqrt{2}a}{4} \ \ (\text{fcc}) \qquad \text{Relationship of Atomic Radii and Unit Cell Edge Lengths} \qquad (8.1)$$

$$r = \frac{\sqrt{3}a}{4} \ \ (\text{bcc})$$

The radius obtained from the structure of a metallic solid is referred to as either the **_metallic radius_** or the **_atomic radius_**.

8.2-3. Determining an Atomic Radius Exercise

8.3 Unit Cell Stoichiometry
Introduction

The number of atoms or ions in a unit cell of a compound does not have to be the same as the number of atoms in the formula of the compound, but the stoichiometry of the unit cell must be the same as the stoichiometry of the compound. Thus, a unit cell of NaCl may have many sodium and chloride ions, but the number of each ion must be the same because their stoichiometric ratio is 1:1 in the compound. However, when determining the unit cell stoichiometry, you cannot simply count all of the atoms or ions that form the unit because many of the particles may be part of more than one unit cell. In this section, we explain how to determine the stoichiometry of a unit cell.

Objectives
- Determine the fraction of an atom that lies in a unit cell given the lattice site occupied by the atom.
- Determine the number of atoms, molecules, or ions in a unit cell.

8.3-1. Unit Cells Share Particles

A particle in a face contributes 1/2 particle to each unit cell, one on an edge contributes 1/4 to a unit cell, and one on a corner contributes 1/8 per cell.

The structure of the unit cell is useful for understanding the stoichiometry of the compound. The stoichiometry of a compound can be determined by considering the number of particles (atoms, molecules, or ions) that make up the unit cell. However, most atoms in a unit cell are shared by several unit cells, so the contribution of a particle to any one unit cell is usually less than one.
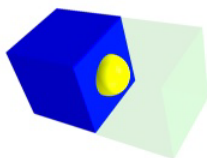
Figure 8.4a: Particle Contributions to Unit Cell Stoichiometry A particle on a **face center** is shared by two unit cells, so it contributes 1/2 particle to each.
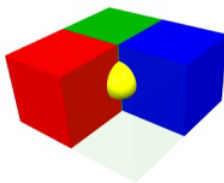
Figure 8.4b: Particle Contributions to Unit Cell Stoichiometry A particle on an **edge** is shared by four unit cells, so it contributes 1/4 particle to each.
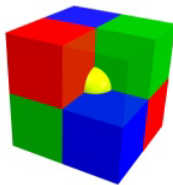
Figure 8.4c: Particle Contributions to Unit Cell Stoichiometry A particle on a **corner** is shared by eight unit cells, so it contributes 1/8 particle to each.

8.3-2. Contributions per Unit Cell

The particles on the eight corners combine to contribute 1 particle to a unit cell. Particles in the six face centers combine to contribute 3 particles to a unit cell. Those on twelve edges combine to contribute 3 particles per unit cell.

Atoms that are entirely within a unit cell each contribute a full atom to the cell stoichiometry, but the atoms in the faces, corners, and edges are shared by more than one unit cell, and the number of atoms they contribute to each unit cell is given below.

$$\frac{8 \text{ corners}}{\text{unit cell}} \times \frac{1 \text{ atom}}{8 \text{ corners}} = \frac{1 \text{ atom}}{\text{unit cell}}$$ Atoms located on the *corners* of the unit cell contribute 1 atom per unit cell.

$$\frac{6 \text{ faces}}{\text{unit cell}} \times \frac{1 \text{ atom}}{2 \text{ faces}} = \frac{3 \text{ atoms}}{\text{unit cell}}$$ Atoms located on the *faces* of the unit cell contribute 3 atoms per unit cell.

$$\frac{12 \text{ edges}}{\text{unit cell}} \times \frac{1 \text{ atom}}{4 \text{ edges}} = \frac{3 \text{ atoms}}{\text{unit cell}}$$ Atoms located on the *edges* of the unit cell contribute 3 atoms per unit cell.

8.3-3. Determining the Number of Atoms in a Unit Cell Exercise

EXERCISE 8.2:

How many atoms are in each of the three cubic unit cells?

sc = _____   bcc = _____   fcc = _____

# 8.4 Coordination Number and Geometry
Introduction

The ***coordination number*** (CN) is the number of nearest neighbors of a given particle in the crystal lattice. It determines the nature of the bonding in a crystal. The most common coordination numbers are 4, 6, 8, and 12.
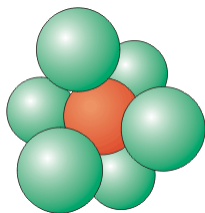
Objectives
- Define the term coordination number.
- Determine the coordination number of an atom or ion in a unit cell.

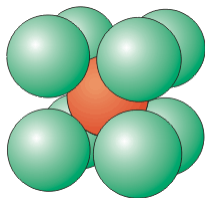## 8.4-1. Common Coordination Numbers and their Geometries
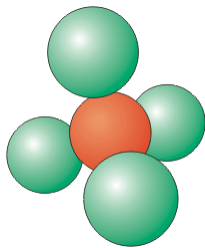
Figure 8.5a: Coordination Number of 4

Four atoms around a central atom are located at the corners of a tetrahedron.

Figure 8.5b: Coordination Number of 6

Six atoms around a central atom are located at the corners of an octahedron. An atom on the corner of a simple cubic unit cell has a coordination number of six.

Figure 8.5c: Coordination Number of 8

Eight atoms around a central atom are located at the corners of a cube. The atom in the center of a body-centered unit cell has a coordination number of eight.
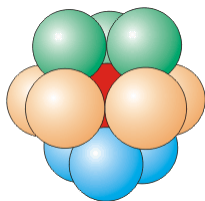
Figure 8.5d: Coordination Number of 12

Each atom in a face-centered cubic unit cell has a coordination number of 12. The 12 particles, which make up the *coordination sphere* of the red particle lie in three planes. The three planes can be seen in either of two ways:

- The top and bottom planes each have three particles, while the plane in the middle contains the central particle and six others forming a belt around it.
- The top and bottom planes each have four particles, while the plane in the middle contains the central particle and four others. The central plane is the face of a face-centered cube.

The packing of equal sized particles shown for the coordination number of twelve represents the tightest possible packing arrangement and is frequently described as the *closest packed* geometry.

8.4-2. Coordination Number Exercise

EXERCISE 8.3:

The mineral rutile is an oxide of titanium that crystallizes in the tetragonal ($a = b > c$, $\alpha = \beta = \gamma = 90°$) unit cell. Use the unit cell shown below to determine the following for titanium oxide.
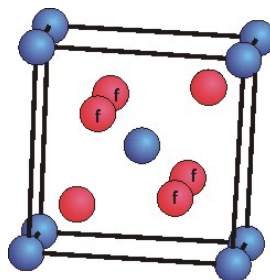
Ti atoms are blue and O atoms are red. The four O atoms marked "f" are in the cell face, but the other two are in the cell body.

number of Ti atoms in the uc = _____

number of O atoms in the uc = _____

simplest formula of titanium oxide = _____

coordination number of Ti = _____

8.5 Density and Packing Efficiency
Introduction

It is impossible to pack spheres without introducing some ***void space*** (space that is not occupied). How well the atoms pack a unit cell depends upon the unit cell type and is given by the packing efficiency of the unit cell. Solids with tightly packed unit cells are more dense than those with low packing efficiencies. In this section, we examine the packing efficiencies of the cubic unit cells and show how to determine the density of a solid from its crystal structure.

