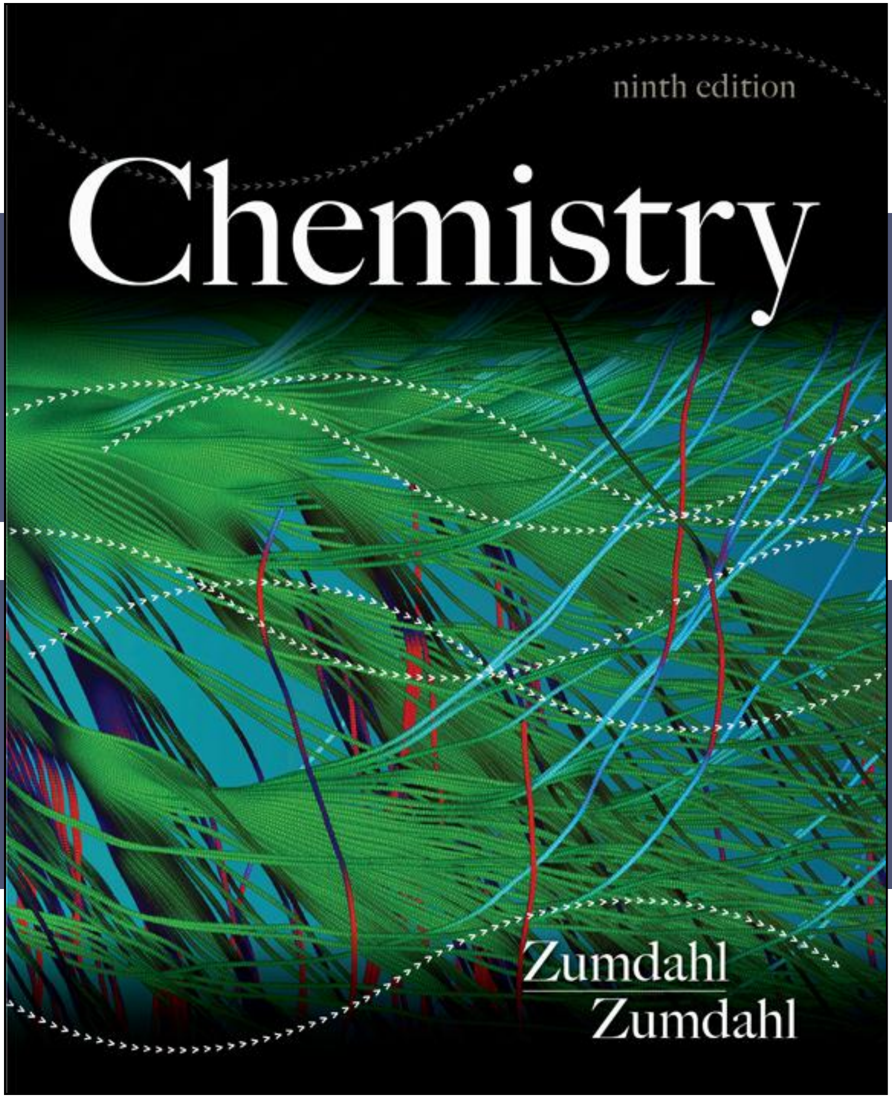
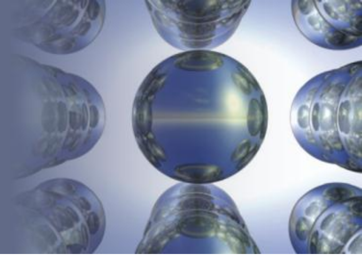
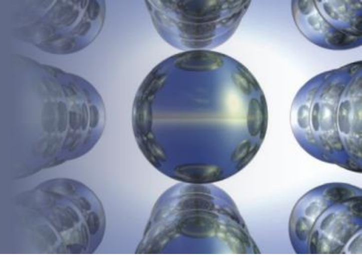


Chapter 10

Liquids and Solids

Chapter 10
Table of Contents





Chapter 10

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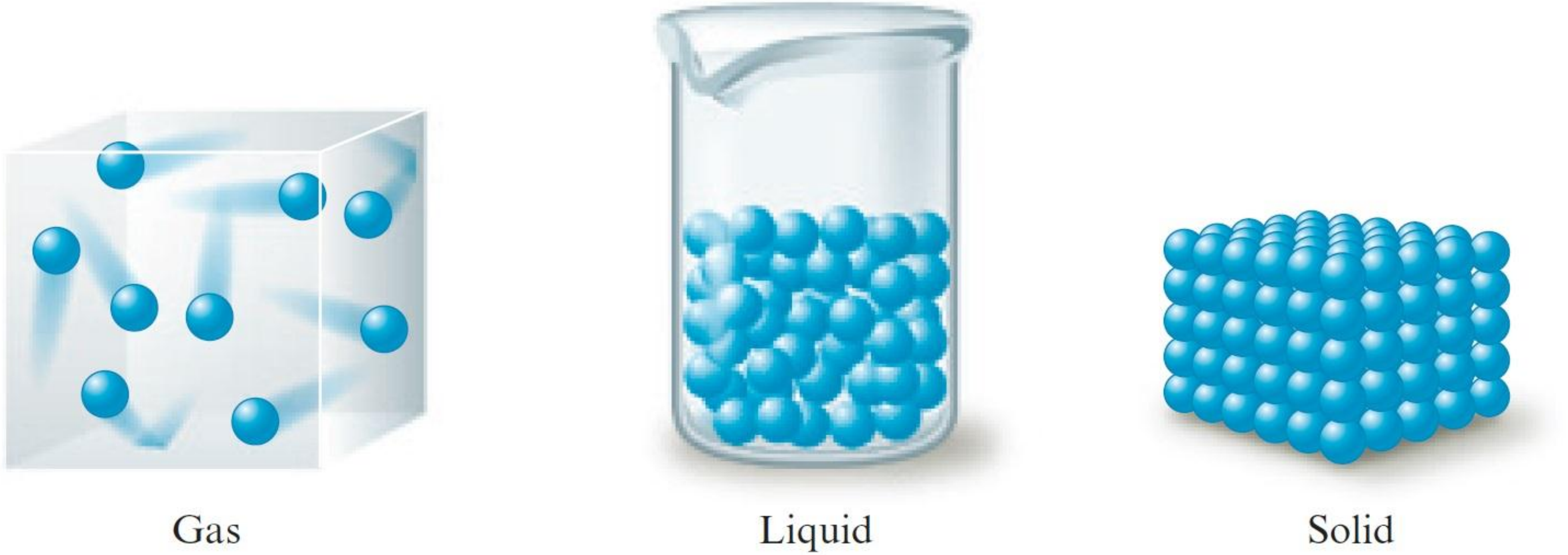
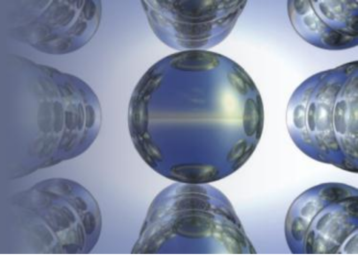
Figure 10.1 - Schematic Representations of the Three States of Matter



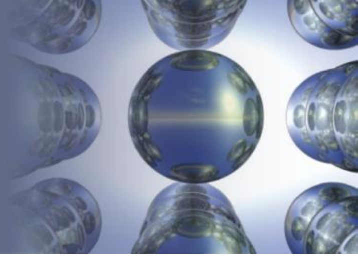


Intramolecular and Intermolecular Bonding

- Intramolecular bonding - Occurs within molecules
- **Condensed states** of matter - Liquids and solids
  - Forces involved
    - Covalent bonding
    - Ionic bonding
    - **Intermolecular bonding**: Occurs between molecules

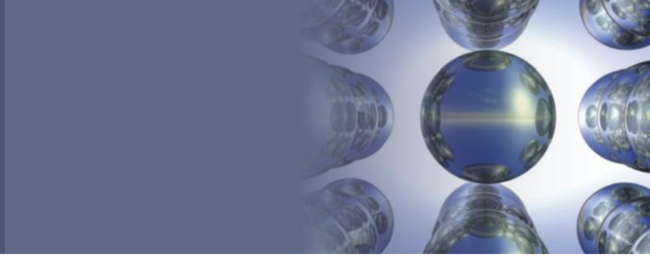
Changes in States

- When a substance changes from solid to liquid to gas, the molecules remain intact
- Caused by the changes in the forces among the molecules and not within the molecules
  - When energy is added to ice, the motion of the molecules increases
    - Results in greater movement and disorder characteristic of liquid water



Changes in States (Continued)

- When more energy is added to water, gaseous state is eventually reached
    - Intermolecular distance increases and intermolecular interaction decreases
- More energy is required to overcome the covalent bonds and decompose the water molecules into their component atoms

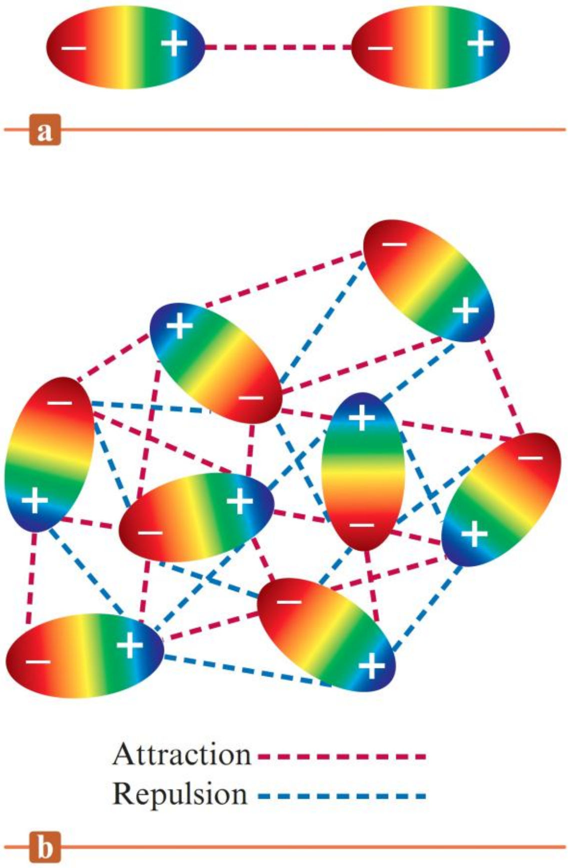


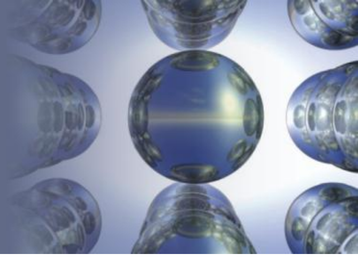
Dipole–Dipole Forces

- Forces that act between polar molecules
- **Dipole–dipole attraction**: Electrostatic attraction between molecules with dipole moments
  - Molecules orient themselves in a way that the positive and negative ends are close to each other
  - In a condensed state, dipoles find the best compromise between attraction and repulsion

Characteristics of Dipole–Dipole Forces

- Approximately 1% as strong as covalent or ionic bonds
- Strength of the forces decreases as the distance between the dipoles increases





Hydrogen Bonding

- Significantly strong dipole–dipole forces
- Prevalent in molecules that have a hydrogen atom bound to a highly electronegative atom
- Causative factors
  - Polarity of the bond
  - Proximity of the dipoles
    - Influenced by the size of the hydrogen atom
- Influences physical properties of molecules

