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Chapter 9
Liquids and Solids

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Chemistry
Principles and Reactions Sixth Edition
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Outline

1. Liquid-vapor equilibrium
2. Phase diagrams
3. Molecular substances; intermolecular forces
4. Network covalent, ionic and metallic solids
5. Crystal structures

Recall Gases

- At ordinary temperatures and pressures, all gases follow the ideal gas law
- There is no equivalent equation of state that can be written to correlate the properties of liquids and solids

Liquids and Solids Differ from Gases

1. Molecules are much closer together in liquids and solids than in gases
    - In gases, molecules are separated by ten or more molecular diameters
    - In liquids and solids, the molecules are in contact with each other
2. Intermolecular forces play a major role in the behavior of liquids and solids, whereas they are negligible in gases

Behavior of Liquids and Solids

- Phase equilibria
    - Gas-liquid
        - Vapor pressure
        - Boiling point
        - Critical properties
- Relationships
    - Particle structure
    - Interparticle forces
    - Physical properties

Figure 9.1 – Surface Tension of Water

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Liquid-Vapor Equilibrium

- Vaporization
  - Liquid is converted into a gas
  - In an open container, evaporation continues until all the liquid is converted into vapor
  - In a closed container, the process of vaporization is countered by the process of condensation:
    - Liquid ⇌ Vapor
    - The double arrow indicates a *dynamic equilibrium*

Equilibrium

- When the rate at which the liquid vaporizes is equal to the rate at which the vapor condenses, a *dynamic equilibrium is established*
- The *liquid level in the container does not change*
- Molecules are entering the vapor phase from the liquid and condensing from the vapor phase to the liquid at the same rate

Equilibrium in Bromine

Vapor Pressure

- Once equilibrium between a liquid and its vapor is reached, the number of molecules per unit volume does not change with time
  - The pressure exerted by the vapor over the liquid remains constant
- The vapor pressure is temperature dependent

Pressure and Volume

- As long as both liquid and vapor are present, the vapor pressure is independent of the volume of the container

Example 9.1

Example 9.1   Graded

A "cool-mist" vaporizer with capacity 2.00 L is used to add moisture to dry air in a room at 25°C. The room has dimensions 12 ft by 12 ft by 8 ft. The vapor pressure of water at 25°C is 24 mm Hg. Take the density of water at 25°C to be 1.00 g/mL.

- ∗(a) If the vaporizer runs until it is empty, what is the vapor pressure of water in the room?
- ∗∗(b) How much water is required to completely saturate the air at 25°C?
- ∗∗∗(c) A relative humidity of 33% is desirable in heated space on wintry days. What volume of water is left in the vaporizer when the room's relative humidity reaches that level? (Relative humidity = $100 \times P/P^o$, where P is the actual pressure of water vapor and P^o is the vapor pressure at saturation.)

Example 9.1, (Cont'd)

SOLUTION

(a) Assume that all the water is vaporized and use the ideal gas law to calculate vapor pressure. To use the ideal gas law, you will need:

$$V = (12 \times 12 \times 8)\ \text{ft}^3 \times \frac{28.32\ \text{L}}{1\ \text{ft}^3} = 3.3 \times 10^4\ \text{L}$$

and

$$n_{H_2O} = 2.00\ \text{L} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{1.00\ \text{g}}{1\ \text{mL}} \times \frac{1\ \text{mol}}{18.02\ \text{g}} = 111\ \text{mol}$$

Now substitute into the ideal gas law:

$$P = \frac{nRT}{V} = \frac{(111\ \text{mol})(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\text{K})}{3.3 \times 10^4\ \text{L}} = 0.082\ \text{atm} = 62\ \text{mm Hg}$$

It is impossible to have a vapor pressure larger than 24 mm Hg at 25°C. Thus, the assumption that all the water is vaporized is wrong. The pressure in the room is 24 mm Hg.

(b) The vapor pressure of water vapor in air that is saturated with water vapor is 24 mm Hg. We now need to find, with the help of the ideal gas law, the mass of water required.

$$n_{H_2O} = \frac{PV}{RT} = \frac{(24/760)\ \text{atm} \times 3.3 \times 10^4\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\text{K})} = 43\ \text{mol}$$

$$\text{mass}_{H_2O} = 43\ \text{mol} \times 18.02\ \text{g/mol} = 7.7 \times 10^2\ \text{g}$$

Example 9.1, (Cont'd)

(c) A relative humidity of 33% means that the actual pressure P of water vapor must be

$$P = \frac{\text{relative humidity}}{100} \times P^0 = \frac{33}{100} \times 24\ \text{mm Hg} = 7.9\ \text{mm Hg}$$

