

Chapter 10

The Liquid and Solid States



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1

Introduction

- How do the properties of liquid and solid substances differ?
- How can we predict properties based on molecular-level structure?



Figure 10.3



Figure 10.1

Glasses
Wires
Reshaping

2

Chapter 10 Topics

1. Changes of State
2. Intermolecular Forces
3. Properties of Liquids
4. Properties of Solids



Figure 10.1

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Solids, Liquids, and Gases: How do they differ?

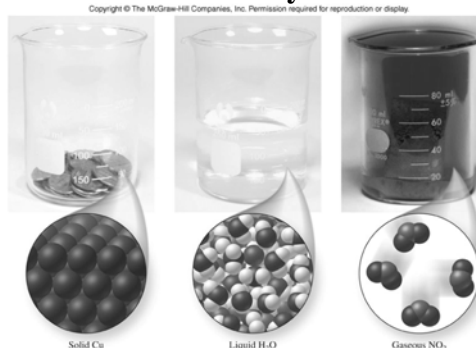


Figure 10.4

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Physical State of a Substance



Copper melts above 1083°C.

Figure 10.5



Water exists in all three physical states under normal conditions.

Figure 10.6

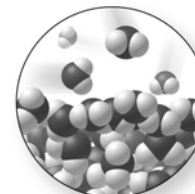
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Liquid-Gas Phase Changes

- Evaporation, or vaporization
 - Evaporation occurs because some surface liquid molecules have high enough KE to escape to the gas phase.
 - Endothermic



Figure 10.8



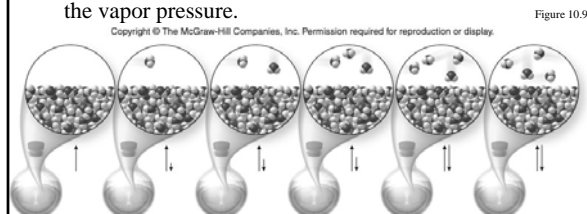
Evaporation

Figure 10.7

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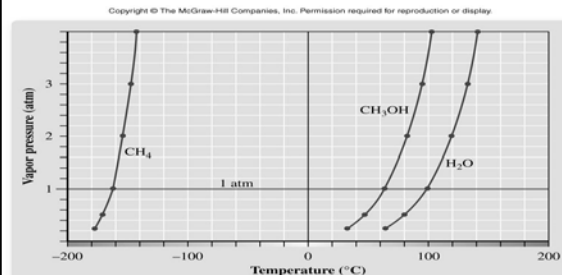
Liquid-Vapor Equilibrium

- A liquid placed in a closed container will evaporate only until an equilibrium is reached.
 - Liquid \rightleftharpoons gas
- The pressure exerted by the vapor at equilibrium is the vapor pressure.

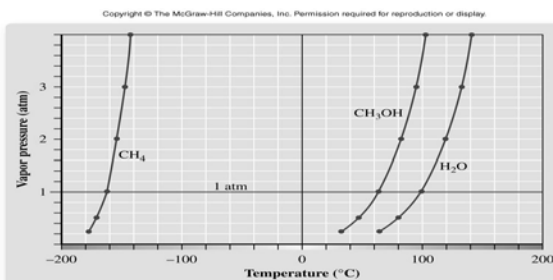


Vapor pressure depends on molecular structure and temperature.

Figure 10.10

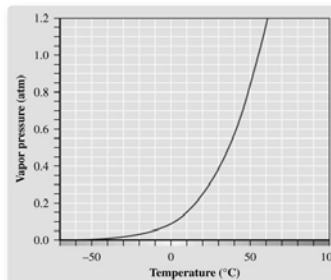


The temperature at which vapor pressure equals the external pressure of the atmosphere is the normal boiling point.



EXAMPLE 10.1 Vapor Pressure and Boiling Point

Consider the following vapor pressure curve for acetone, which is used in fingernail polish removers.



What is the normal boiling point of acetone? What is its boiling point at 0.50 atm?