Objectives
- Determine relative packing efficiencies of cubic unit cells.
- Determine the density of a solid from its crystal structure.

8.5-1. Density

Density is the mass-to-volume ratio of a substance.

$$d = \frac{\text{mass of substance}}{\text{volume of substance}} \qquad \text{Density} \tag{8.2}$$

Densities of metals range from 0.53 g/cm^3 for lithium to 22.65 g/cm^3 for iridium.

8.5-2. Packing Efficiency

Packing efficiency is the fraction of the unit cell that is occupied by particles. Closest packed spheres pack with a packing efficiency of 74%.

Spheres cannot be packed without creating some void space, but the amount of void space depends upon how well they are packed. ***Packing efficiency*** (PE) is that fraction of the unit cell volume that is actually occupied by particles, not void space.

Thus, the packing efficiency of a unit cell is

$$\text{Packing Efficiency} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} \times 100\%$$

$$\text{PE} = \frac{N \times (4/3)\pi r^3}{a^3} \times 100\%$$

(8.3)

- a = the length of a side of the unit cell, so a^3 is the volume of the unit cell.
- r = the radius of the atoms that occupy the unit cell, so $(4/3)\pi r^3$ is the volume of a single atom in the unit cell.
- N = the number of atoms in the unit cell, so $N(4/3)\pi r^3$ is the volume occupied by all of the atoms in the unit cell.

The unit cell size (a) is directly proportional to the atom size (r), so one can be defined in terms of the other and then canceled in the above expression. Consequently, the packing efficiency depends only upon the cell type, not its size. As shown in the next sections, the relationship between a and r depends only upon the unit cell type.
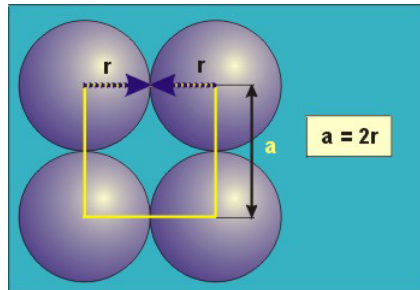
8.5-3. Packing in Simple Cubes

Figure 8.6

In the *simple cubic unit cell*, the spheres touch along the cell edge. Consequently, the edge length is two atomic radii ($a = 2r$).

The properties of the simple cubic unit cell:

- $r = 0.5a$
- $N = 1$ atom/unit cell
- packing efficiency = 52%
- coordination number = 6

8.5-4. Packing in Face-Centered Cubes
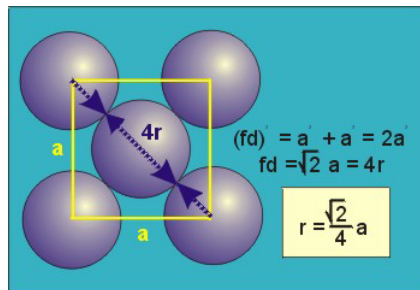

Figure 8.7

Particle contact in the *face-centered cubic unit cell* is along the face diagonal (fd). The face diagonal is four atomic radii ($fd = 4r$) and is related to the unit cell edge length (a) by the Pythagorean theorem.

The properties of the face-centered cubic unit cell:

- $r = \dfrac{\sqrt{2}}{4}a = 0.354a$
- $N = 4$ atoms/unit cell
- packing efficiency = 74%
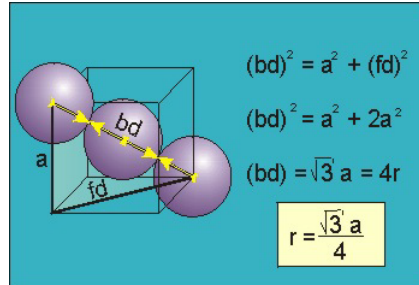- coordination number = 12

8.5-5. Packing in Body-Centered Cubes

$$(bd)^2 = a^2 + (fd)^2$$
$$(bd)^2 = a^2 + 2a^2$$
$$(bd) = \sqrt{3}\,a = 4r$$
$$r = \dfrac{\sqrt{3}\,a}{4}$$

Figure 8.8

For the *body-centered cubic unit cell*, the spheres make contact along the body diagonal (bd), which is four atomic radii (each yellow arrow is one atomic radius), i.e., $bd = 4r$. The body diagonal is related to the face diagonal (fd) and the cell edge (a) by the Pythagorean theorem. The relationship between the cell edge and the face diagonal was derived in the discussion of the fcc unit cell.

The properties of the body-centered cubic unit cell:

- $r = \dfrac{\sqrt{3}}{4}a = 0.433a$
- $N = 2$ atoms/unit cell
- packing efficiency = 68%
- coordination number = 8

8.5-6. Packing Efficiency and Coordination Number

As shown in the previous sections, the packing efficiency of a unit cell depends only on the cell type; it is independent of edge length and atomic radius because both cancel in the calculation. Table 8.2 gives the packing efficiencies of the cubic unit cells and coordination numbers of the atoms in them. As might be expected, the packing efficiency increases as the number of atoms in the unit cell and the number of atoms that are packed around each atom (coordination number) increases.

Lattice Type	Packing Number	Coordination Efficiency
Simple	52%	6
Body-centered	68%	8
Face-centered	74%	12

Table 8.2: Packing Efficiencies and Coordination Numbers of Cubic Lattices

8.5-7. Packing Efficiency and Crystal Properties

Table 8.3 shows the unit cell types, metallic radii, and densities of selected metals that adopt cubic unit cells. Almost half of the volume of a sc unit cell is void space, so the sc unit cell is not a favorable way to pack and metals do not generally crystallize in sc lattices. Indeed, the only known example of a metal adopting the sc unit cell is a form of polonium. The densities of the Group 1A elements are all quite low because their atoms are not very dense (they have the greatest volume and smallest mass of any atom in their period) and because they pack in the less efficient bcc lattice. The impact of packing efficiency on the density can be seen by comparing K and Ca, which

are next to one another in the periodic chart and have nearly identical metallic radii. Ca is almost 60% more dense because it crystallizes in the more efficient fcc unit cell. The effect can also be seen by comparing two forms of iron. Iron normally crystallizes with a bcc structure known as α-iron, but it also can be made to adopt a more efficiently packed fcc structure called γ-iron by adding small amounts of carbon and manganese or nickel and chromium. The tighter packing of γ-iron makes it so corrosion-resistant that it is known as stainless steel.