Again, use the ideal gas law to find the mass of water that must be vaporized to reach the calculated pressure (7.9 mm Hg). Subtract the mass of vaporized water from the mass of water in the vaporizer, and use density to calculate the volume of water in the vaporizer.

$$n_{H_2O} = \frac{PV}{RT} = \frac{(7.9/760)\ \text{atm} \times 3.3 \times 10^4\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\text{K})} = 14\ \text{mol}$$

The volume of water vaporized is thus

$$14\ \text{mol} \times \frac{18.02\ \text{g}}{1\ \text{mol}} = 2.5 \times 10^2\ \text{g} = 0.25\ \text{L}$$

The volume of water left in the vaporizer is therefore

$$2.00\ \text{L} - 0.25\ \text{L} = 1.75\ \text{L}$$

Reality Check The calculations in (b) show that about 770 grams are required for saturation (100% relative humidity). To get 33% relative humidity, you would expect to need about a third of that amount, which is what the calculations in (c) do give.

Vapor Pressure and Temperature

- The vapor pressure of a liquid increases as the temperature rises
  - Increase in P is not linear with temperature
  - Water
    - VP is 24 mmHg at 25° C
    - VP is 92 mmHg at 50° C
- To make a linear plot, the natural logarithm is required

Figure 9.2 – Exponential and Logarithmic Plots
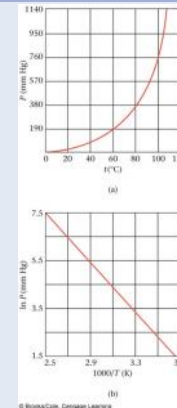
Vapor Pressure Equation

$$\ln P = -\frac{\Delta H_{vap}}{RT} + b$$

The Clausius-Clapeyron Equation

- For many purposes, a two-point equation is useful
  - Two pressures
  - Two temperatures

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

- Notes:
  - Temperatures must be in Kelvin
    - R = 8.31 J/mol·K
    - H_{vap} must be in J for use with this value for R

Example 9.2

Example 9.2 Benzene has a vapor pressure of 183 mm Hg at 40°C. Taking its heat of vaporization to be 30.8 kJ/mol, calculate its vapor pressure at 25°C.

Strategy It is convenient to use the subscript 2 for the higher temperature and pressure. Substitute into the Clausius-Clapeyron equation, solving for P_1. Remember to express temperature in K and take $R = 8.31$ J/mol · K.

SOLUTION

$$\ln \frac{183 \text{ mm Hg}}{P_1} = \frac{30.8 \times 10^3 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}} \left[\frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}} \right] = 0.596$$

Taking inverse logs: $\dfrac{183 \text{ mm Hg}}{P_1} = 1.81; P_1 = 101 \text{ mm Hg}$

Reality Check This value is reasonable in the sense that lowering the temperature should reduce the vapor pressure.

Boiling Point

- When heat is applied to a liquid in an open container, bubbles eventually form at the bottom
  - At a certain temperature, large bubbles form throughout the liquid; i.e., the liquid boils
  - The temperature at which a liquid boils depends on the pressure above it
    - If the *pressure is 1 atm, the temperature at which the liquid boils is called the normal boiling point*
    - When the term *boiling point is used, the normal boiling point is implied*
  - *The boiling point is the temperature at which the vapor pressure equals the prevailing pressure*

Boiling Point and Prevailing Pressure

- Variation on atmospheric pressure will change the boiling point
  - At high elevation, atmospheric pressure is lower, so the boiling point is lower
  - To elevate the boiling point and allow food to cook more quickly, a pressure cooker can be used
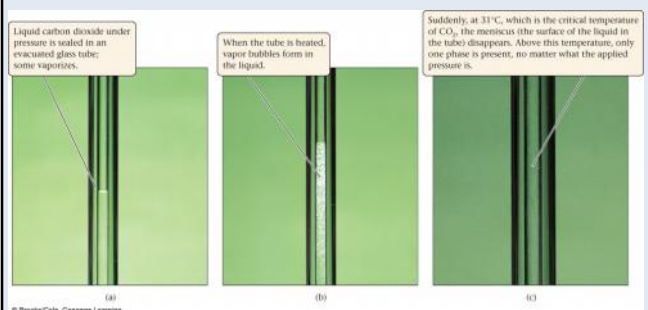
Figure 9.3 - Boiling