Liquid-Solid Phase Changes

- The temperature at which the liquid and solids states coexist in equilibrium is called the freezing point or the melting point. Solid \rightleftharpoons liquid



Melting

- When ice melts, the water molecules stay intact but flow past one another
- When the ionic compound NaCl melts, ionic bonds are broken and ions flow freely.

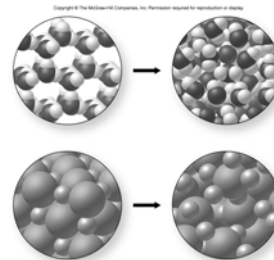


Figure 10.12

Solid-Gas Phase Changes

- Under certain conditions, substances can go directly from the solid state to the gas state: sublimation. CO_2 and I_2 do under normal conditions.

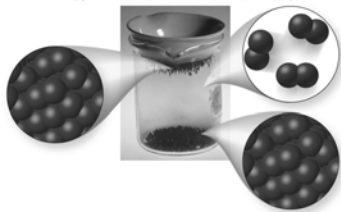


Figure 10.13

Melt CO₂ 13

- Cooling Curve
 - Heat is removed to cause phase changes.
- Heating Curve
 - Heat is added to cause phase changes.

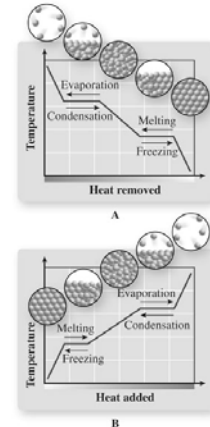


Figure 10.14

Cooling Curve

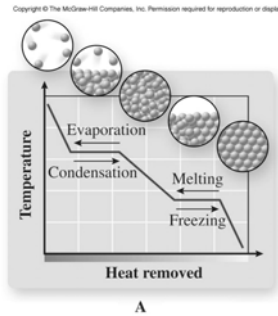


Figure 10.14

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10.2 Intermolecular Forces

- Why is CO_2 a gas at room temperature and H_2O a liquid?
- Why do liquids have different boiling points?
- What causes molecules to stick together when in the liquid state?
 - Attractive forces, called intermolecular forces, exist between molecules.

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Intermolecular Forces

- Three types of intermolecular forces:
 - London dispersion forces
 - Dipole-dipole forces
 - Hydrogen bonding

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London Dispersion Forces

- London dispersion forces exist in all substances.
- It is the only intermolecular force present in nonpolar substances.
- London dispersion forces are a result of temporary electron cloud distortions and temporary polarity (dipoles).

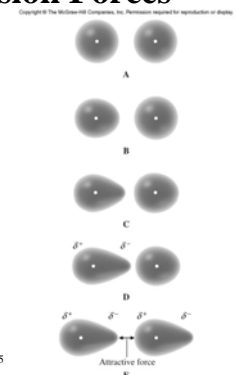


Figure 10.15

London

London Dispersion Forces

Figure 10.16

- The larger the electron cloud, the more it can be distorted.
 - The larger the molecule, the stronger the London dispersion forces.

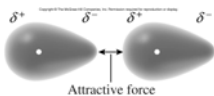
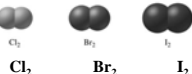
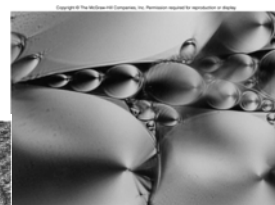
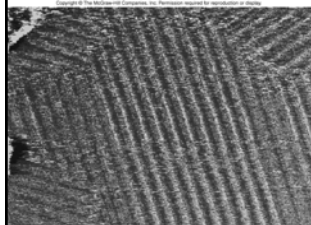


Figure 10.15



Liquid Crystals

- Long, very large molecules can be held together by London forces



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London Dispersion Forces

- For each pair, determine which has the stronger London dispersion forces?
 - He or Kr
 - HCl or HBr
 - CH_4 or C_2H_6

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London Dispersion Forces

- Relative boiling points tell us about intermolecular force strength.
- The stronger the forces, the higher the temperature needed to overcome them.