Metal	Unit Cell	Radius (Å)	Density (g/cm³)
Ag	fcc	1.44	10.5
Al	fcc	1.43	2.70
Au	fcc	1.46	19.3
Ba	bcc	2.48	3.59
Ca	fcc	2.35	1.55
Cu	fcc	1.28	8.96
K	bcc	2.35	0.86
Li	bcc	1.55	0.53
Na	bcc	2.35	0.97
Ni	fcc	1.25	8.90
Pb	fcc	1.75	11.35
Pt	fcc	1.39	21.45
Rb	bcc	2.48	1.53
Sr	fcc	2.15	2.6

Table 8.3: Unit Cell Type, Metallic Radii, and Densities of Selected Metals with Cubic Unit Cells

8.5-8. Exercise on Determining Packing Efficiency

EXERCISE 8.4:

Rhodium (Rh, M_m = 102.9 g/mol) crystallizes in a face-centered cubic unit cell that is 3.79 Å on a side. Determine the atomic radius, packing efficiency, and density of the unit cell based on these data. See Section 8.5-4. for help with fcc unit cell packing. Express your answers with three digits.

The atomic radius of Rh is $r =$ _____ Å

The volume of one Rh atom is $V =$ _____ Å^3

The number of Rh atoms present in one unit cell is $n =$ _____

The volume of all of the atoms in the unit cell is $V =$ _____ Å^3

The volume of the unit cell is $V =$ _____ Å^3

The packing efficiency of the cell based on these numbers is PE = _____ %

The mass of all atoms in the unit cell is $m =$ _____ g

The volume of the unit cell in cm^3 is $V =$ _____ cm^3

The density of Rh derived from these data is $d =$ _____ g/cm^3

8.6 Band Theory of Simple Metals
Introduction

The **metallic bond** is the interaction that holds metal atoms in the solid. The strength of the metallic bond varies considerably depending upon the metal. Consequently, metals vary from very high-melting substances such as iron (mp = 1535 °C) to low-melting substances such as mercury (mp = −39 °C).

Metals have low ionization energies and readily lose their valence electrons to become positively charged ions. In a metallic bond, valence electrons from all of the metal atoms in the solid are *delocalized* over the entire metal. The metal cations are immersed in the sea of valence electrons, and the electrostatic force exerted between the cations and the surrounding electrons holds the positively charged metal ions in place.

Bonding and electrical conduction in metals is best understood in terms of **band theory**, which is the extension of molecular orbital theory (Section 6.5) to the very large number of atoms found in a metal.

Objectives
- Describe a metallic bond.
- Explain what is meant by an *energy band*.
- Define the *Fermi level* and identify it in a band diagram.
- Explain how a metal can be a conductor even when all of its valence orbitals are full.
- Define the *band gap*.
- Distinguish between a *valence band* and a *conduction band*.
- Distinguish between a metallic conductor, a semiconductor, and an insulator based on their band structures.

8.6-1. Introduction to Band Theory

The molecular orbital description of the delocalized electrons in metallic bonds provides a more complete picture of metallic bonding as well as an explanation for the electrical conductivity of metals. The explanation, which is called band theory, applies the concepts presented in the molecular orbital discussion in Chapter 6 to a very large number of orbitals. The orbitals in the solid are constructed in the same way as those in a molecule, but they apply to a crystal rather than a molecule, so they are called crystal orbitals rather than molecular orbitals. As the number of orbitals increases, the adjacent orbitals become more similar, and the resulting energy levels get closer together. In a piece of metal, the number of atoms and atomic orbitals in each crystal orbital is enormous (on the order of Avogadro's number), so the energy levels are so close that they can no longer be distinguished and the system is described in terms of energy bands rather than energy levels. The formation and properties of bands is the topic of this section.

8.6-2. Properties of Multi-Orbital Systems

Increasing the number of orbitals in a molecular orbital increases the energy spread of the molecular orbitals while decreasing the energy separation between adjacent orbitals.

Orbital X in Figure 8.9 has nine bonding interactions, while orbital A has only one. Each bonding interaction lowers the energy of the orbital, so X is at lower energy. Orbital Z has nine antibonding interactions, while orbital B has only one. Thus, Z is at a higher energy than B. We conclude that increasing the number of orbitals increases the energy difference between the highest and lowest energy orbitals; i.e., increases their energy spread ($\Delta E_2 > \Delta E_1$).
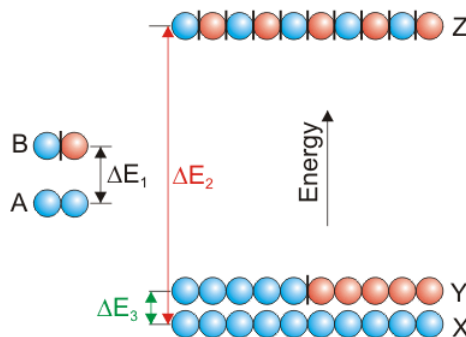

Figure 8.9: Energy Levels in Two- and Ten-Orbital Systems Only the two orbitals at lowest energy and the one at highest energy of the ten-orbital system are shown.

Orbital A is completely bonding, but orbital B is completely antibonding. They are very different types of orbitals, so their energies are very different. Orbital X has nine bonding interactions, while orbital Y has eight bonding interactions and one antibonding interaction. Orbitals X and Y are both strongly bonding, so they are close in energy.

8.6-3. The Definition of a Band

The energy levels in a metal are so close that they are represented by a band of energy.

As the number of orbitals increases, the energy spread of the molecular orbitals continues to increase, while the energy separation between adjacent levels continues to decrease. In a piece of metal, the number of atoms and orbitals is so large (on the order of Avogadro's number) that the energy levels are so close that they can no longer be distinguished. At this point, the energy levels are said to form an **energy band**. Energy bands are represented by rectangles that show the spread in energy between the lowest and highest energy orbitals. Although the separation between levels is so small that discreet levels are not shown, they do exist and the electrons fill the levels in a band with the same rules as they do the levels in an atom (lowest energy, Pauli Exclusion Principle).
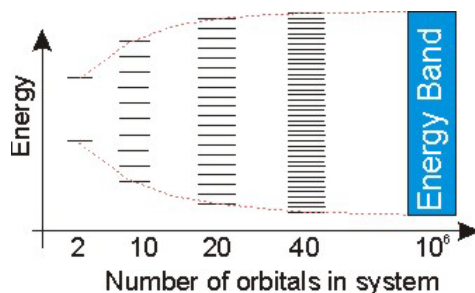

Figure 8.10: Band Formation The dotted lines represent the energy spread and show that the top and bottom energies begin to level off as the number of orbitals gets large.

8.6-4. Fermi Level

The highest-energy occupied level in a metal is called the Fermi level.

The electrons in a band occupy the lowest energy levels available, and their occupation is represented by shading the occupied portion of the band. The occupied level of greatest energy is called the **Fermi level**. The band in Figure 8.11 is half-filled, so the Fermi level is the middle level of the band.