Figure 10.3 - Hydrogen Bonding in Water

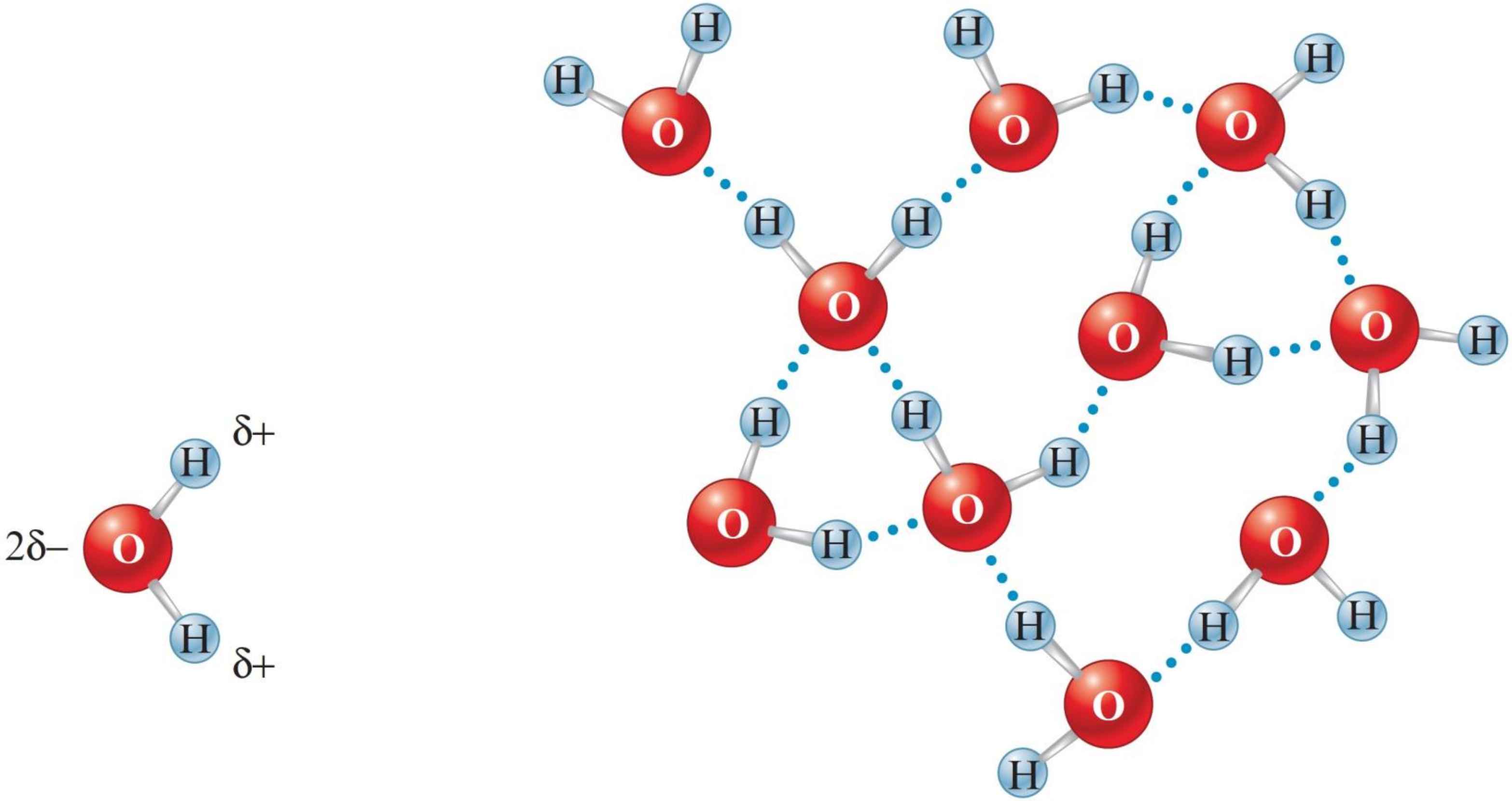
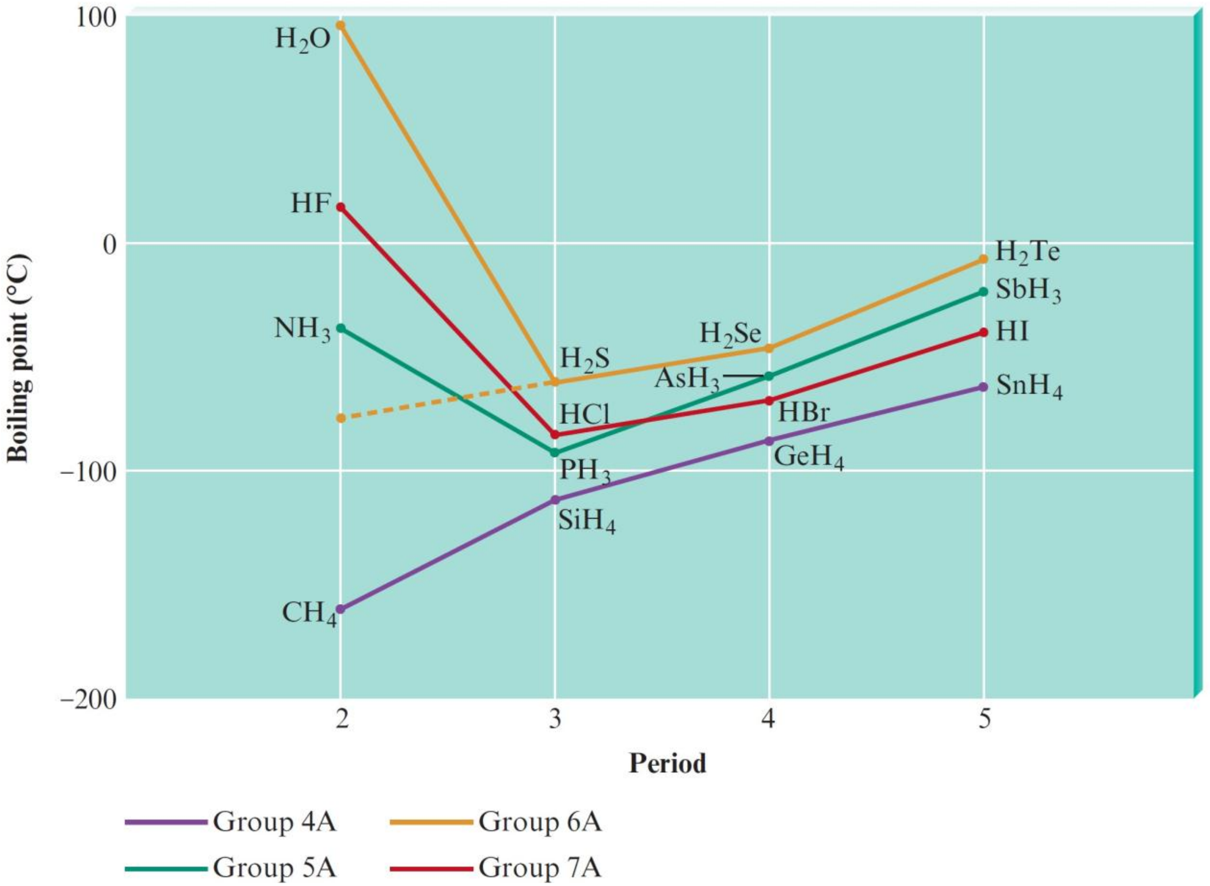
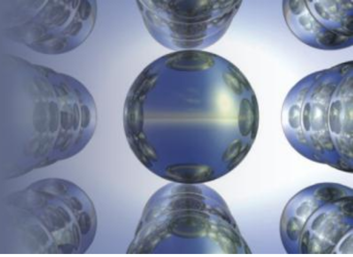


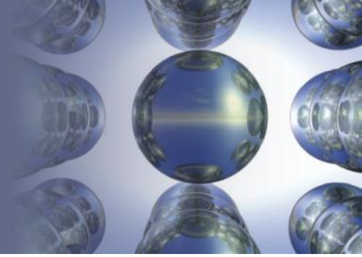
Figure 10.4 - Boiling Points of the Covalent Hydrides of the Elements in Groups 4A, 5A, 6A, and 7A





London Dispersion Forces

- Forces that exist among noble gas atoms and nonpolar molecules
- An accidental instantaneous dipole that occurs in an atom can induce a similar dipole in a neighboring atom
    - Leads to an interatomic attraction that is weak and short-lived
        - Can be significant for large atoms



London Dispersion Forces (Continued)

- Polarizability - Indicates the ease with which the electron cloud of an atom can be distorted to give a dipolar charge distribution
    - As the atomic number increases, the number of electrons increases
        - Increases the probability of the occurrence of momentary dipole interactions
- Used by nonpolar molecules to attract each other

Critical Thinking

- You have learned the difference between intermolecular forces and intramolecular bonds
  - What if intermolecular forces were stronger than intramolecular bonds?
    - What differences could you observe in the world?

Liquids

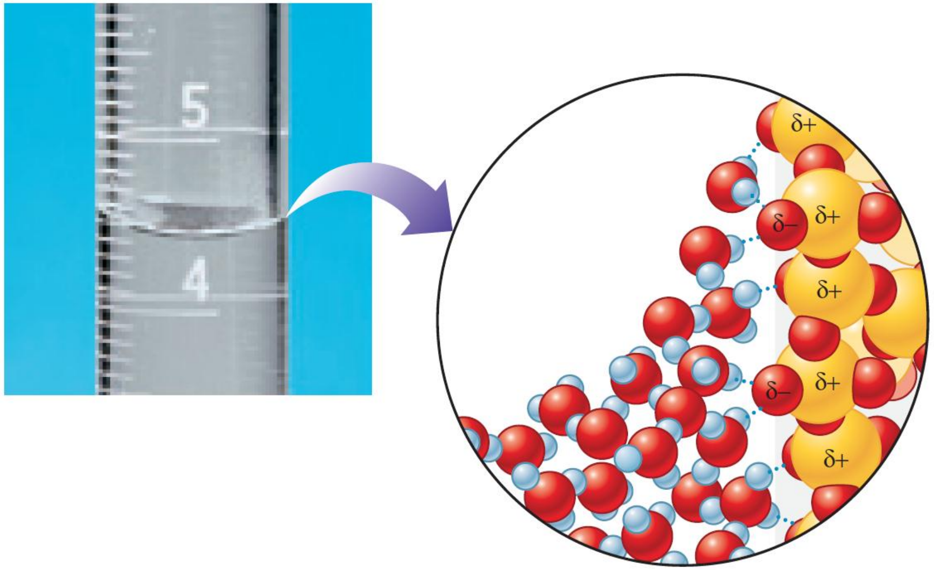
- Possess low compressibility, lack rigidity, and have high density compared with gases
- **Surface tension**: Resistance of a liquid to an increase in its surface area
    - Liquids with large intermolecular forces tend to have high surface tensions

Liquids (Continued)

- Polar liquids exhibit capillary action
  - **Capillary action**: Spontaneous rising of a liquid in a narrow tube
    - Cohesive forces - Intermolecular forces among the molecules of the liquid
    - Adhesive forces - Forces between the liquid molecules and the walls of the container