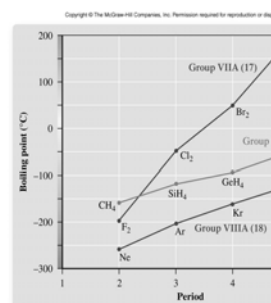


Figure 10.19

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Boiling Points of Hydrocarbons

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TABLE 16.2 Petroleum Fractions

Fraction	Boiling Range (°C)	Composition Range	Uses
Natural gas	<20	CH_4 to C_4H_{10}	Fuel, petrochemicals
Petroleum ether	20-60	C_5H_{12} , C_6H_{14}	Solvent
Ligroin, or naphtha	60-100	C_6H_{14} , C_7H_{16}	Solvent, raw material
Gasoline	40-220	C_6H_{10} to $\text{C}_{13}\text{H}_{28}$, mostly C_7H_{14} to C_9H_{18}	Motor fuel
Kerosene	175-325	C_8H_{16} to $\text{C}_{14}\text{H}_{30}$	Heating fuel and jet fuel
Gas oil	>275	C_7H_{16} to $\text{C}_{18}\text{H}_{38}$	Diesel fuel and heating fuel
Lubricating oils and greases	High: Viscous liquids	$>\text{C}_{18}\text{H}_{38}$	Lubrication
Paraffin	High: Melting point 50-60	$\text{C}_{25}\text{H}_{52}$ to $\text{C}_{30}\text{H}_{60}$	Wax products
Asphalt or petroleum coke	High: Solid residue		Roofing, paving, fuel, reducing agent

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Dipole-Dipole Forces

- Dipole-dipole forces exist between polar molecules.
 - A polar molecule has a positive and negative end, so it is considered a dipole.
 - SO_2 is polar so it experiences dipole-dipole forces in the liquid state, in addition to London dispersion forces.



Figure 10.18

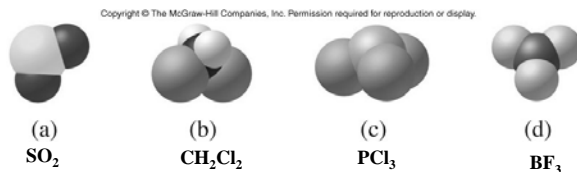
Dipole-Dipole

Dipole-dipole attractions

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Dipole-Dipole Forces

- Which of the following molecules experience dipole-dipole forces?



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Dipole-Dipole Forces

- Which is more polar? HCl or HBr ?
- Which has the stronger dipole-dipole forces?
- Boiling Point of HBr is higher than HCl .
 - How can we explain this?

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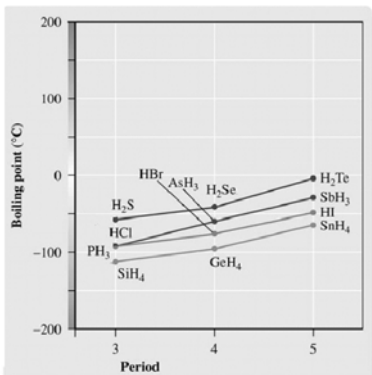


Figure 10.20

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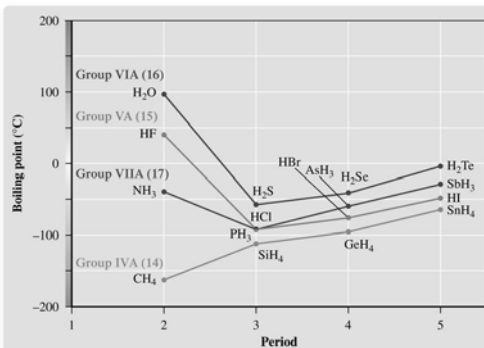


Figure 10.20

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Hydrogen Bonding

- The irregularity in boiling point trends in Figure 10.20 is due to a particularly strong dipole-dipole force called hydrogen bonding.
- Hydrogen bonding occurs between molecules that contain hydrogen covalently bonded to either nitrogen, oxygen, or fluorine:
 - N-H , O-H , or F-H
- Hydrogen bonding causes boiling points to be much higher than expected.