Metals conduct electricity when the electrons are free to move, but they are free only when there are empty orbitals into which they can move. A partially filled band like the one in the figure is formed when the atomic orbitals used to construct it are not full. Since the energy separation between adjacent levels in a band is so small, the separation between the highest energy filled orbitals and the lowest energy unfilled orbitals is nearly zero in a partially filled band. Thus, electrons near the Fermi level of a partially filled band can move easily into empty orbitals. Since these orbitals are delocalized over the entire metal, the electrons are free to move through the entire metal, and the metal conducts electricity. Metals with this band structure (partially filled bands) are called metallic **conductors**.
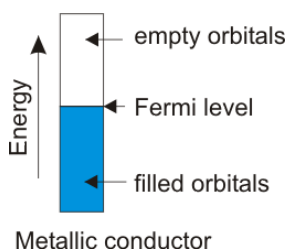
Figure 8.11: Band Structure for a Metallic Conductor Note: the shaded portion of the rectangle indicates the portion of the band that contains filled orbitals.

8.6-5. Valence Band, Conduction Band, and the Band Gap

The band gap is the energy separation between the valence and conduction bands.

Both occupied and unoccupied orbitals of a metal can combine to form bands. Electrons can move in bands that are not full, but they cannot move through a band that is full. The filled band at highest energy is occupied by valence electrons, so it is called the **valence band**. The unfilled band of lowest energy is called the **conduction**

band because it is the band in which electrons are free to move. The energy separation between the valence and conduction band is called the **band gap**. As we show in the next section, the conductivity properties of the metal are determined by the magnitude of the band gap.
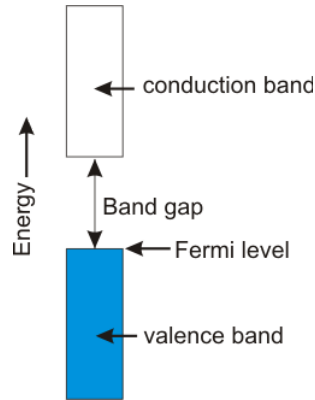

Figure 8.12: The Band Gap

8.6-6. Conductivity

Conductors have no band gap, semiconductors have moderate band gaps, and insulators have large band gaps.

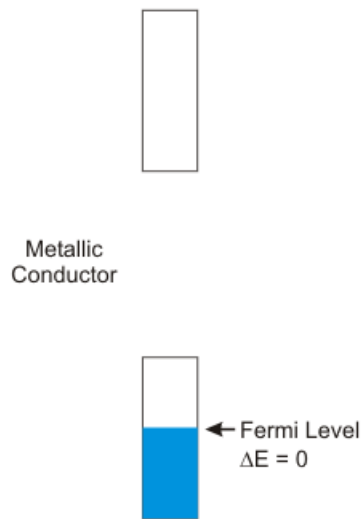The electrical conductivity properties of a metal depend upon its band gap.

Figure 8.13

Metallic conductors have partially filled bands, so they have no band gap. Bands at higher energy are irrelevant to their conductivity.
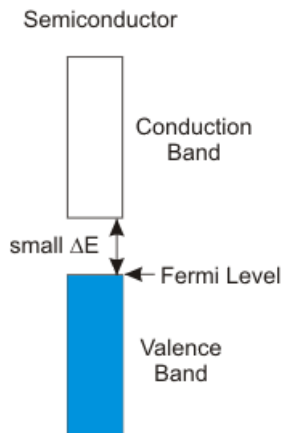
Figure 8.14

Semiconductors have band gaps that are not zero but are small enough that the conduction band can be populated at reasonable temperatures. The conductivity of semiconductors increases as the temperature is increased because the number of electrons in the conduction band increases as their thermal energy increases.
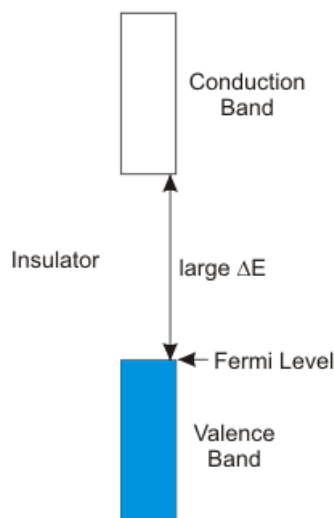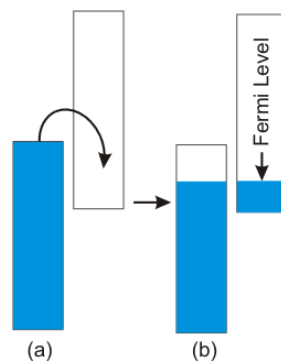

Figure 8.15

Insulators have band gaps that are so large that no electrons can occupy the conduction band at reasonable temperatures.

8.6-7. Band Overlap

A metal with filled orbitals can be a conductor if the bottom of a band formed from empty orbitals overlaps the top of the band formed from filled orbitals.

Metals with no unfilled orbitals can contain partially filled bands if the band formed from the filled atomic orbitals overlaps with a band formed from empty orbitals. This is the reason that metallic elements, such as zinc, that have no partially filled orbitals in their atoms can still be conductors. For example, Figure 8.16 shows the band structure of zinc. The filled 4s band and the unoccupied 4p band overlap, so the highest energy electrons in the 4s band move to lower energy in the 4p band to produce two partially filled bands. The partially filled bands make zinc a conductor.

Figure 8.16: A Metallic Conductor Produced from Overlapping Bands

Partially filled bands can be formed in atoms with no partially filled sublevels if the band formed with filled atomic orbitals overlaps with one formed from empty atomic orbitals.

8.7 Ionic Solids and Ionic Radii
Introduction

The ionic bond (Chapter 4) is the interaction that holds the ions of an ionic substance in the solid state. In order to melt or break an ionic crystal, ionic bonds must be broken, and ionic bonds are usually quite strong. Consequently, ionic substances are typically hard and have high melting points, which means that they are typically solids at room conditions. However, the strength of an ionic bond depends upon the charge of the ions and their separation (Coulomb's Law). Thus, ionic compounds with small ions (small separation) that are highly charged have higher melting points than ionic compounds with large ions that carry lower charges. For example, the melting point of MgO (small ions with +2 and −2 charges) is 2852 °C, while that of CsI (large ions with +1 and −1 charges) is 626 °C. In this section, we examine the structure of some simple ionic compounds.

Objectives
- Describe the sodium chloride structure.
- Distinguish between the NaCl and CsCl structures.
- Determine the radius of an ion given the ionic radius of the other ion and the distance between the ions in a compound.