Concave Meniscus Formed by Polar Water

- Adhesive forces toward glass are stronger than cohesive forces in the liquid



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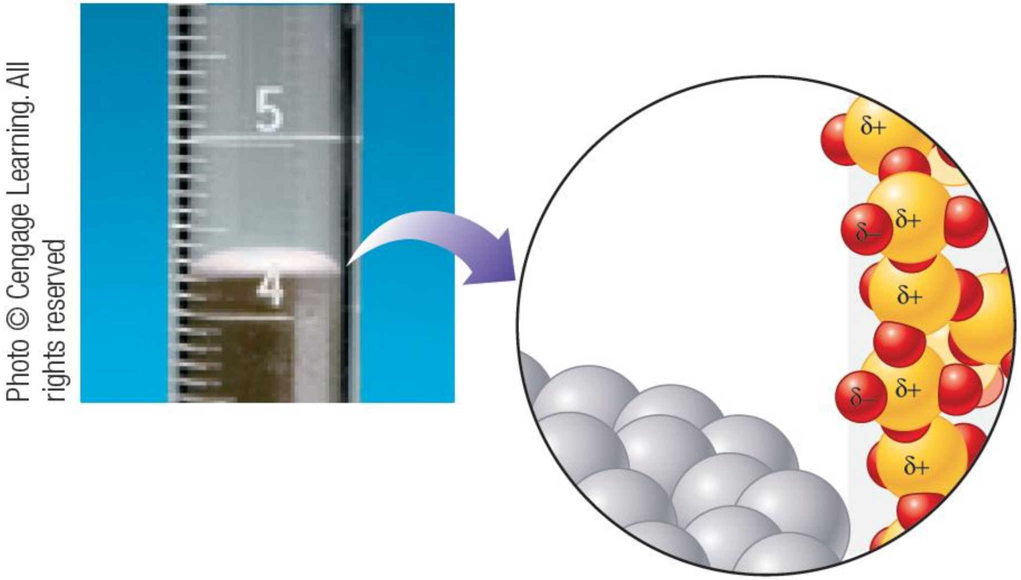
Convex Meniscus Formed by Nonpolar Liquid Mercury

- Cohesive forces in the liquid are stronger than adhesive forces toward glass



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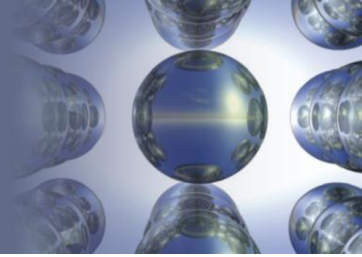
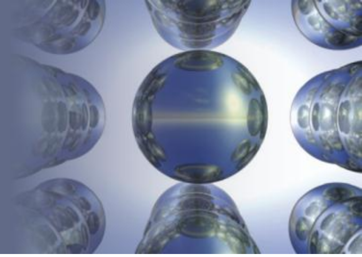


Viscosity

- Measure of a liquid’s resistance to flow
- Liquids with large intermolecular forces and complex molecules tend to be highly viscous
    - Example - Glycerol and grease



Structural Model for Liquids

- Have strong intermolecular forces and significant molecular motions
- Contain a large number of regions
  - Arrangement of the components are similar to those that are present in solids, but with more disorder
  - Holes are present in a few regions
  - Regions are subject to rapid fluctuations

Classification of Solids

- **Amorphous solids**: Have considerable disorder in their structures
- **Crystalline solids**: Characterized by highly regular arrangement of components
  - Positions of components are represented by lattices
    - **Lattice**: Three-dimensional system of points designating positions of components that make up the substance
    - **Unit cell**: Smallest repeating unit of a lattice

Figure 10.9 - Three Cubic Unit Cells and the Corresponding Lattices

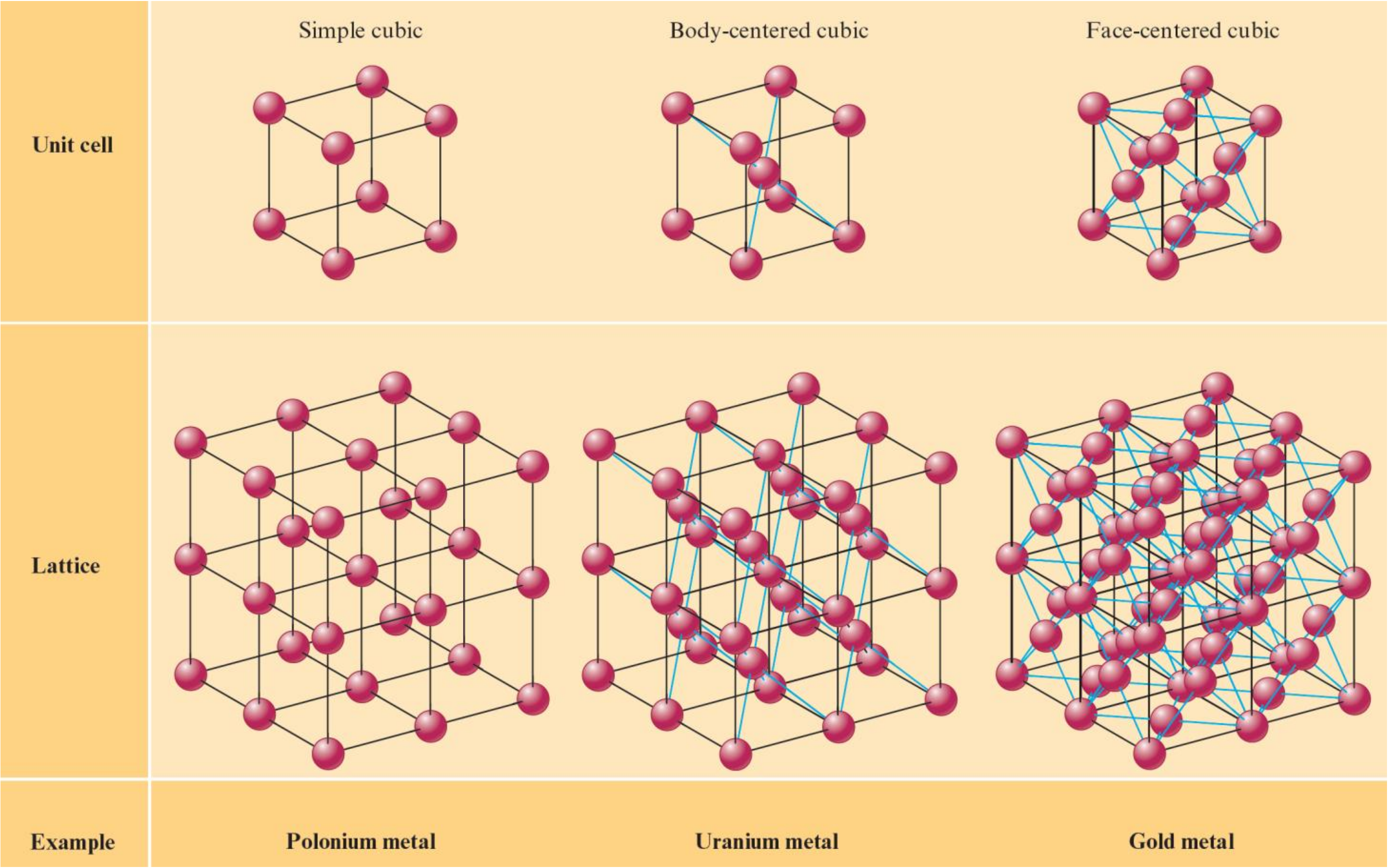
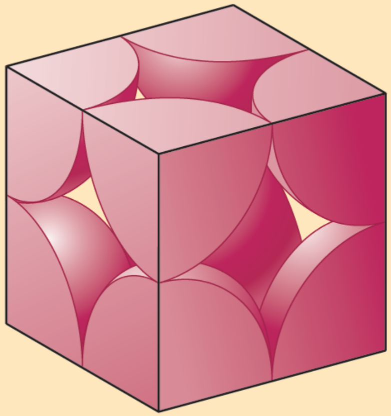
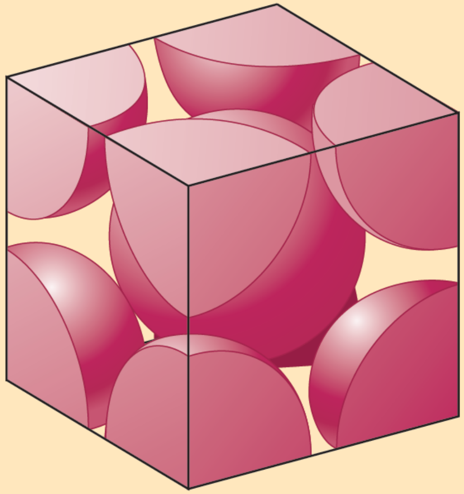
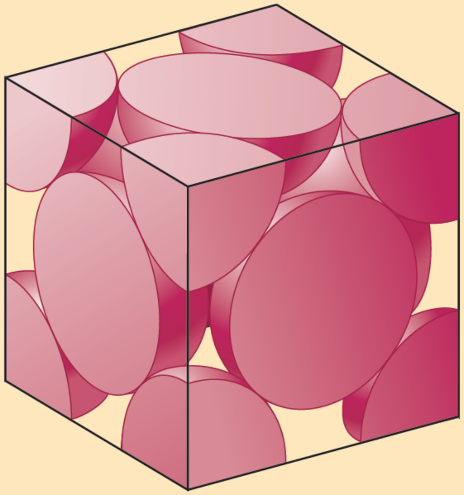


Figure 10.9 - Three Cubic Unit Cells and the Corresponding Lattices (Continued)

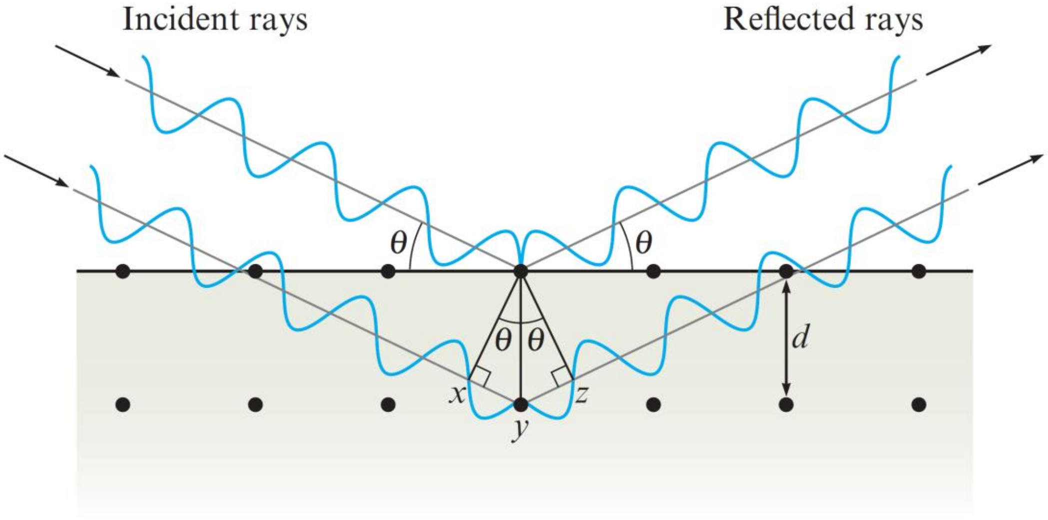
Space-filling unit cell			
Example	**Polonium metal**	**Uranium metal**	**Gold metal**

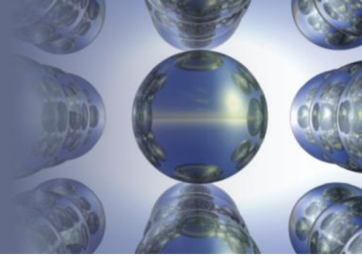
X-Ray Analysis of Solids

- **X-ray diffraction**: Helps determine the structures of crystalline solids
- Diffraction occurs due to:
  - Constructive interference when parallel beam waves are in phase
  - Destructive interference when waves are out of phase

Bragg Equation

- Used to determine interatomic spacings
- Consider two in-phase waves being reflected by atoms in two different layers in a crystal



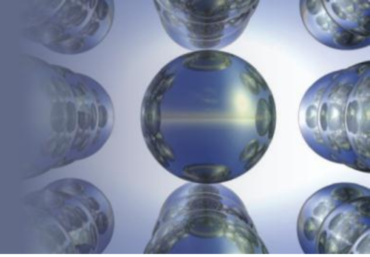


Bragg Equation (Continued 1)