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Hydrogen Bonding (shown by the dotted lines)

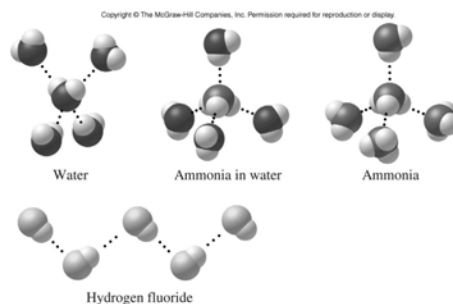


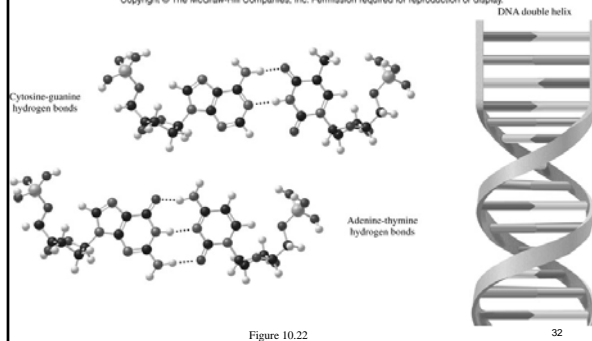
Figure 10.21

HF

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Hydrogen bonding is the strong force that holds together the DNA double helix.

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Hydrogen Bonding

- Hydrogen bonding in H_2O causes ice to be less dense than the liquid state.

Figure 10.25

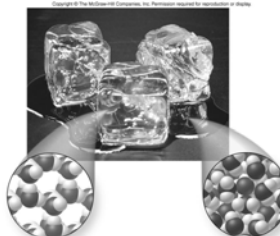
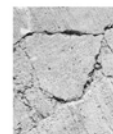


Figure 10.24

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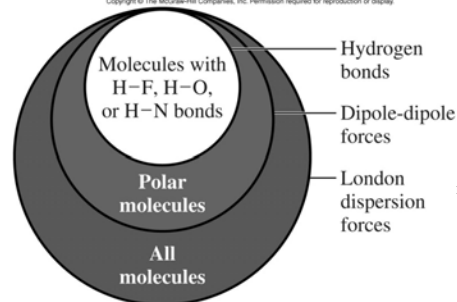
Hydrogen Bonding

- Which of the following hydrogen bond in the pure liquid state?
 - CH_3NH_2
 - NF_3
 - $\text{CH}_3\text{-O-CH}_3$
 - $\text{CH}_3\text{CH}_2\text{OH}$
 - HCl

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Summary of Intermolecular Forces

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Trends in Intermolecular Force Strength

- When determining which substance has the stronger total intermolecular forces or the higher boiling point, follow the following guidelines:
 - First look to see if the substance can hydrogen bond. If so it likely has the strongest intermolecular forces.
 - If you are comparing two molecules of different molar masses, London dispersion forces are more important.
 - If you are comparing two molecules of very similar molar masses, dipole-dipole forces are more important.

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Trends in Boiling Point

- Which of the following should have the highest boiling point?
 - CH_3OH or CH_3SH
 - I_2 or SO_2
 - CO or N_2

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10.3 Properties of Liquids

- Vapor Pressure
- Density
- Viscosity
- Surface tension
- Capillary action

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Trends in Vapor Pressure

- How is vapor pressure related to intermolecular force strength?

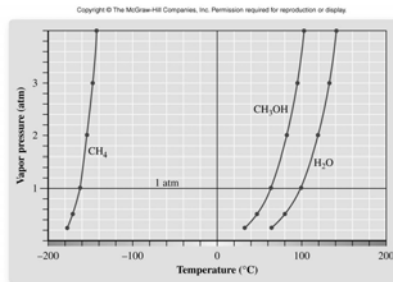
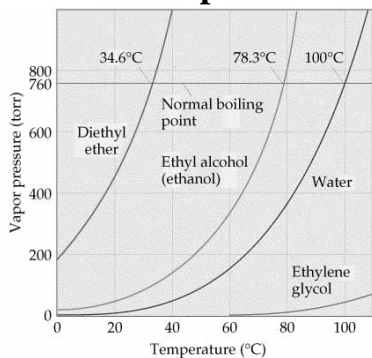