8.7-1. Ionic Radii

The distance between two adjacent ions in a crystal is equal to the sum of their ionic radii. For example, the distance between Li^{1+} and I^{1-} ions in a crystal of LiI is 2.96 Å, so we can write $r_{Li} + r_I = 2.96$Å. Ionic radii have been determined by examining many such distances. The ionic radii of the alkali metal ions (Group 1A) and the halide ions (Group 7A) are given in Table 8.4.

Cation	Radius (Å)	Anion	Radius (Å)
Li^{1+}	0.90	F^{1-}	1.19
Na^{1+}	1.16	Cl^{1-}	1.67
K^{1+}	1.52	Br^{1-}	1.82
Rb^{1+}	1.66	I^{1-}	2.06
Cs^{1+}	1.81		

Table 8.4: Ionic Radii of Group 1A and 7A Ions

8.7-2. Ionic Radii Exercise

EXERCISE 8.5:

What is the ionic radius of Mg^{2+}, if the Mg–Cl distance in $MgCl_2$ is 2.53 Å?

the ionic radius of Cl^{1-} from Table 8.4 = _____ Å

r_{Mg} = _____ Å

8.7-3. LiI

Not all of the particles in an ionic solid are identical, but the same structural descriptions that are applied to metallic solids can be used to understand the crystal structure of many ionic compounds. For example, most of the alkali halides have a preference for a structure in which the anions pack in a face-centered cubic unit cell, as shown in Figure 8.17a, with the cations filling the void space as in Figure 8.17b.
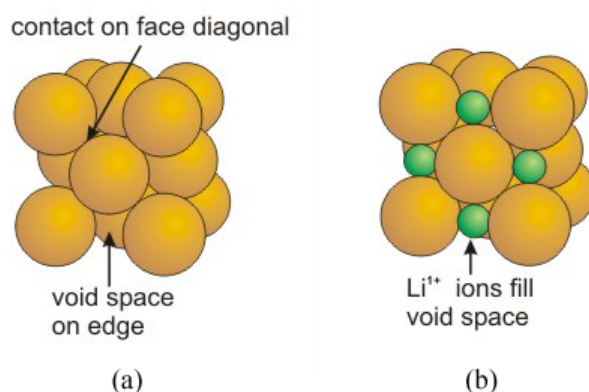

Figure 8.17

The three anions along a diagonal of a face touch in a fcc unit cell, but there is void space along each of the cell edges and in the body center and much smaller cations fill the space. Using geometry, we can calculate that to fill the void space perfectly, the radius of the cation should be a little less than half the radius of the anion $(r_{cation} = 0.414 r_{anion})$.

LiI nearly adopts the ideal structure $(r_{Li}/r_I = 0.44)$ and has a very high packing efficiency. However, the Li^{1+} ions are slightly too large to fit into the holes, so the I^{1-} ions are pushed apart slightly, so they no longer make contact.
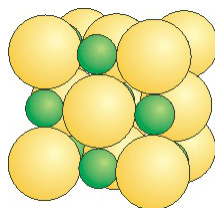
## 8.7-4. LiCl

Figure 8.18: LiCl Unit Cell

Chloride ions are smaller than iodide ions, so their fcc arrangement has even smaller holes along the edge. Consequently, they must be pushed apart even farther to accommodate the Li^{1+} ions (Figure 8.18). The distance by which the chloride ions are separated is determined in the following exercise.

8.7-5. Packing Exercise

EXERCISE 8.6:

Use ionic radii ($r_{Li} = 0.90$ Å; $r_{Cl} = 1.67$ Å) and the figure to determine the void space (highlighted in red) between chloride ions in LiCl.
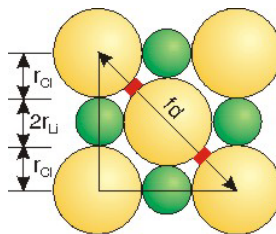
the unit cell edge is $a =$ _____ Å

the face diagonal is $fd =$ _____ Å

four chloride ionic radii $=$ _____ Å

the void space $=$ _____ Å

8.7-6. NaCl

Sodium chloride adopts the same structure type as lithium chloride. In fact, this structure type is called the sodium chloride structure, and LiCl is said to crystallize in the sodium chloride structure. In sodium chloride, the sodium cation is considerably larger than the ideal hole created by closest packed chloride anions. As shown in Figure 8.19, the chloride anions are moved even farther apart to accommodate the larger sodium ions. While this expansion of the packing in the unit cell lowers the packing efficiency, there is little energetic cost because each ion is still in direct contact with six ions of opposite charge. The major change in this expanded structure is that the like charges (anion-anion and cation-cation) are further separated, which is energetically favorable.
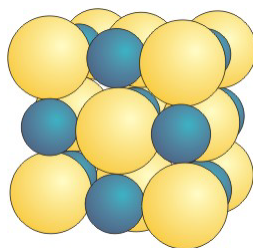

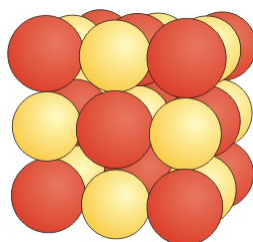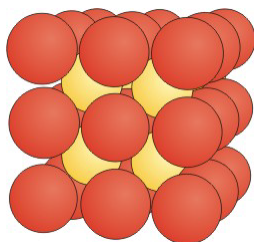**Figure 8.19: NaCl Structure**

8.7-7. CsCl

Figure 8.20a: CsCl Unit Cell CsCl in NaCl structure

In CsCl, the radius of the cesium ion is slightly larger than the radius of the chloride anions of the fcc lattice. Because the cations and anions are now nearly the same size, the fcc lattice is pushed apart. The packing efficiency

drops down to that of a simple cube in which four of the corners are occupied by cations and four are occupied by anions. CsCl can be made to crystallize with the sodium chloride only under certain conditions.

Figure 8.20b: CsCl Unit Cell The CsCl structure

Under normal conditions, the packing efficiency of these nearly equally sized ions is optimized in the arrangement, as shown in the figure. This structure, known as the cesium chloride structure, can be described as having chloride anions forming a simple cube with a cesium cation in the body center. Alternatively, it can be described as a simple cube of cesium cations with a chloride anion in the body center.

8.8 Network Covalent Solids
Introduction

Covalent solids are like ionic solids in that they are very large networks of particles rather than discrete molecules. They differ from ionic solids in that the particles are atoms, not ions, and they are held in their lattice sites by covalent bonds rather than ionic bonds. Because the atoms in the lattice are attached by strong covalent bonds, the materials have very high melting points and are very hard. In this section, we examine the structures of several common network covalent solids.

Objectives
- Describe the structure of graphite and explain why graphite is a lubricant.
- Describe the structures of diamond and the semiconductors Si and Ge.
- Describe the similarity between the structure of diamond and the semiconductors ZnS, GaAs, and IP.

8.8-1. Graphite

The carbon atoms in graphite are sp^2 hybridized and covalently bound together into a two-dimensional array in which the C–C distances are 1.4 Å (see Figure 8.21a). Layers of the two-dimensional arrays are held together loosely (3.4 Å between layers as shown in Figure 8.21b) by intermolecular interactions.