External pressure, P_2

Vapor bubbles

Pressure in the vapor bubble, P_1
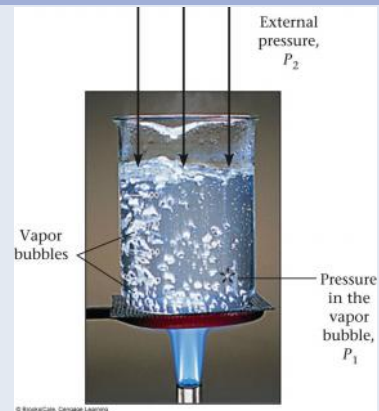
Carbon Dioxide

- Consider carbon dioxide
  - CO_2 as a liquid is sealed into an evacuated glass tube
  - As the tube is heated, some liquid is converted to vapor, and the pressure rises to 44 atm at 10 °C
  - At 31 °C, the pressure is 73 atm
  - Suddenly, the meniscus between liquid and vapor disappears and only vapor is present

Figure 9.4

Liquid carbon dioxide under pressure is sealed in an evacuated glass tube; some vaporizes.

When the tube is heated, vapor bubbles form in the liquid.

Suddenly, at 31°C, which is the critical temperature of CO_2, the meniscus (the surface of the liquid in the tube) disappears. Above this temperature, only one phase is present, no matter what the applied pressure is.

(a)   (b)   (c)

Critical Temperature and Pressure

- For every liquid, there is a temperature above which only vapor can exist
  - This is the *critical temperature*
- At this temperature, the pressure is called the *critical pressure*
  - Together, the critical temperature and pressure are called the *critical point*

Table 9.1 – Critical Temperatures

Table 9.1	Critical Temperatures (°C)				
Permanent Gases		**Condensable Gases**		**Liquids**	
Helium	−268	Carbon dioxide	31	Ethyl ether	194
Hydrogen	−240	Ethane	32	Ethyl alcohol	243
Nitrogen	−147	Propane	97	Benzene	289
Argon	−122	Ammonia	132	Bromine	311
Oxygen	−119	Chlorine	144	Water	374
Methane	−82	Sulfur dioxide	158		

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Permanent Gases

- Permanent gases are substances with critical temperatures below 25 ° C.
  - Usually stored in cylinders at 150 atm or greater
  - Only vapor is present in the tank
 - Pressure in the tank drops as the gas is released

Condensable Gases

- Condensable gases have critical temperatures above 25 ° C.
  - Carbon dioxide
  - Hydrocarbon gases
  - Ammonia
  - Chlorine
  - Sulfur dioxide
- For these substances, the liquid-vapor equilibrium accounts for the pressure in the tank
  - Pressure will not change until all the liquid is gone

Phase Diagrams

- Phase diagrams are graphical representations of the pressure and temperature dependence of a pure substance
  - Pressure on the y-axis
  - Temperature on the x-axis
- Three places to consider
  - In a region, one phase exists
  - On a line, two phases exist in equilibrium
  - At a point, three phases exist in equilibrium

Figure 9.5 – A Phase Diagram
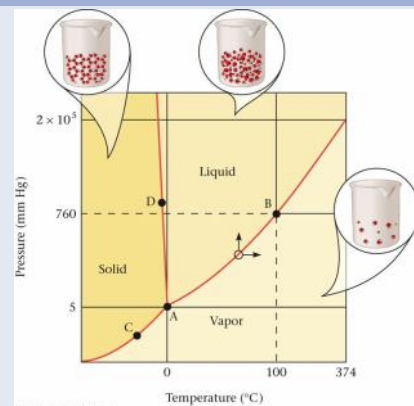
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Phase Diagram of Water

- Curve AB is the vapor pressure-temperature curve
- Curve AC is the vapor pressure curve of ice
- Line A-D gives the temperature-pressure dependence for ice in equilibrium with water
- Point A is the *triple point*
  - All three phases are in equilibrium
  - There is only one triple point for a pure substance
  - For water, the triple point is at 0.01 ° C

Example 9.3

Example 9.3   Conceptual

Consider a sample of H_2O at point A in Figure 9.5.

(a) What phase(s) is (are) present?
(b) If the temperature of the sample were reduced at constant pressure, what would happen?
(c) How would you convert the sample to vapor without changing the temperature?

Strategy   Use the phase diagram in Figure 9.5. Note that P increases moving up vertically; T increases moving to the right.

SOLUTION

(a) A is the triple point; ice, liquid water, and water vapor are present.
(b) Move to the left to reduce T. This penetrates the solid area, which implies that the sample freezes completely.
(c) Reduce the pressure to below the triple point value, perhaps to 4 mm Hg.