Figure 10.10

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Trends in Vapor Pressure



Trends in Vapor Pressure

- Which of the following should have the highest vapor pressure (at a given temperature)?
 - CH_3OH or CH_3SH
 - I_2 or SO_2
 - CO or N_2

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Viscosity

Viscosity - resistance to flow

Figure 10.5

- Values depend on size and intermolecular force strength.
- Large molecules get tangled in each other to increase viscosity.
- How does viscosity change when the temperature is increased?

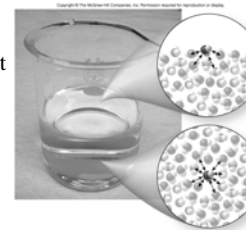


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Surface Tension

- Surface tension causes a liquid to try to minimize its surface area.
- Surface molecules have fewer molecules to interact with than the inner molecules.

Figure 10.27



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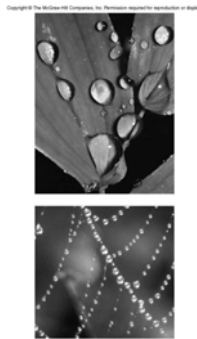
Surface Tension

Figure 10.26

- How is surface tension important in these photos?



Figure 10.28



Capillary Action

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Figure 10.30



Figure 10.29



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10.4 Properties of Solids

- The particles in the solid state are held together in specific positions – there is no translational motion.
- Crystalline solids are well ordered.
- Amorphous solids lack regular form.

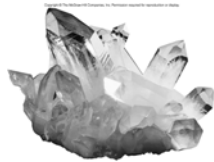


Figure 10.31

B

Crystals and Crystal Lattices

- A crystalline solid is composed of a repeating, 3-dimensional array of particles.
- The pattern formed is called a crystal lattice.
- Atoms, molecules, or ions pack together efficiently to maximize attractive forces and bonding interactions.

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Gold Atoms in 2 Dimensions (Close Packing)

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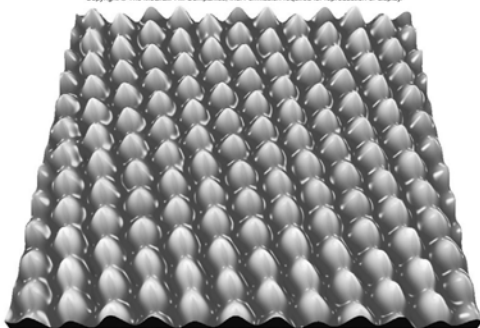


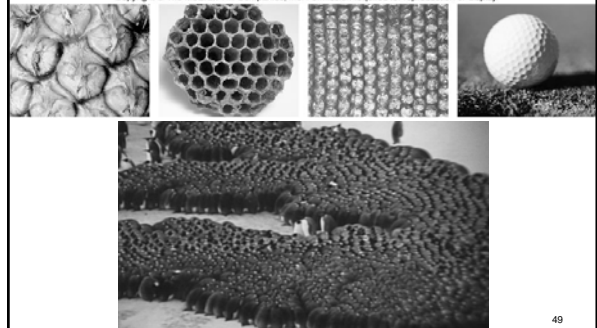
Figure 10.32

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Close-Packing in Nature

Figure 10.33

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Close Packing in 3 Dimensions

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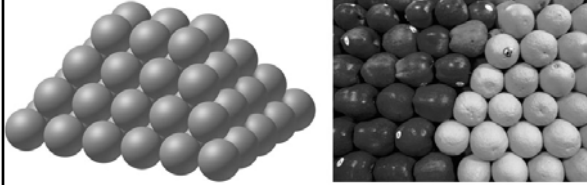


Figure 10.34

CCP

50

Types of Crystalline Solids (See Table 10.3)