The covalent bonding within the layer gives graphite a high melting temperature. The large number of covalent bonds also produces band structures that make it a good conductor. However, the interaction between the layers is weak, so the layers can slip over each other, which makes graphite an excellent lubricant.
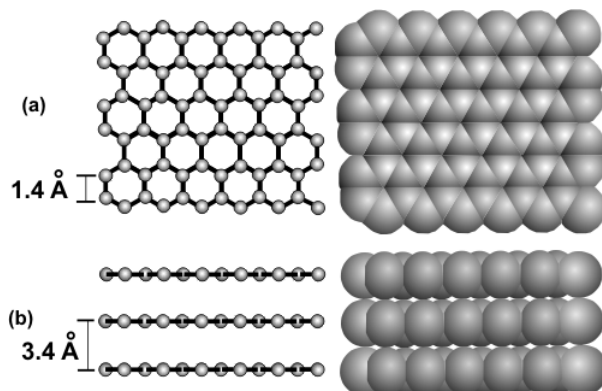
Figure 8.21: Graphite Ball-and-stick and space filling models of graphite that show a small portion of three layers.

8.8-2. Buckyball

Fullerenes are carbon compounds with structures based on the graphite structure. The most common fullerene is C_{60}, which is called buckminster-fullerene (or buckyball) after the architect of the geodesic dome. Buckyball was discovered in the early 1980's. It contains 20 hexagons and 12 pentagons and is the shape of a soccer ball. The hexagons are the same units that form the basis of graphite, but the pentagons are required for closure. A great deal of research was done on fullerenes to develop new technologies. For example, efforts were made to use it as a molecular ball-bearing lubricant, and to encapsulate drugs in its cavity, so they could be released slowly in the body. Buckyball is also a superconductor, so efforts were made to take advantage of this property as well. However, no practical uses of buckyball have yet been developed.


(a)　　　　　**(b)**
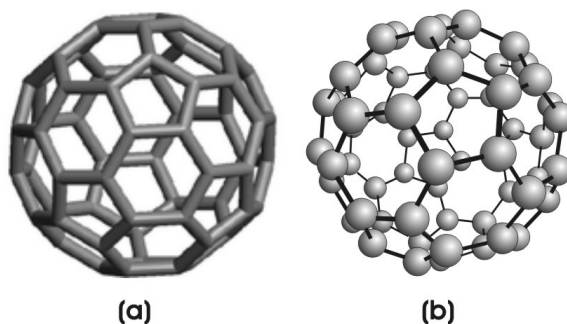
Figure 8.22: Buckyball Figure (a) shows the stick model of Buckyball that includes only the bonds to emphasize the hexagons and pentagons. Figure (b) is the ball-and-stick model that includes the carbon atoms.

8.8-3. Nanotubes

Nanotubes are based on the graphite structure. They are basic building blocks in molecular electronics.

A carbon nanotube is a rolled-up sheet of graphite that is only nanometers wide but up to a centimeter long. Nanotubes are very strong, and, depending on how the graphite sheets are rolled (straight across or at a diagonal), they are conductors or semiconductors. Single nanotubes have been used to make molecular wires, diodes, and transistors, and groups of nanotubes have been integrated into logic circuits, fundamental computer components. These devices are a hundred times smaller than those on present-day computer chips. Nanotubes are a basic building block in the new field of molecular electronics. Indeed, a new technology, one based on devices that measure less than 1000 nanometers, is currently being developed. This new technology is referred to as nanotechnology.


(a)

(b)
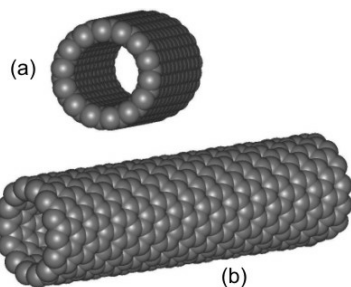
Figure 8.23: Nanotube The tube is viewed down its axis in a and along its side in b.

8.8-4. Diamond

Its strong bonds and structure make diamond the strongest substance known.

Directional sp^3 hybridized orbitals are used to create the three-dimensional framework of diamond. The directional bonds result in a much lower packing efficiency than in metals or ionic compounds where the spherical nature of the atoms and ions allows for much tighter packing. The figure shows one unit cell.
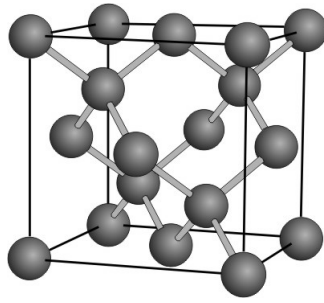
Figure 8.24: Diamond Structure

The electrons of the covalent bonds are delocalized over the entire structure, diamond has valence and conduction bands. Consequently, the diamond structure type is found for several common semiconductors (Si and Ge). Diamond, however, is an insulator because its band gap is very large.

8.8-5. Zinc Blende

The zinc blende structure is common amongst semiconductors.

The zinc blende structure differs from the diamond structure in that there are two sets of atoms (Zn and S) instead of one (C). However, the two sets occupy the same positions as do the carbon atoms in diamond: the corners and face-centers are occupied by one type of atom, but the four sites within the cell are occupied by another. The zinc blende structure type is the structure adopted by the most common semiconductors (ZnS, GaAs, InP).
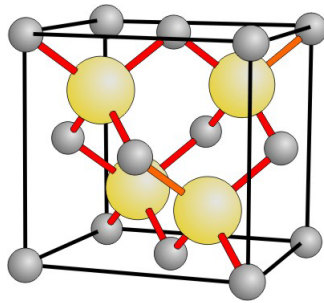
Figure 8.25: Zinc Blende Structure

8.8-6. Silica

Silica, silicon dioxide, is encountered most commonly as sand, which is used to make glass, cement, and ceramics. The crystalline form of silica that is found at room conditions is known as quartz. Quartz is based on a three-dimensional covalent network of SiO_4 tetrahedra. A high temperature form of SiO_2 (known as high cristobalite) is shown in the Figure 8.26. The silicon atoms (the gray spheres) also adopt the diamond-type structure but, in this structure, there is an oxygen atom (red sphere) located between each pair of silicon atoms.
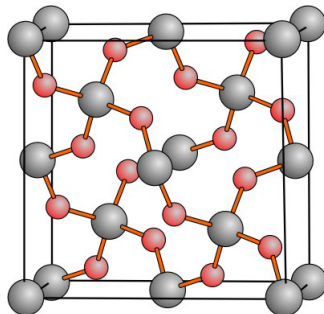

Figure 8.26: Structure of High Cristobalite, a Form of Quartz

8.8-7. Zeolite Structure

Zeolites are characterized by molecular scale channels.