- If the sum of *xy* and *yz* gives the extra distance traveled by the lower wave, the waves will be in phase after reflection if

$$xy + yz = n\lambda \qquad (10.1)$$

  - *n* is an integer
  - λ is the wavelength of the X rays



Bragg Equation (Continued 2)

- Using trigonometry, it can be shown that

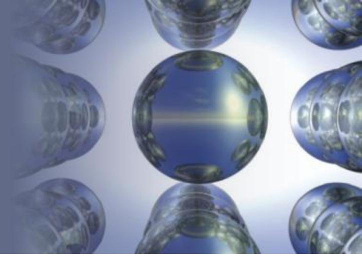
$$xy + yz = 2d\ \sin\theta \qquad (10.2)$$

  - *d* is the distance between the atoms
  - θ is the angle of incidence and reflection
- Combining equations 10.1 and 10.2 gives Bragg's equation

$$n\lambda = 2d\ \sin\theta$$

Diffractometer

- Used to conduct X-ray analysis of crystals
- Rotates the crystal based on the X-ray beam
  - Collects data produced by the scattering of X rays from the various planes of atoms in the crystal
- Helps gather data on bond lengths and angles



Interactive Example 10.1 - Using the Bragg Equation

- X rays of wavelength 1.54 Å were used to analyze an aluminum crystal
    - A reflection was produced at $\theta = 19.3$ degrees
    - Assuming $n = 1$, calculate the distance d between the planes of atoms producing this reflection

Interactive Example 10.1 - Solution

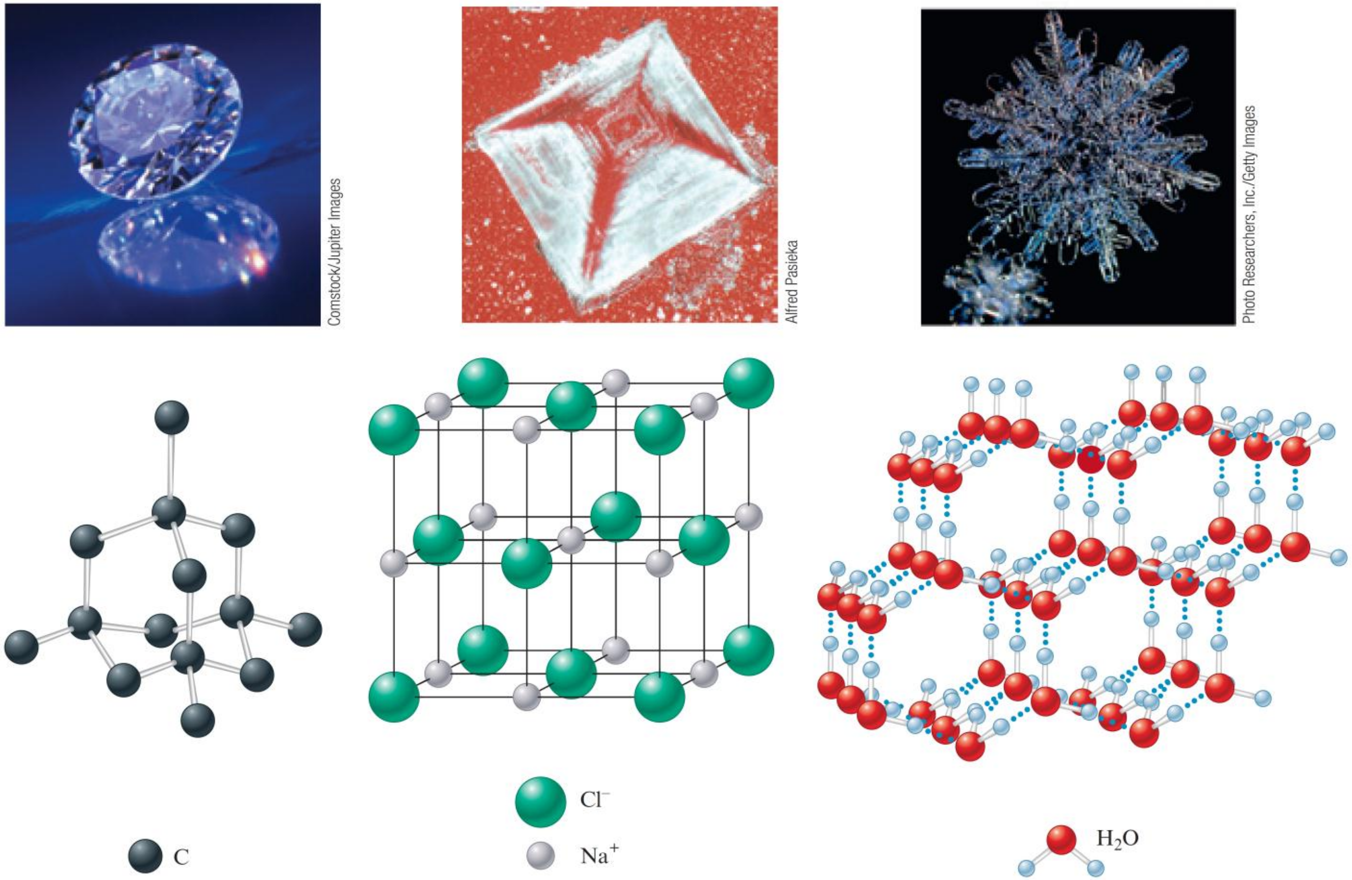
- To determine the distance between the planes, use the Bragg equation
  - $n = 1$
  - $\lambda = 1.54$ Å
  - $\theta = 19.3$ degrees

$$d = \frac{n\lambda}{2\sin\theta} = \frac{(1)(1.54\ \text{Å})}{(2)(0.3305)} = 2.33\text{Å} = 233\text{pm}$$

Types of Crystalline Solids

- **Ionic solids**: Possess ions at the lattice points that describe the structure of the solid
- **Molecular solids**: Possess discrete covalently bonded molecules at the lattice points
- **Atomic solids**: Possess atoms at the lattice points that describe the structure of the solid

Figure 10.22 - Examples of Three Types of Crystalline Solids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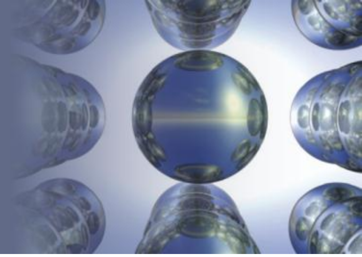
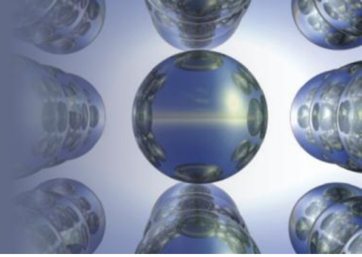


Classification of Atomic Solids

- Metallic solids - Possess a special type of delocalized nondirectional covalent bonds
- Network solids - Possess atoms bonded by strong directional covalent bonds
  - Bonds lead to giant molecules of atoms
- Group 8A solids - Possess noble gas elements that are attracted to each other by London dispersion forces



Closest Packing Model

- **Closest packing** arrangement
  - Characterized by layers of uniform hard spheres that efficiently use available space
    - Each sphere is surrounded by six others
  - Types of arrangement
    - The *aba* arrangement
    - The *abc* arrangement

The *aba* Arrangement

- Spheres in every third layer lie directly over spheres in the first layer
- Resulting structure is called the **hexagonal closest packed (hcp) structure**

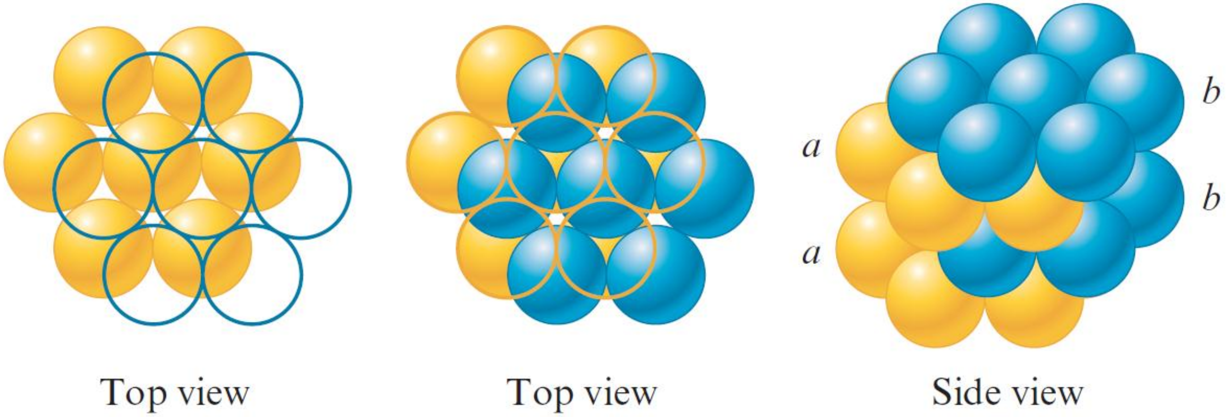
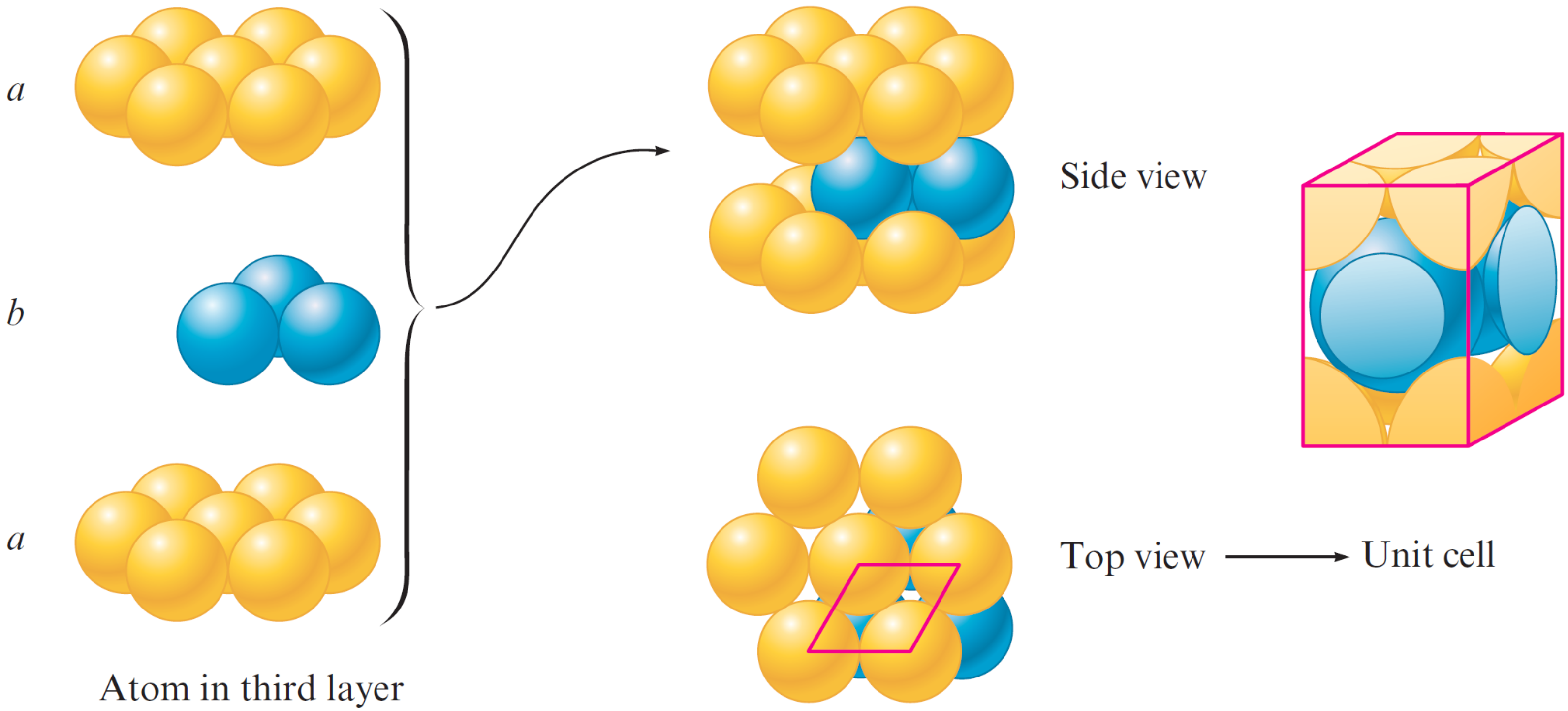


Figure 10.14 - Hexagonal Closest Packing



Atom in third layer
lies over atom in
first layer.