- **Metallic**
 - Pure metals and alloys; composed of atoms
 - Metallic bonding
- **Ionic**
 - Ionic compounds; composed of ions
 - Ionic bonding
- **Molecular**
 - Molecular compounds or nonmetal elements; composed of molecules or atoms
 - Intermolecular forces
- **Network**
 - Molecular compounds or nonmetal elements;
 - All atoms are connected by covalent bonds

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Metallic Solids

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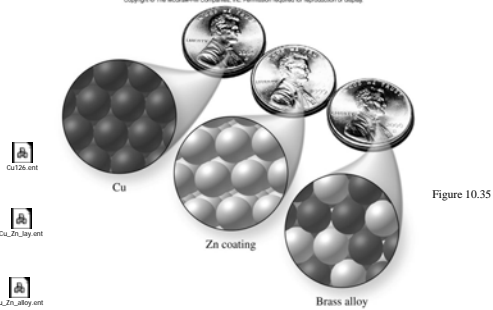


Figure 10.35

Cu126.ent

Cu_Zn_alloy.ent

Cu_Zn_alloy.ent

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Ionic Solids

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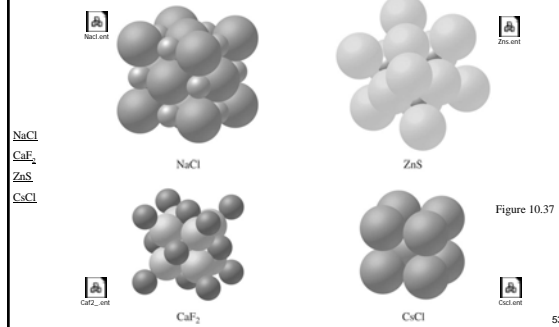


Figure 10.37

NaCl
CaF₂
ZnS
CaCl₂

CaF₂.ent

CaCl₂.ent

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Molecular Solids

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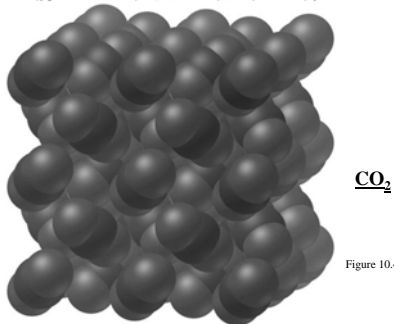


Figure 10.40

CO₂

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Network Solids

The Diamond Form of Carbon

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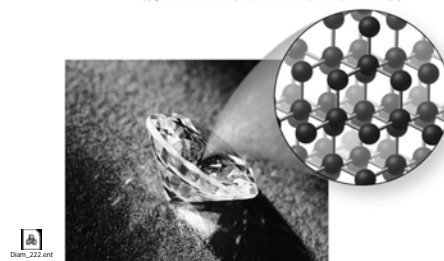


Figure 10.41

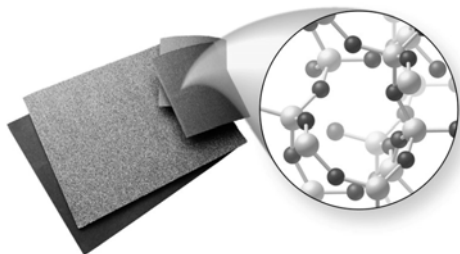
Diam_222.ent

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Network Solids

Silicon dioxide, very high melting point

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sil2_large.ort

Figure 10.42

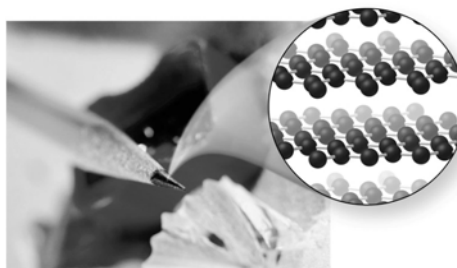
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Network Solid in 2 Dimensions

Graphite Form of Carbon

Figure 10.43

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graphite_4.ort

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Types of Solids

■ Predict the type of solid for each:

- a) CO_2 sublimes at -78.4°C
- b) Br_2 mp = -7.2°C
- c) C (diamond) mp = 3550°C
- d) MgO mp = 2800°C

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