Natural zeolites are aluminosilicates, extended networks that are built from tetrahedral AlO_4 and SiO_4 units that are bridged by oxygen atoms (each oxygen atom is part of two units). The structure of zeolites is filled with cavities (pores) and channels that are only a few angstroms wide (1 angstrom = 10 nm). The aluminosilicate framework is anionic, so natural zeolites are commonly found as their sodium salts. The cations sit inside the cavities. Small molecules can also get into the channels and interact with the oxygen atoms in the aluminosilicate framework, which leads to many uses for zeolites.
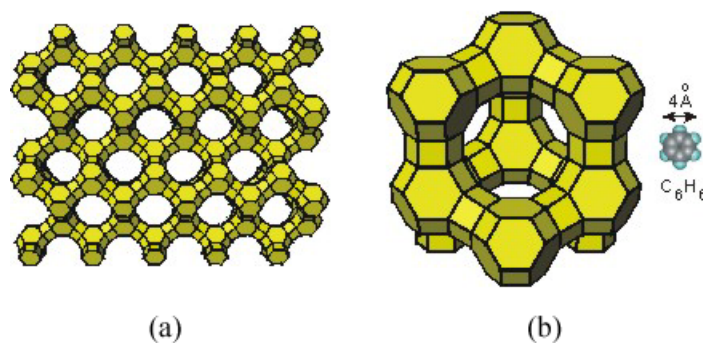
Figure 8.27: Zeolite (a) A section of a zeolite showing a series of channels. Al or Si atoms sit at the end of each line with O atoms bridging them. The openings in the structure that are too small for other molecules to enter are shown as closed surfaces. (b) The pore of this zeolite is formed by a ring that contains 12 atoms (Si and Al) and is 7 Å in diameter. A benzene molecule, which is about 4 Å across, is shown for comparison.

8.8-8. Zeolite Function

Molecular sieves

- The interaction between small molecules in the cavities and the oxygen atoms in the framework keeps the small molecules from leaving, so zeolites are used as molecular sieves. One common use is as a drying agent because water is small and interacts very strongly with the walls via hydrogen bonding. Consequently, when zeolite is added to a wet liquid, the water molecules enter the cavities but do not exit. The molecular sieves are then filtered out of the liquid to leave a dry liquid behind. The sieves can be restored by placing them in a hot oven where the thermal energy is sufficient for the water molecules to break their interactions with the framework.

Ion exchange

- The sodium ions are only loosely bound in the cavities, so they are easily displaced by other ions. Thus, zeolites can also be used for ion-exchange. Perhaps the most common ion-exchanger is the water softener. Water hardness is due to Ca^{2+} and Mg^{2+}. When "hard water" is passed through a zeolite column, the Ca^{2+} and Mg^{2+} displace Na^{1+} because the more highly charged ions interact more strongly. Thus, the water that leaves the column contains Na^{1+} rather than Ca^{2+} and Mg^{2+}, so it is "soft water."

Catalysts

- Chemistry can take place inside the pores. Indeed, some reactions that occur with difficulty on their own occur with relative ease within the cavities of a zeolite. The enhanced reactivity results because interactions with the aluminosilicate framework can make substances more reactive, i.e., zeolites can function as catalysts. The pore size dictates the size of both the reactants and the products, so chemists can select to react only certain molecules in a mixture by selecting a zeolite with the appropriate pore size to exclude larger molecules. Chemists also create zeolites with chemical groups attached to them that enhance certain reactions; i.e., they functionalize zeolites.

Molecular confinement

- Confinement and transportation of large amounts of gases presently requires a combination of very large volumes, very high pressures, and/or very low temperatures. However, storing the gases in the cavities of zeolites is presently being pursued by chemists and engineers. The process would involve synthesizing a zeolite with the cavity size appropriate for the gas and mixing the gas with the zeolite to get the gas molecules into the pores. Once the zeolite is saturated with the gas, the conditions (temperature, pressure, cation, or other method) would be changed to cause a structural change in the zeolite that would trap the gas. Restoring the original conditions would restore the original zeolite structure, so the gas would be released.

8.8-9. Clays

Clays are the most abundant minerals found in soils, rocks, and waters. Like zeolites, they are usually aluminosilicates. However, Mg is substituted for Al in many clays, and Fe fills certain of the Al sites in some clays to give them a red color. All clays exhibit a two-dimensional layered lattice structure rather than the porous network structure of zeolites. As shown in the following figures, the two major types of clays, kaolinite and smectite clays, differ in the organization of tetrahedral (SiO_4) and octahedral (AlO_6 or MgO_6) building blocks. The differences in their structure in turn result in dramatically different properties for these two types of clays.

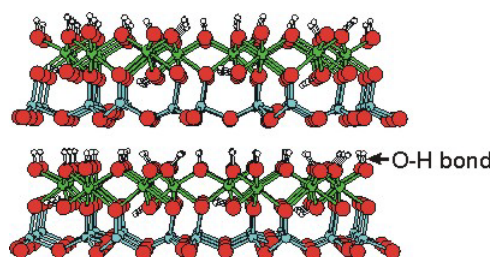**Figure 8.28a: Kaolinite Clay**

Kaolinite clays consist of aluminosilicate sheets composed of a silicate layer (SiO_4 tetrahedra shown in blue) and an aluminate layer (AlO_6 octahedra shown in green). In their sedimentary formation, kaolinite clays may have water between the aluminosilicate layers. However, upon heating (firing) the water is driven out from between the layers, leaving only OH bonds on the surface formed by the aluminate layers. These terminal OH groups from strong hydrogen bonds to the oxygen atoms of the silicate portion of the neighboring layer providing a rigid material, which is why kaolinite clay is the main component of china clay.
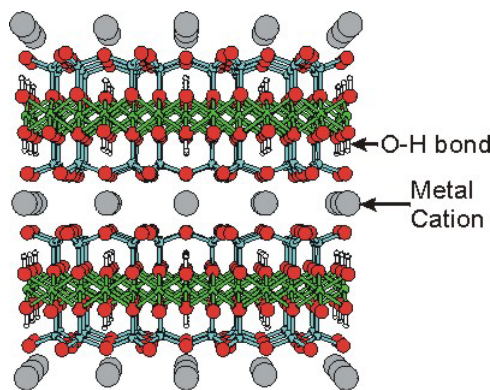

Figure 8.28b: Smectite Clay

Smectite (or swelling) clays consist of sheets composed of a layer of aluminate octahedra sandwiched between two layers of silicate tetrahedra. Other cations surrounded by water (hydrated metal ions), represented by the larger gray spheres in Figure 8.28b, often fill the space between these layers. There are fewer OH groups in this type of structure, and those that are present are "buried" on the aluminate layer between the two silicate layers, which effectively shields them from forming inter-layer hydrogen bonds. As a result, the layers in a smectite clay are not tightly held together, and other ions and molecules can penetrate in between these layers and force the sheets apart.