The *abc* Arrangement

- No spheres in the third layer lie over ones in the first layer
- Resulting structure is called the **cubic closest packed (ccp) structure**

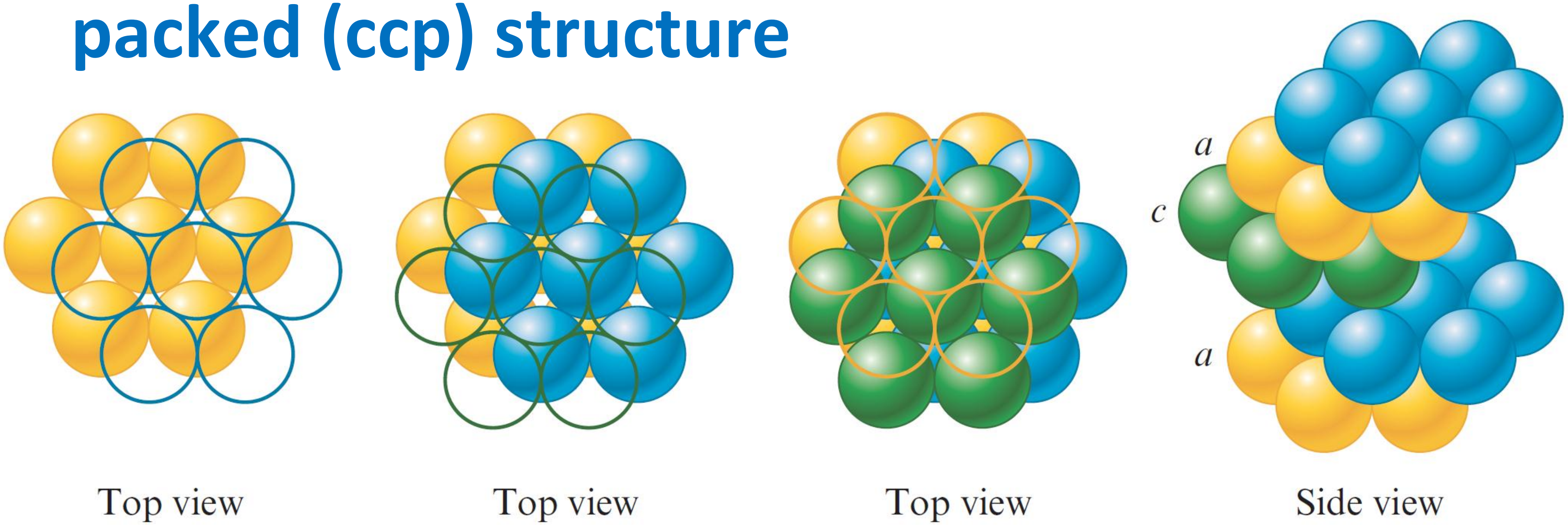
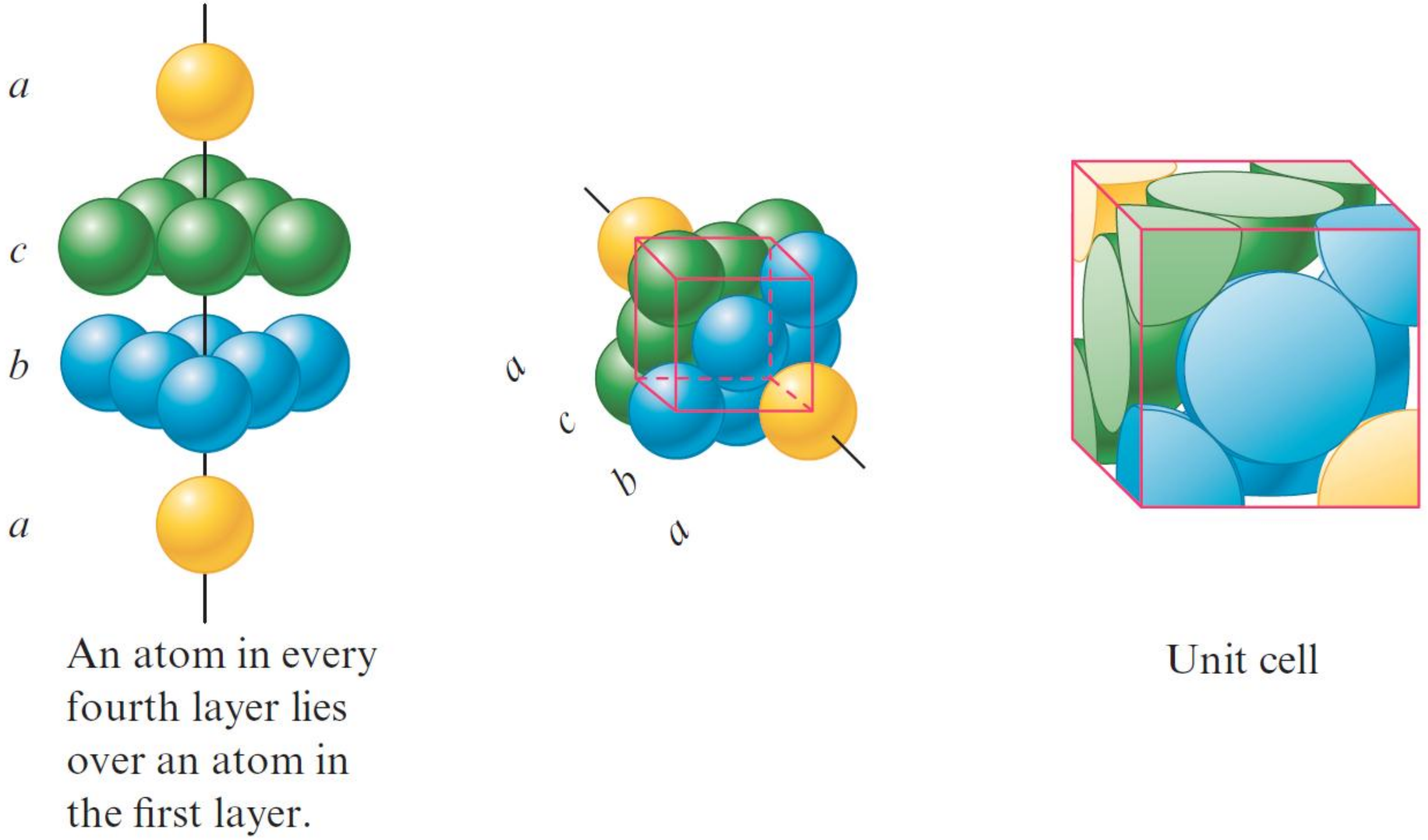


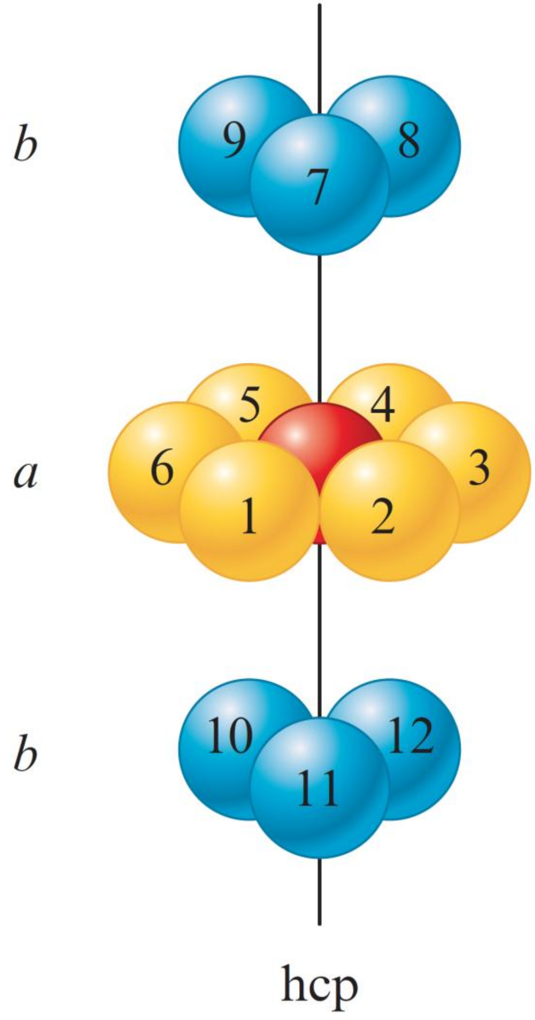
Figure 10.15 - Cubic Closest Packing



An atom in every fourth layer lies over an atom in the first layer.

Nearest Neighbors of a Sphere

- Each sphere has 12 equivalent nearest neighbors



Net Number of Spheres in a Face-Centered Cubic Unit Cell

- A unit cell is defined by the centers of the spheres on the corners of the cube
- Net number of spheres in a face-centered cubic unit would be

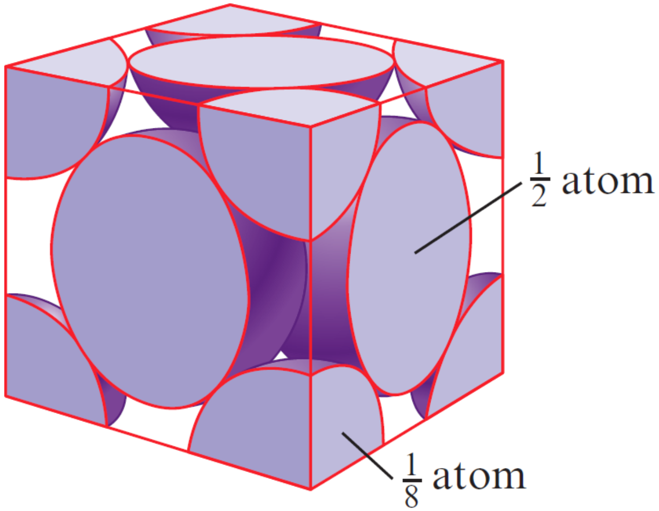
$$\left(8\times\frac{1}{8}\right)+\left(6\times\frac{1}{2}\right)=4$$