Sublimation

- Sublimation is the process by which a solid passes directly into the vapor phase without first being converted to a liquid
  - Sublimation can happen only at a temperature below the triple point
  - Water can sublime if the pressure is reduced
    - Freeze drying
    - Cold winter days
 - Iodine sublimes readily because its triple point pressure is much higher than that of water

Figure 9.6

Melting Point

- For a pure substance, the melting point and freezing point are identical
  - The effect of pressure on the freezing point is very small
  - An increase in pressure favors the more dense phase
    - This is usually the solid phase
    - Water is denser than ice, so water is anomalous
    - The slope of the solid-liquid line depicts the behavior of the freezing point as pressure is increased or decreased
      - Positive slope: solid is denser than liquid
      - Negative slope: liquid is denser than solid

Figure 9.7
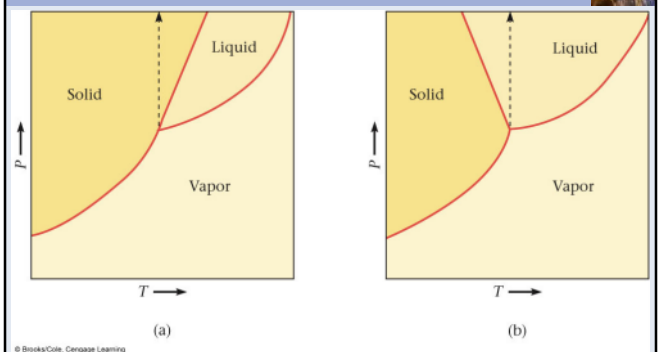
Molecular Substances; Intermolecular Forces

- Many gases, most liquids and many solids are molecular
  - Molecules are the structural units of such matter
  - Properties of molecular substances include
    - They are nonconductors of electricity when pure
    - They are insoluble in water but soluble in nonpolar solvents such as CCl_4 or benzene
    - They have low melting points
  - These properties depend on the intermolecular forces between the molecules of the substance

Dispersion Forces

- All substances have dispersion forces
  - Also called London or van der Waals forces
  - Stem from induced dipoles in molecules
  - Motion of electrons in the molecule causes transient dipoles to form
  - Increase with the number of electrons in the molecule
  - As molar mass increases, dispersion forces become stronger
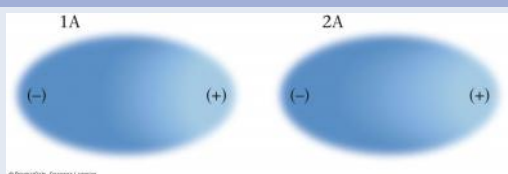
Figure 9.8 and Table 9.2

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Table 9.2 Effect of Molar Mass on Boiling Points of Molecular Substances

| Noble Gases* | | Halogens | | | Hydrocarbons | | |
MM (g/mol)	bp (°C)		MM (g/mol)	bp (°C)		MM (g/mol)	bp (°C)
He	4	−269	F_2	38	−188	CH_4	16	−161
Ne	20	−246	Cl_2	71	−34	C_2H_6	30	−88
Ar	40	−186	Br_2	160	59	C_3H_8	44	−42
Kr	84	−152	I_2	254	184	$n\text{-}C_4H_{10}$	58	0

*Strictly speaking, the noble gases are "atomic" rather than molecular. However, like molecules, the noble-gas atoms are attracted to one another by dispersion forces.

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Dipole Forces

- Molecules with permanent dipoles display dipole forces
  - Dispersion forces are also present but are much weaker
  - Adjacent molecules line up so that the negative pole of one molecule is as close as possible to the positive pole of another molecule
  - Result is an electrostatic attractive force that causes molecules to associate with each other
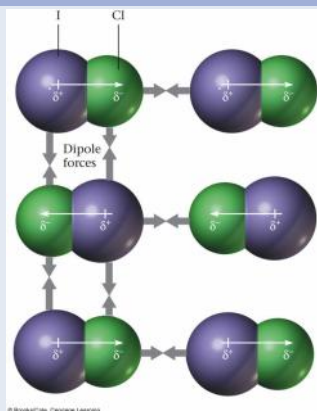
Figure 9.9

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Table 9.3

Table 9.3 Boiling Points of Nonpolar Versus Polar Substances

| | Nonpolar | | | Polar | |
Formula	MM (g/mol)	bp (°C)	Formula	MM (g/mol)	bp (°C)
N_2	28	−196	CO	28	−192
SiH_4	32	−112	PH_3	34	−88
GeH_4	77	−90	AsH_3	78	−62
Br_2	160	59	ICl	162	97

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Example 9.4

Explain, in terms of intermolecular forces, why

(a) the boiling point of O_2 ($-183°C$) is higher than that of N_2 ($-196°C$).
(b) the boiling point of NO ($-151°C$) is higher than that of either O_2 or N_2.