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This property makes them chemically important for the same reasons as zeolites. The major difference being that the 3-D network of zeolites provides greater size and shape selectivity than the 2-D structure of clays. Interestingly, when a smectite clay is fired, the water can also be driven out of the crystal lattice. However without strong hydrogen bonding between the layers, the fired materials result in the flaky material mica, rather than the more robust china or porcelain.

8.9 Molecular Solids and Atomic Radii
Introduction

Molecular compounds form molecular solids. The molecules are held in the condensed states by relatively weak intermolecular forces (Table 7.2: Relative Strengths of Interaction). Because these forces are usually much weaker than those responsible for ionic or covalent solids, molecular solids tend to have lower melting points and are usually softer than the other solids. However, their properties can be quite diverse, as evidenced by the fact that hydrogen, water, table sugar ($C_{12}H_{22}O_{11}$), dry ice, and iodine form molecular solids that have melting points that range from $-259\ °C$ for H_2 to $186\ °C$ for sugar, a range of over $400\ °C$. In addition, the intermolecular forces are typically tens of kilojoules, while covalent bond strengths are hundreds of kilojoules. Thus, covalent bonds are not broken when a substance melts, so molecules retain their identity in the liquid state.

8.9-1. Van der Waals Distance and Bond Length

Atoms that are closer than the sum of their van der Waals radii are interacting.

Unlike ionic or network covalent solids, individual molecules are easily identified in a molecular solid (Figure 8.29). Adjacent molecules interact through intermolecular forces (dotted lines in figure), while atoms within a molecule interact through much stronger covalent bonds (red rods in figure). Molecules are easily identified because the distance between atoms on adjacent molecules, which is called the van der Waals distance (d_{vdw}), is much greater than the distance between atoms within a molecule, which is called the bond length (L). In a network covalent solid such as SiO_2 (Figure 8.26), all Si–O distances between adjacent atoms are the same, so there are no identifiable SiO_2 molecules.

There are two X–X distances shown in crytalline X_2, and each defines a different atomic radius. The covalent radius of X is defined as one-half of the X–X bond length ($L = 2r_{\mathrm{cov}}$), and the **van der Waals radius** of X is defined as one-half of the X–X van der Waals distance. The van der Waals radius of an atom is viewed as its "interaction distance." Two atoms closer than the sum of their van der Waals radii are assumed to be interacting.
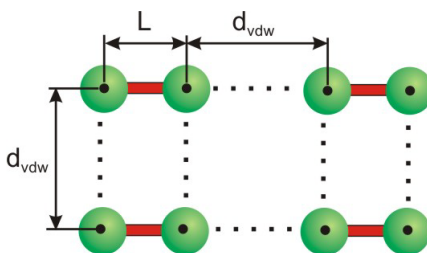

Figure 8.29: Four Molecules in Crystalline X_2

8.9-2. Representing Molecules with van der Waals Radii

The radii of the atomic spheres used in space-filling models are proportional to their van der Waals radii. The definition of the van der Waals radius is clarified in Figure 8.30, which is identical to Figure 8.29 except that space-filling representations are used rather than ball-and-stick. Note that the atomic spheres of X penetrate one another in an X_2 molecule, which means that the two atoms are much closer than the sum of their van der Waals radii. Two atoms much closer than the sum of their van der Waals radii are interacting strongly, so there is a bond between the two X atoms. The spheres on adjacent molecules are touching but not penetrating, so the X atoms of different X_2 molecules interact, but only weakly.
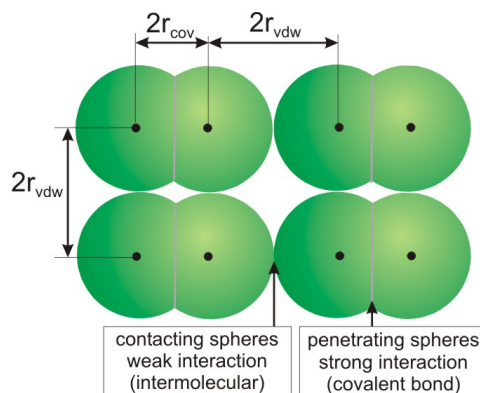
Figure 8.30: van der Waals Radii
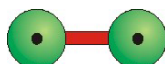
8.9-3. Comparing Molecular Representations

Figure 8.31a: Molecular Representations In the ball-and-stick representation, spheres are used to indicate the positions but not the sizes of the atoms.
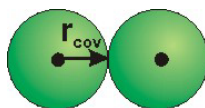

Figure 8.31b: Molecular Representations When atomic size is represented by the covalent radii, bonds are shown as the contact of spheres
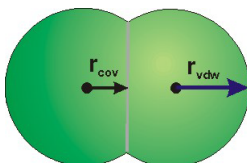

Figure 8.31c: Molecular Representations When atomic size is given with van der Waals radii (space-filling), bonds are indicated by the penetration of spheres.

8.9-4. Table of Radii

	H
r_{cov}	0.32
r_{vdw}	1.2

	C	**N**	**O**	**F**
r_{cov}	0.77	0.75	0.73	0.72
r_{vdw}	1.70	1.5	1.40	1.35

	Si	**P**	**S**	**Cl**
r_{cov}	1.11	1.06	1.02	0.99
r_{vdw}	2.10	1.9	1.85	1.80

	Ge	**As**	**Se**	**Br**
r_{cov}	1.22	1.20	1.17	1.14
r_{vdw}		2.0	2.00	1.95

Table 8.5: Covalent and van der Waals Radii in Å
(1 Å = 100 pm) of Selected Nonmetals

8.9-5. Radii Exercise

> **EXERCISE 8.7:**
> What is the van der Waals distance in graphite as shown in Figure 8.21?
> $d_{\mathrm{vdw}} =$ —————————— Å
>
> What is the van der Waals radius of carbon as determined from this distance?
> $r_{\mathrm{vdw}} =$ —————————— Å

8.9-6. Bond Length Exercise

> **EXERCISE 8.8:**
>
> Use the covalent radii in Table 8.5 to determine the Ge–Cl bond length.
>
> $r =$ —————————— Å

8.10 Comparison of Solid Types
Introduction
Objectives
- Determine the relative melting points of two substances based on the type of solid they form.

8.10-1. Comparison of Solid Types

Type of Solid	Particles	Force of Interaction	Strength of Interaction*	Examples
Metallic	Atoms	Metallic Bonds	Variable	Na, Cu, Ag
Ionic	Ions	Ionic Bonds	Strong	NaCl, NH_4Br
Covalent	Atoms	Covalent Bonds	Strong	ZnS, C, SiO_2
Molecular	Molecules	Intermolecular	Weak to Moderate	CO, H_2O, CCl_4

*The strength of interaction dictates the melting and boiling points and the hardness of the substance.

Table 8.6: Summary of Solid Types

8.10-2. Questions

> **EXERCISE 8.9:**
>
> Choose the substance in each pair that has the higher melting point.
>
> NaF   NaCl SiO_2
> MgO Cl_2 SO_2

8.11 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.