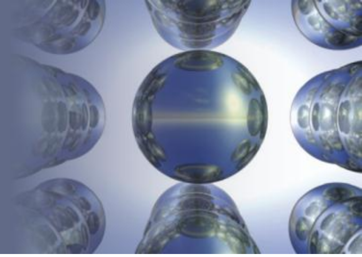
Number of corners in a cube

Number of spheres that lie inside a unit cell

Number of faces in a cube

Number of central spheres that lie inside a unit cell



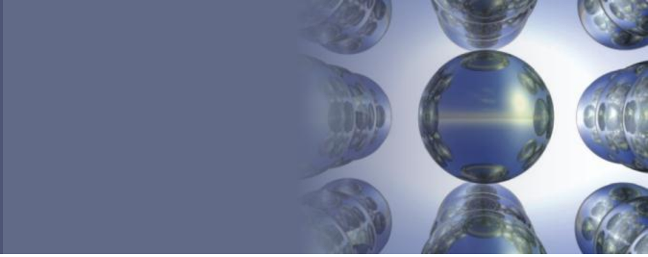


Interactive Example 10.2 - Calculating the Density of a Closest Packed Solid

- Silver crystallizes in a cubic closest packed structure
    - The radius of a silver atom is 144 pm
    - Calculate the density of solid silver

Interactive Example 10.2 - Solution

- Density is mass per unit volume
  - We need to know how many silver atoms occupy a given volume in the crystal
  - The structure is cubic closest packed, which means the unit cell is face-centered cubic
  - We must find the volume of this unit cell for silver and the net number of atoms it contains



Interactive Example 10.2 - Solution (Continued 1)

- Note that in this structure the atoms touch along the diagonals for each face and not along the edges of the cube
    - Length of the diagonal is $r + 2r + r$, or $4r$
    - We use this fact to find the length along the edge of the cube by the Pythagorean theorem

Interactive Example 10.2 - Solution (Continued 2)

$$d^2 + d^2 = (4r)^2$$

$$2d^2 = 16r^2$$

$$d^2 = 8r^2$$

$$d = \sqrt{8r^2} = r\sqrt{8}$$

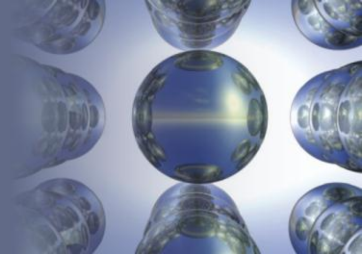
- Since *r* = 144 pm for a silver atom,

$$d = (144\text{ pm})\left(\sqrt{8}\right) = 407\text{ pm}$$

Interactive Example 10.2 - Solution (Continued 3)

- The volume of the unit cell is d^3, which is (407 pm)^3, or 6.74×10^7 pm^3
  - Converting this to cubic centimeters,

$$6.74 \times 10^7\,\text{pm}^3 \times \left(\frac{1.00 \times 10^{-10}\,\text{cm}}{\text{pm}}\right)^3 = 6.74 \times 10^{-23}\,\text{cm}^3$$

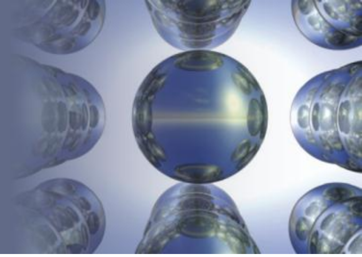


Interactive Example 10.2 - Solution (Continued 4)

- Since we know that the net number of atoms in the face-centered cubic unit cell is 4, we have 4 silver atoms contained in a volume of 6.74×10^{-23} cm^3
- Therefore, the density is

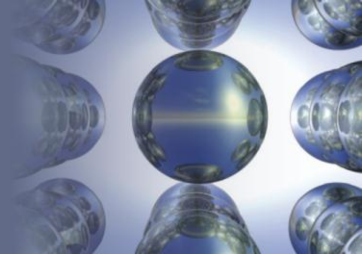
$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \left(\frac{(4\text{ atoms})(107.9\text{ g / mol})(1\text{ mol} / 6.022 \times 10^{23}\text{ atoms})}{6.74 \times 10^{-23}\text{ cm}^3} \right)$$

$$= 10.6\text{ g / cm}^3$$



Bonding Models for Metals

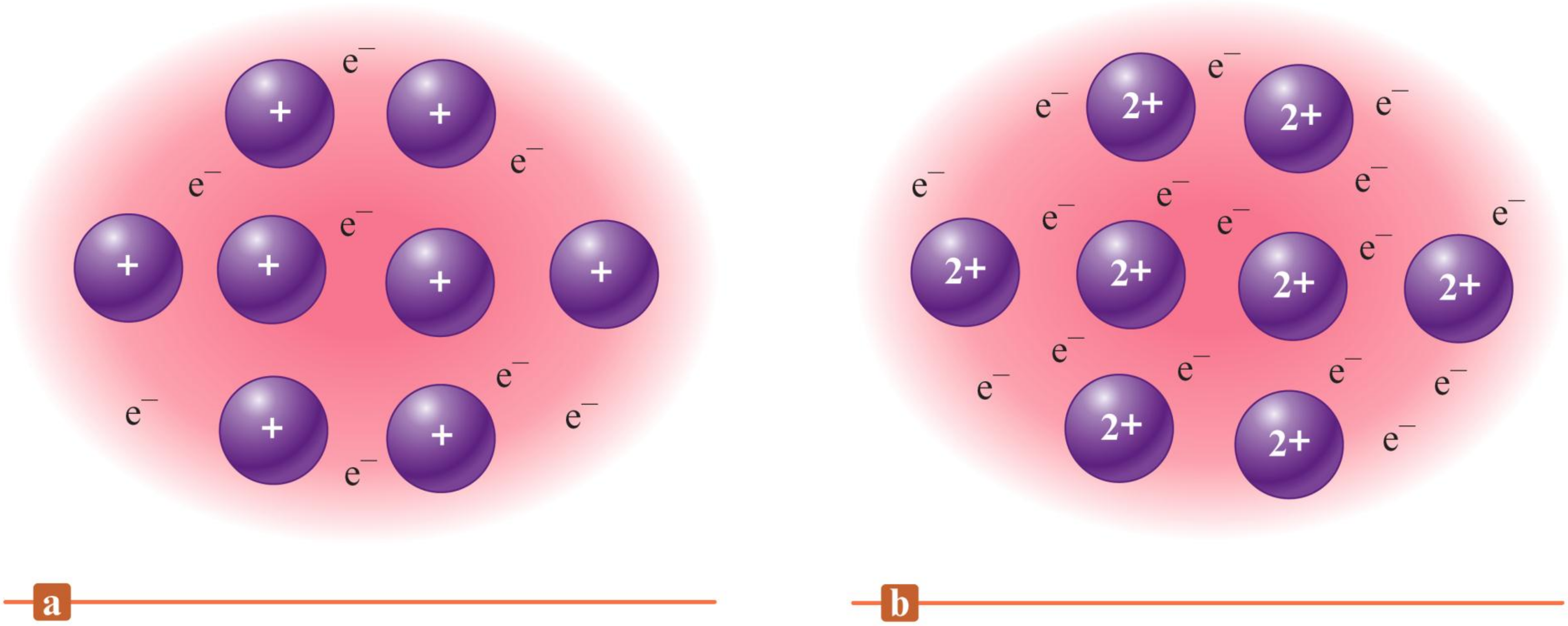
- A successful bonding model for metals must consider:
  - Malleability
  - Ductility
  - Efficient and uniform conduction of heat and electricity



Electron Sea Model

- Envisions a regular array of metal cations in a sea of valence electrons
    - Mobile electrons conduct heat and electricity
    - Metal ions freely move around as the metal is hammered into a sheet or drawn into a wire

Figure 10.8 (a) and (b) - Depiction of Electron Sea Model



Representation of an alkali metal (Group 1A) with one valence electron

Representation of an alkaline earth metal (Group 2A) with two valence electrons

Band Model or Molecular Orbital (MO) Model

- Electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms

Figure 10.19 - Molecular Orbital Energy Levels Produced When Various Numbers of Atomic Orbitals Interact

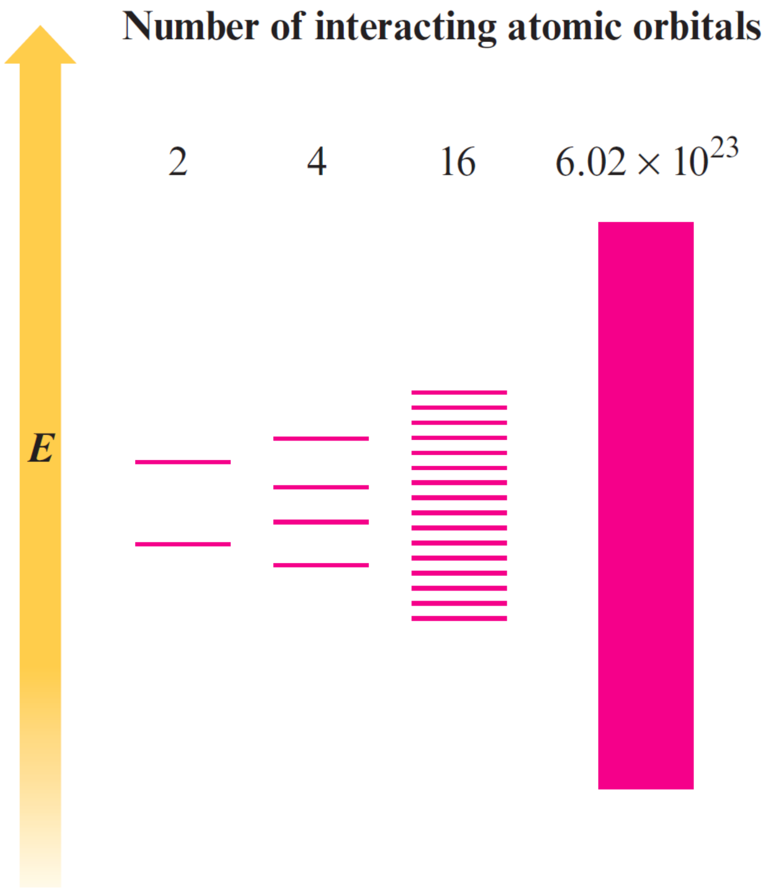
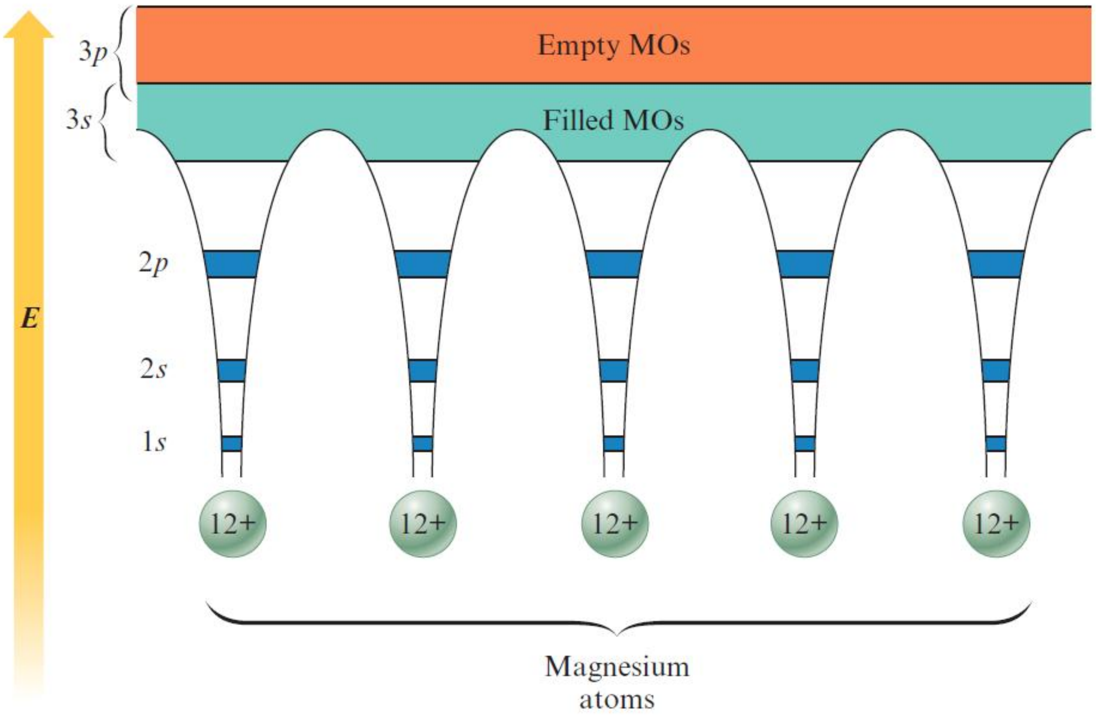