Strategy Determine whether the molecule is polar or nonpolar and identify the intermolecular forces present. Remember, dispersion forces are always present and increase with molar mass.

Example 9.4, (Cont'd)

SOLUTION

(a) Only dispersion forces are involved with these nonpolar molecules. The molar mass of O_2 is greater (32.0 g/mol versus 28.0 g/mol for N_2), so its dispersion forces are stronger, making its boiling point higher.
(b) Dispersion forces in NO (30 g/mol) are comparable in strength to those in O_2 and N_2. The polar NO molecule shows an additional type of intermolecular force not present in N_2 or O_2: the dipole force. As a result, its boiling point is the highest of the three substances.

Hydrogen Bonding

- Unusually strong type of dipole force
  - H attached to a N, O, or F
  - The H from one molecule can bond to the negative end of the dipole of another
    - Dipole arises from the difference in the electronegativity between H and (N, O, or F)
    - Small size of H allows the unshared pair from the negative end of the dipole to approach the H closely
  - HF, H_2O and NH_3: unusually high boiling points as a result of hydrogen bonding

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Table 9.4

Table 9.4 Effect of Hydrogen Bonding on Boiling Point

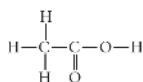|	bp (°C)		bp (°C)		bp (°C)
NH_3	-33	H_2O	100	HF	19
PH_3	-88	H_2S	-60	HCl	-85
AsH_3	-63	H_2Se	-42	HBr	-67
SbH_3	-18	H_2Te	-2	HI	-35

Note: Molecules in blue show hydrogen bonding.

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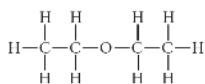

Example 9.5

Example 9.5 Would you expect to find hydrogen bonds in
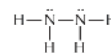
(a) acetic acid?

(b) diethyl ether?

(c) hydrazine, N_2H_4?

Strategy For hydrogen bonding to occur, hydrogen must be bonded to F, O, or N. In (c), draw the Lewis structure first.

Example 9.5, (Cont'd)

SOLUTION

(a) There should be hydrogen bonds in acetic acid because an H atom is bonded to oxygen.
(b) All the hydrogen atoms are bonded to carbon in diethyl ether, so there should be no hydrogen bonds.
(c) The Lewis structure of hydrazine is

Because hydrogen is bonded to nitrogen, hydrogen bonding can occur between neighboring N_2H_4 molecules. The boiling point of hydrazine ($114°C$) is much higher than that of molecular O_2 ($-183°C$), which has the same molar mass.

Reality Check In acetic acid, the H atom bonded to oxygen in one molecule forms a hydrogen bond with an oxygen in an adjacent molecule. The same situation applies in hydrazine if you substitute nitrogen for oxygen.

Water

- Hydrogen bonding in water accounts for
  - High specific heat
  - High boiling point
  - Higher density of the liquid phase relative to the solid

Figure 9.10
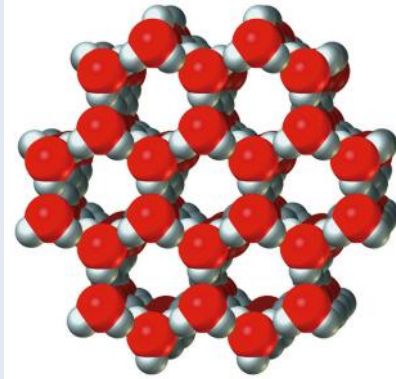
Example 9.6

Example 9.6   **Conceptual**

What types of intermolecular forces are present in nitrogen, N_2? Chloroform, $CHCl_3$? Carbon dioxide, CO_2? Ammonia, NH_3?

Strategy   Determine whether the molecules are polar or nonpolar; only polar molecules show dipole forces. Check the Lewis structures for H atoms bonded to F, N, or O. All molecules have dispersion forces.

SOLUTION   The N_2 and CO_2 molecules are nonpolar (Chapter 7), so only dispersion forces are present. Both $CHCl_3$ and NH_3 are polar molecules. Chloroform contains dipole forces as well as dispersion forces. Ammonia contains hydrogen bonds as well as dispersion forces.