Figure 10.20 - Representation of Energy Levels in a Magnesium Crystal



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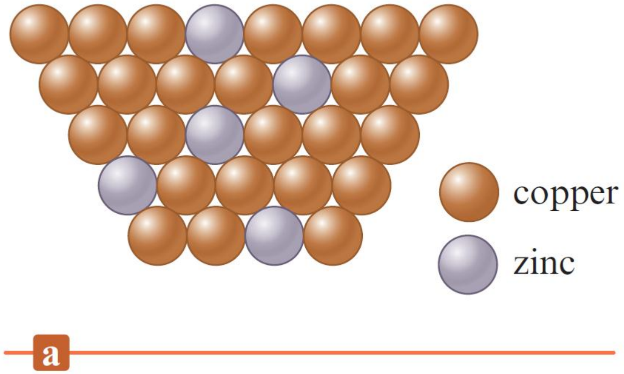
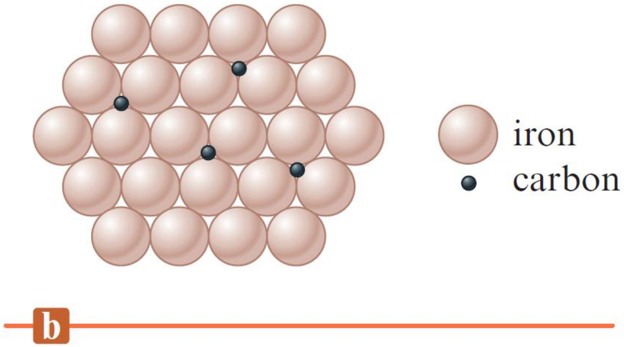
Metal Alloys

- **Alloy**: Substance that contains a mixture of elements and possesses metallic properties
  - **Substitutional alloy**: Some host metal atoms are replaced by other metal atoms of similar size
  - **Interstitial alloy**: Some of the interstices in the closest packed metal structure are occupied by small atoms

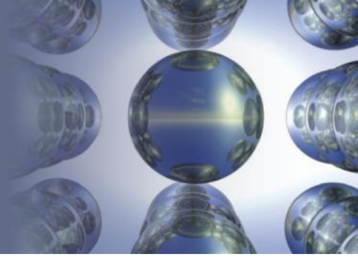
Figure 9.21 - Two Types of Alloys



Brass

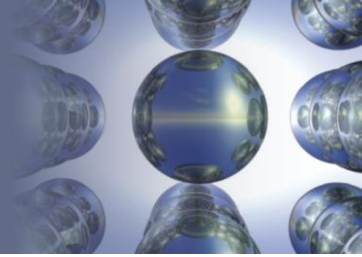


Steel



Influence of Carbon on the Properties of Steel

- Mild steel - Contains less than 0.2% carbon
  - Malleable and ductile
  - Used for nails, cables, and chains
- Medium steel - Contains 0.2 to 0.6% carbon
  - Used in rails and structural steel beams
- High-carbon steel - Contains 0.6 to 1.5% carbon
  - Tough and hard
  - Used for springs, tools, and cutlery



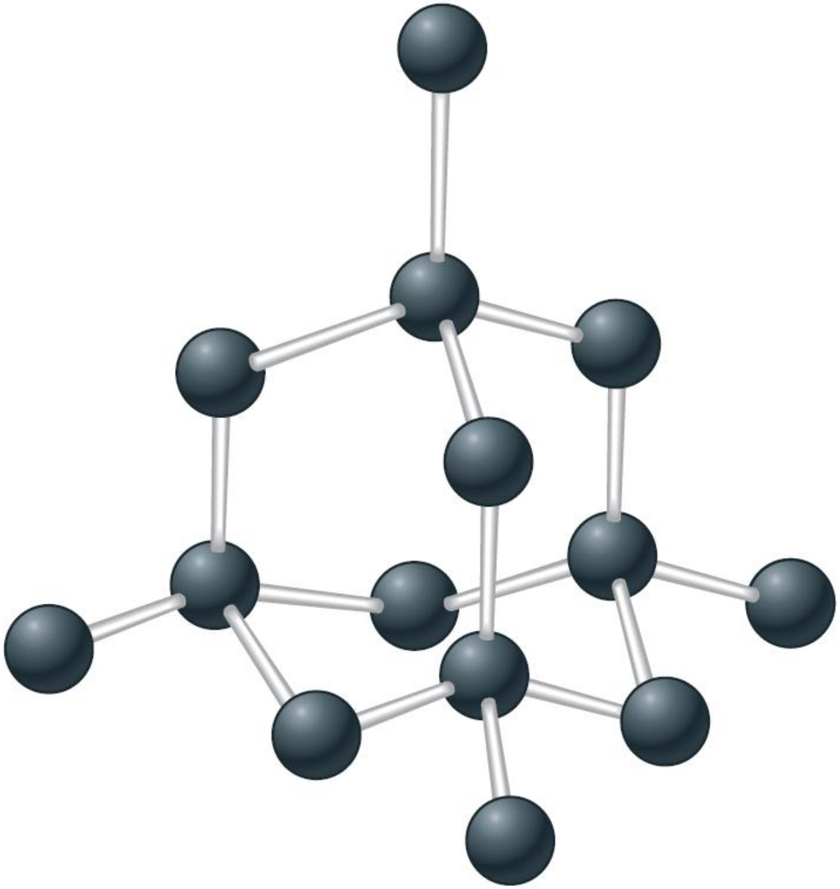
Network Solids

- Atomic solids that contain directional covalent bonds
  - Form solids that are viewed as giant molecules
- Properties
  - Brittle in nature
  - Ineffective conductors of heat and electricity

Diamond

- Each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule
- Structure fits the characteristics of the localized electron model
  - Covalent bonds result in a stable structure
    - Formed by the overlap of sp^3 hybridized carbon atomic orbitals

Figure 10.22 (a) - The Structure of Diamond



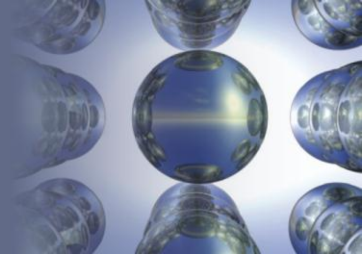
Diamond (Continued)

- Structure according to the MO model
    - A large gap between the filled and empty levels exists
        - Electron transfer is difficult
        - Diamond is not expected to be a good electrical conductor
- Used in industrial cutting implements
    - Graphite can be converted to diamond by applying 150,000 atm of pressure at 2800°C

Figure 10.23 (a) - Partial Representation of the Molecular Orbital Energies in Diamond

Graphite

- Slippery, black, and a conductor of heat and electricity
- Structure is based on layers of carbon atoms arranged in fused six-membered rings
  - Each carbon atom in a layer is surrounded by three other carbon atoms in a trigonal planar arrangement with 120-degree bond angles



Graphite (Continued)

- *sp*^{2} hybridization is predicted by the localized electron model
  - Three *sp*^{2} orbitals on each carbon atom form σ bonds with three other carbon atoms
  - One 2*p* orbital on each carbon remains unhybridized and is perpendicular to the plane
- Used as a lubricant in locks
  - Slipperiness is due to the strong bonding within the layers of carbon atoms rather than between the layers

Figure 10.22 (b) - The Structure of Graphite

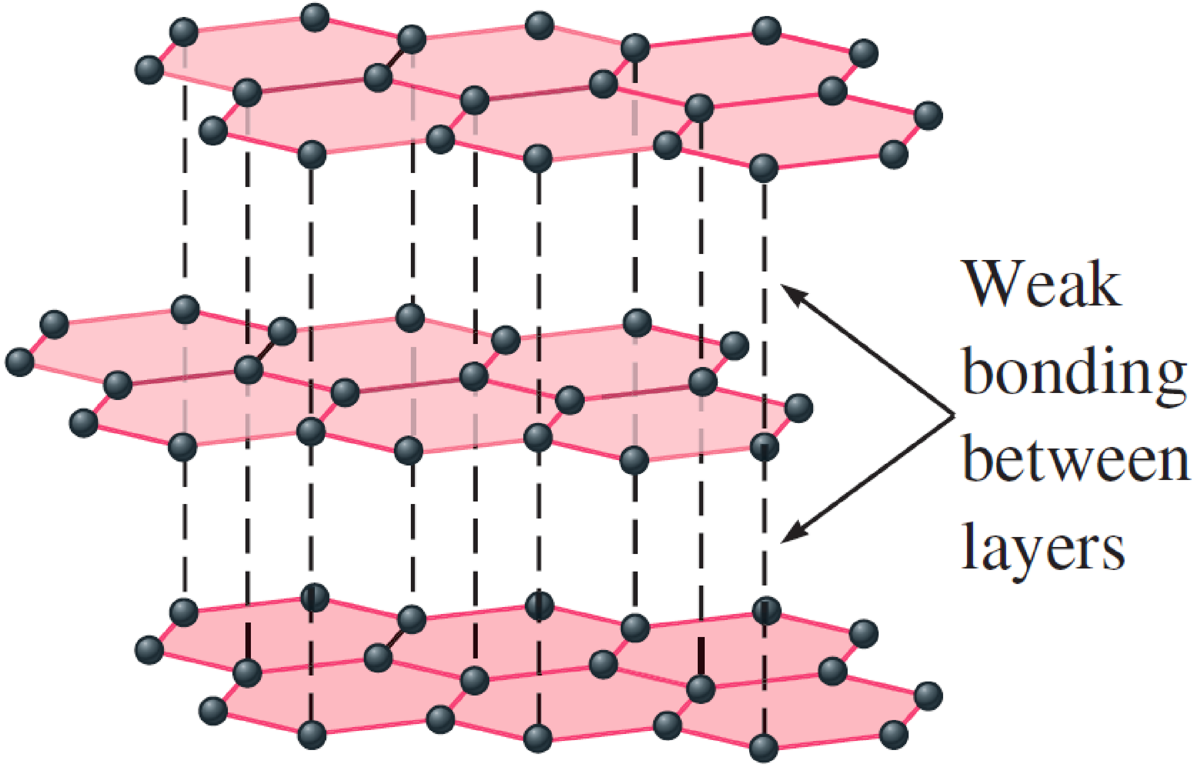
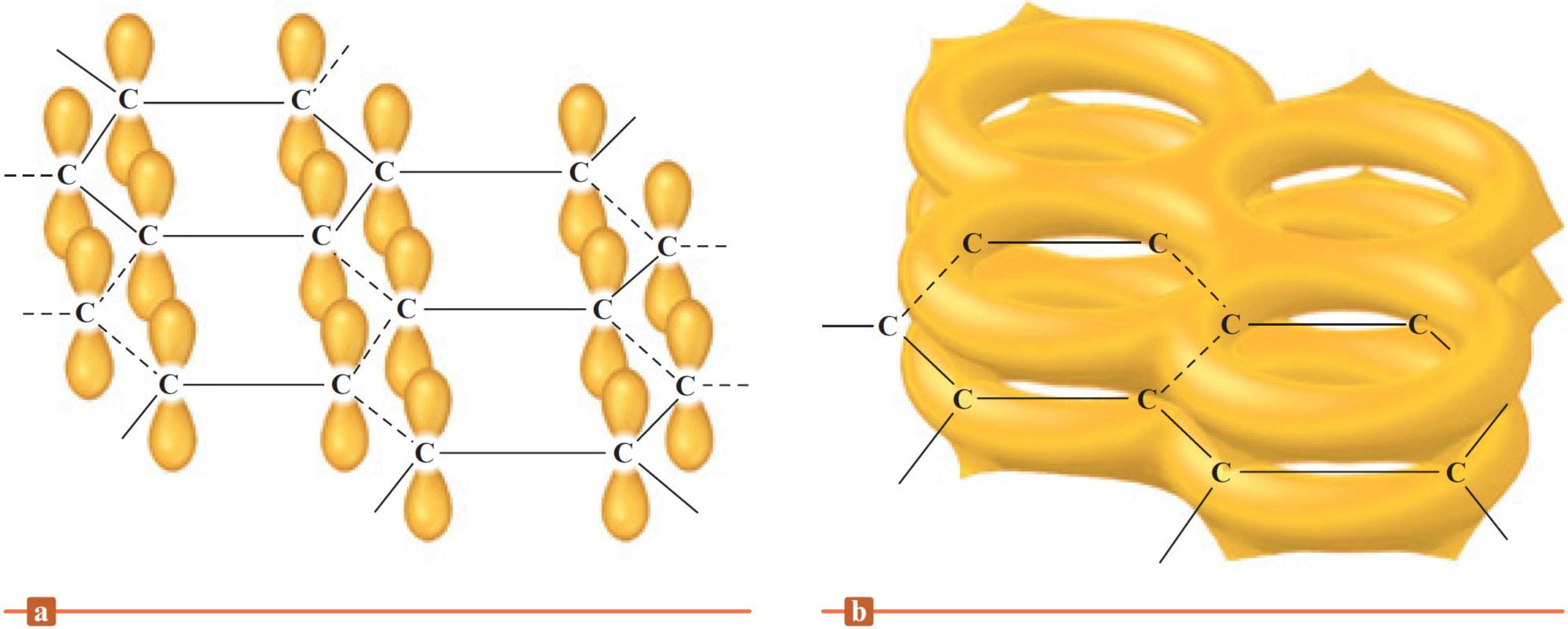