Covalent Bonds vs. Intermolecular Forces

- Three types of intermolecular force
  - Dispersion
  - Dipole
  - Hydrogen bond
- All three intermolecular forces are weak relative to the strength of a covalent bond
  - Attractive energy in ice is 50 kJ/mol
  - Covalent bond in water is 928 kJ/mol

Solids: Network Covalent, Ionic and Metallic

- Network covalent solids
  - Continuous network of covalent bonds
  - Crystal is one large molecule
- Ionic solids
  - Oppositely-charged ions held together by strong electrical forces
- Metallic solids
  - Structural unit are +1, +2 and +3 metals with associated electrons

Figure 9.11
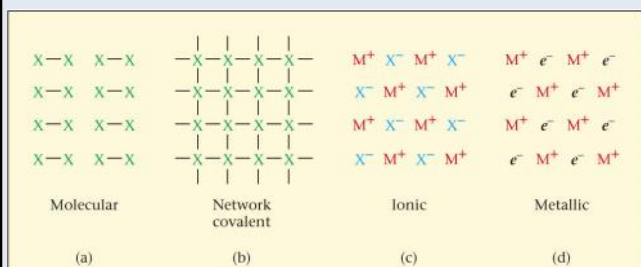
Network Covalent Solids

- Characteristics
  - High melting points, often above 1000 °C
  - Covalent bonds must be broken to melt the substance
- Examples
  - Graphite and diamond: allotropes
    - Diamond is three-dimensional and tetrahedral
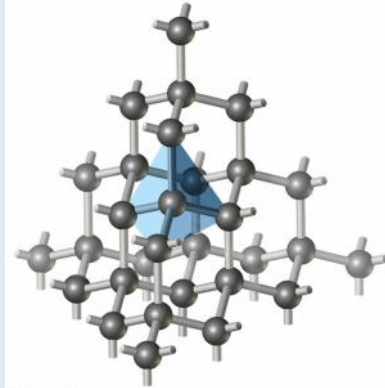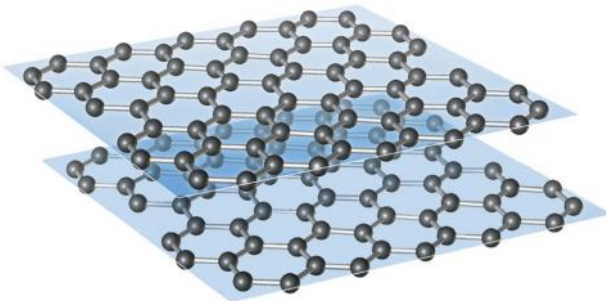   - Graphite is two-dimensional and planar

Figure 9.12

Figure 9.13

Compounds of Silicon

- Quartz
  - SiO_2
    - Major component of sand
    - Glass
  - Layered structures
    - Talc
  - Silicate lattices
    - Chains in 1, 2 and 3 dimensions
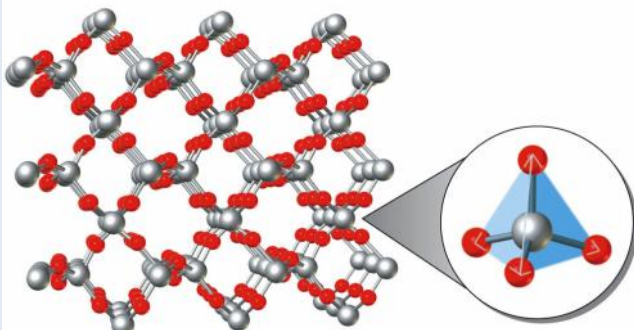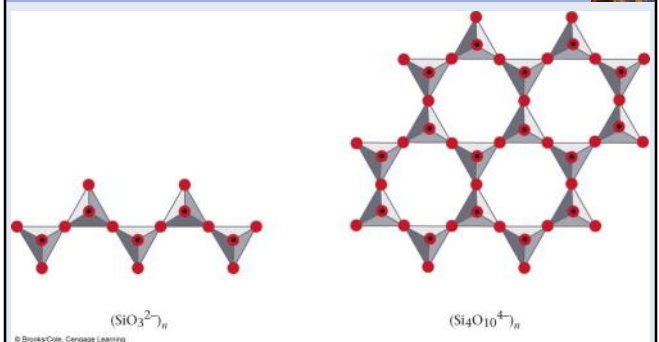   - Zeolites

Figure 9.14

Figure 9.15

$(SiO_3^{2-})_n$ $(Si_4O_{10}^{4-})_n$

Ionic Solids

- Characteristics
  - Nonvolatile; high melting points (600-2000 °C)
  - Nonconductors of electricity in the solid state
    - Conduct when melted or dissolved in water
  - Many are soluble in water but not in nonpolar solvents

Strengths of Ionic Bonds

- Coulomb's Law

$$E = \frac{k \times Q_1 \times Q_2}{d}$$

$$d = r_{cation} + r_{anion}$$

- Strength of ionic bond depends on
  - Charges of the ions (higher charges produce stronger bonds)
  - Sizes of the ions (smaller internuclear distances result in stronger bonds)

Metals

- Characteristics of metals
  - High electrical conductivity
    - Highly mobile electrons in structure
  - High thermal conductivity
    - Heat is carried through the structure by collision between electrons
  - Ductility and malleability
    - Can be drawn into wire or hammered into sheets
  - Luster
    - Polished metal surfaces reflect light
  - Insolubility in water and other common solvents

Solids with Different Structures

Table 9.5
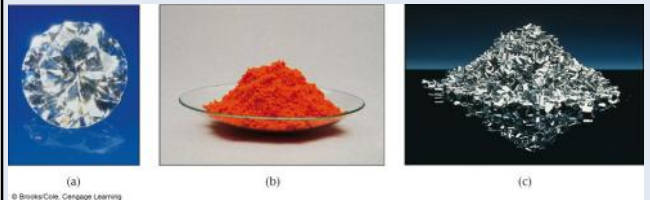
Table 9.5	Structures and Properties of Types of Substances				
Type	Structural Particles	Forces Within Particles	Forces Between Particles	Properties	Examples
Molecular	Molecules				
(a) nonpolar		Covalent bond	Dispersion	Low mp, bp; often gas or liquid at 25°C; nonconductors; insoluble in water, soluble in organic solvents	H₂ CCl₄
(b) polar		Covalent bond	Dispersion, dipole, H bond	Similar to nonpolar but generally higher mp and bp; more likely to be water-soluble	HCl NH₃
Network covalent	Atoms	—	Covalent bond	Hard solids with very high melting points; nonconductors; insoluble in common solvents	C SiO₂
Ionic	Ions	—	Ionic bond	High mp; conductors in molten state or water solution; often soluble in water, insoluble in organic solvents	NaCl MgO CaCO₃
Metallic	Cations, mobile electrons	—	Metallic bond	Variable mp; good conductors in solid; insoluble in common solvents	Na Fe

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Example 9.7

Example 9.7 Conceptual

For each species in column A, choose the description in column B that best applies.

A	B
(a) CO₂	(e) ionic, high-melting
(b) CuSO₄	(f) liquid metal, good conductor
(c) SiO₂	(g) polar molecule, soluble in water
(d) Hg	(h) ionic, insoluble in water
	(i) network covalent, high-melting
	(j) nonpolar molecule, gas at 25°C

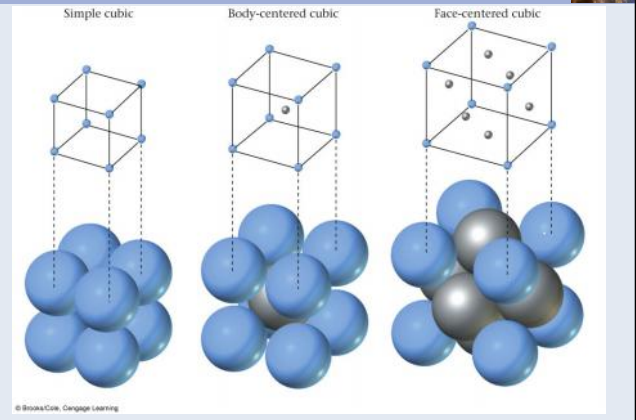**Strategy** Refer to Table 9.5 and the preceding discussion.

SOLUTION

(a) matches (j)   (b) matches (e)
(c) matches (i)   (d) matches (f)

Crystal Structures

- Solids crystallize into definite geometric forms
  - Many times, the naked eye can see the crystal structure
  - NaCl forms cubic crystals

Figure 9.16

Crystal Building Blocks

- Crystals have definite geometric forms because the atoms or ions are arranged in definite, three-dimensional patterns
- Metals crystallize into one of three unit cells
  1. Simple cubic (SC): eight atoms at the corners
  2. Face centered cubic (FCC): simple cubic plus one atom in the center of each face
  3. Body-centered cubic (BCC): simple cubic plus one atom in the center of the cube

Crystal Building Blocks, (Cont'd)

- Three other ways to look at the crystalline unit cells:
  1. Number of atoms per unit cell
     - SC: 1   FCC: 4   BCC: 2
  2. Relation between side of cell (s) and radius of atom or ion (r)
     - SC: $2r = s$ FCC: $4r = s\sqrt{2}$ BCC: $4r = s\sqrt{3}$
  3. Percentage of empty space
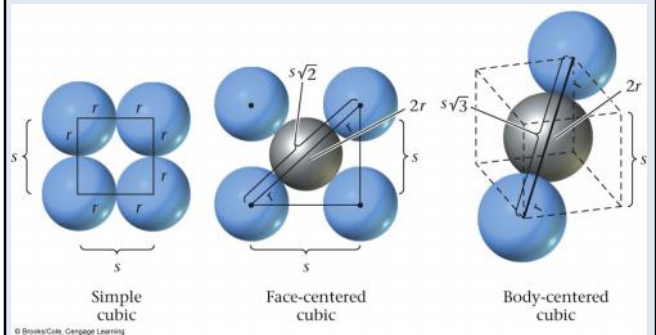   - SC: 47.5   FCC: 32.0   BCC: 26.0

Table 9.6

Table 9.6	Properties of Cubic Unit Cells		
	Simple	BCC	FCC
Number of atoms per unit cell	1	2	4
Relation between side of cell, s, and atomic radius, r	$2r = s$	$4r = s\sqrt{3}$	$4r = s\sqrt{2}$
% of empty space	47.6	32.0	26.0

Figure 9.17

Example 9.8

Silver is a metal commonly used in jewelry and photography. It crystallizes with a face-centered cubic (FCC) unit cell 0.407 nm on an edge.

 * (a) What is the atomic radius of silver in cm? (1 nm = 10^{-7} cm)
 ** (b) What is the volume of a single silver atom? (The volume of a spherical ball of radius r is $V = \frac{4}{3}\pi r^3$.)
 *** (c) What is the density of a single silver atom?

SOLUTION

(a) The equation for the relation between the radius and the length of a side of an FCC cell is

$$4r = s\sqrt{2}$$

Substituting $s = 0.407$ nm and solving for r, we obtain

$$r = \frac{0.407 \text{ nm} \times \sqrt{2}}{4} = 0.144 \text{ nm} \times \frac{10^{-7} \text{ cm}}{1 \text{ nm}} = 1.44 \times 10^{-8} \text{ cm}$$

Example 9.8, (Cont'd)

(b) Because an atom is spherical, the formula in parentheses applies. Using the value of r found in (a), that formula gives

$$V = \frac{4}{3}\pi (1.44 \times 10^{-8} \text{ cm})^3 = 1.25 \times 10^{-23} \text{ cm}^3$$

(c) You will need the mass of a silver atom. To get it, use Avogadro's number and the molar mass of silver, 107.9 g/mol.

$$m_{\text{Ag atom}} = \frac{107.9 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 1.792 \times 10^{-22} \text{ g/atom}$$

$$\text{density}_{\text{Ag atom}} = \frac{1.792 \times 10^{-22} \text{ g/atom}}{1.25 \times 10^{-23} \text{ cm}^3} = 14.3 \text{ g/cm}^3 \cdot \text{atom}$$

Reality Check In FCC unit cells, the fraction of empty space is 0.26. When this is factored into the above, the calculated density of silver becomes $14.3 - (0.26)(14.3) = 10.6$ g/cm^3, which is almost the same as its experimentally determined value: 10.5 g/cm^3.

Ionic Crystals

- Geometry of ionic crystals is more difficult to describe than that of metals
  - LiCl
    - Larger Cl$^-$ ions form a face-centered cube with Li$^+$ ions in the "holes" between the anions
  - NaCl
    - Larger Na$^+$ ions are slightly too large to fit into the holes between the anions, so the Cl$^-$ ions are pushed apart slightly

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Figure 9.18

LiCl   NaCl   CsCl
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Example 9.9

Consider Figure 9.18. The length of an edge of a cubic cell, s, is the distance between the center of an atom or ion at the "top" of the cell and the center of the atom or ion at the "bottom." Taking the ionic radii of Li$^+$, Na$^+$, and Cl$^-$ to be 0.060 nm, 0.095 nm, and 0.181 nm, respectively, determine s for

(a) NaCl   (b) LiCl

Strategy Use Figure 9.18 to determine along what line ions touch.

SOLUTION

(a) Cl$^-$ and Na$^+$ ions touch along an edge of the cell.

$$s = 0.181 \text{ nm} + 2(0.095 \text{ nm}) + 0.181 \text{ nm} = 0.552 \text{ nm}$$

(b) Cl$^-$ ions touch along a face diagonal, which has a length of $s \times 2^{1/2}$.

$$s \times 2^{1/2} = 0.181 \text{ nm} + 2(0.181 \text{ nm}) + 0.181 \text{ nm}$$
$$s = 0.724 \text{ nm}/2^{1/2} = 0.512 \text{ nm}$$

Key Concepts

1. Use the ideal gas law to determine whether a liquid will completely vaporize in a sealed container
2. Use the Clausius-Clapeyron equation to relate vapor pressure to temperature
3. Use a phase diagram to determine the phases present given the pressure and temperature
4. Identify the type of intermolecular forces in different substances
5. Classify substances as molecular, network covalent, or metallic
6. Relate unit cell dimensions to atomic or ionic radii