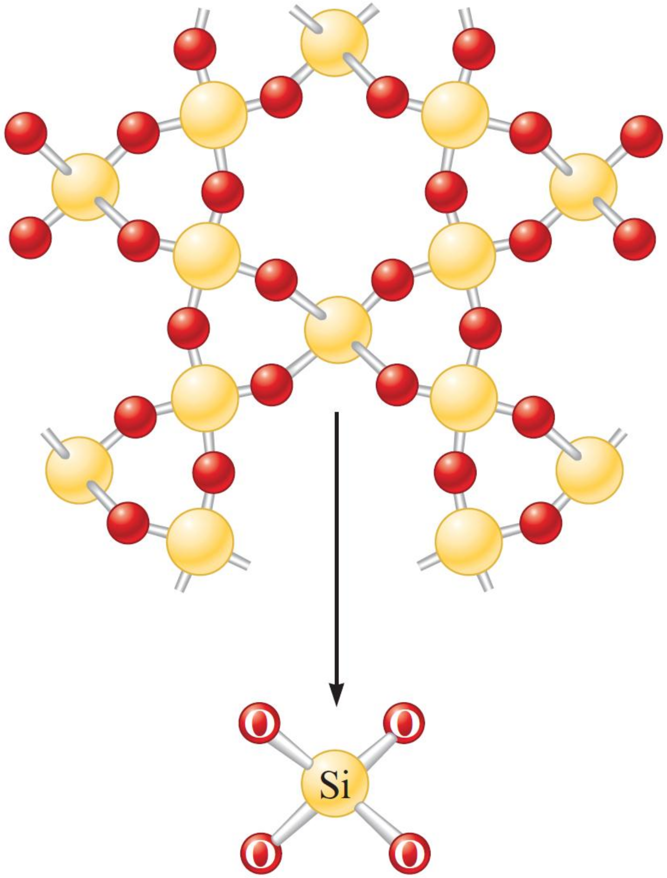
Figure 10.24 (a) and (b) - The *p* Orbitals and the π-Bonding Network in Graphite



Silicon

- An important constituent of the compounds that form the earth’s crust
- Stable silicon compounds involve chains with silicon–oxygen bonds
    - **Silica (SiO_2)**: Fundamental silicon–oxygen compound
- Structure
    - Silicon atom satisfies the octet rule by forming single bonds with four oxygen atoms

Figure 10.26 - Structure of Quartz



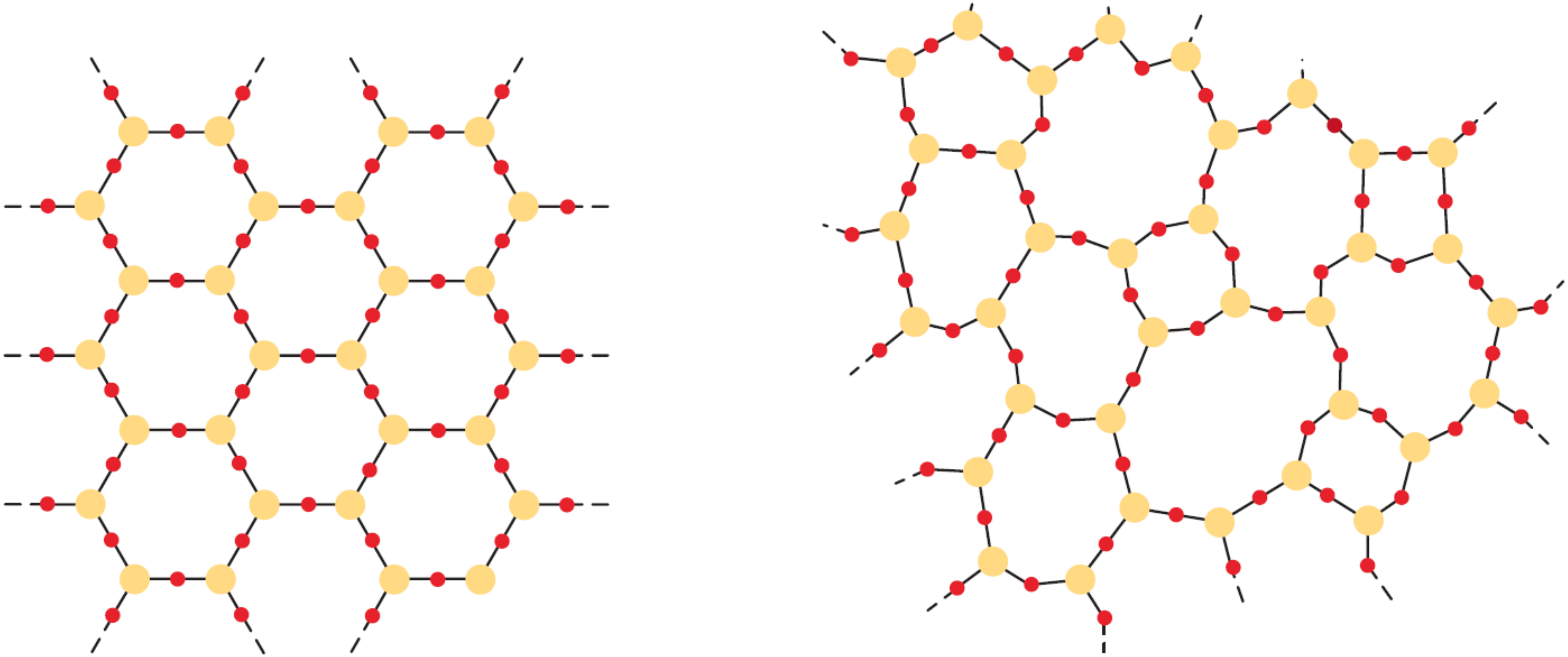
Silicates

- Compounds related to silica
  - Based on interconnected SiO_4 tetrahedra
- Found in rocks, soils, and clays
- Possess O/Si ratios greater than 2:1 and contain silicon–oxygen anions
  - Cations are required to balance the excess negative charge to form neutral silicates

Silicates (Continued)

- **Glass**: Amorphous solid that is formed when silica is heated above 1600° C and cooled rapidly
  - Homogeneous, noncrystalline frozen solution
  - Common glass results when substances like Na_2CO_3 are added to the silica melt and then cooled
  - Properties vary based on the additives

Figure 10.28 (a) and (b) - Two-Dimensional Representations of Quartz Crystal and Quartz Glass



Quartz Crystal

Quartz Glass

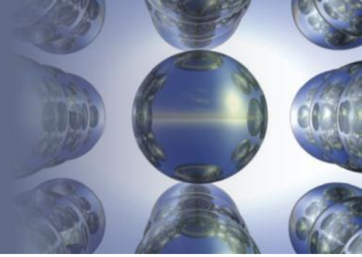
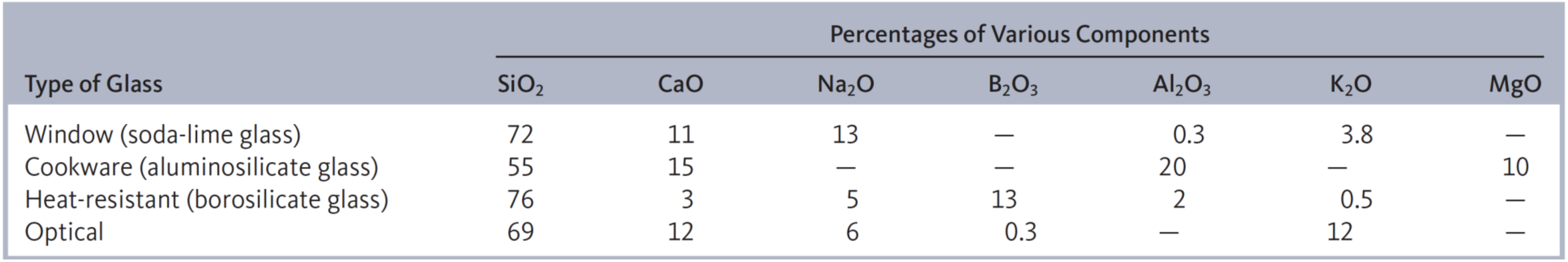


Figure 10.5 - Compositions of Some Common Types of Glass



Type of Glass	Percentages of Various Components						
	SiO_2	CaO	Na_2O	B_2O_3	Al_2O_3	K_2O	MgO
Window (soda-lime glass)	72	11	13	—	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	—	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	—
Optical	69	12	6	0.3	—	12	—

Ceramics

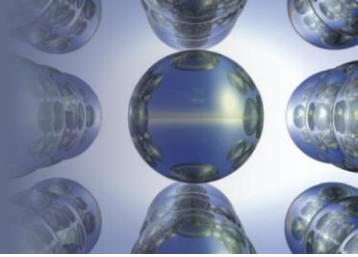
- Made from clays and hardened by firing at high temperatures
- Nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals
- Heterogeneous in nature

Structure of Clay

- Formed by the weathering action of water and carbon dioxide on the mineral feldspar
  - Feldspar - An aluminosilicate that weathers to form kaolinite
    - Kaolinite - Consists of tiny thin platelets with the empirical formula $Al_2Si_2O_5(OH)_4$
    - Platelets interlock as the clay dries
  - During firing, silicates and cations form a glass that binds the crystals of kaolinite

Uses of Ceramics

- Construction of jet and automobile engines
- Flexible ceramics can be obtained by adding small amounts of organic polymers
  - Organic polymers are used to produce durable engine parts, flexible superconducting wires and microelectronic devices, and prosthetic devices



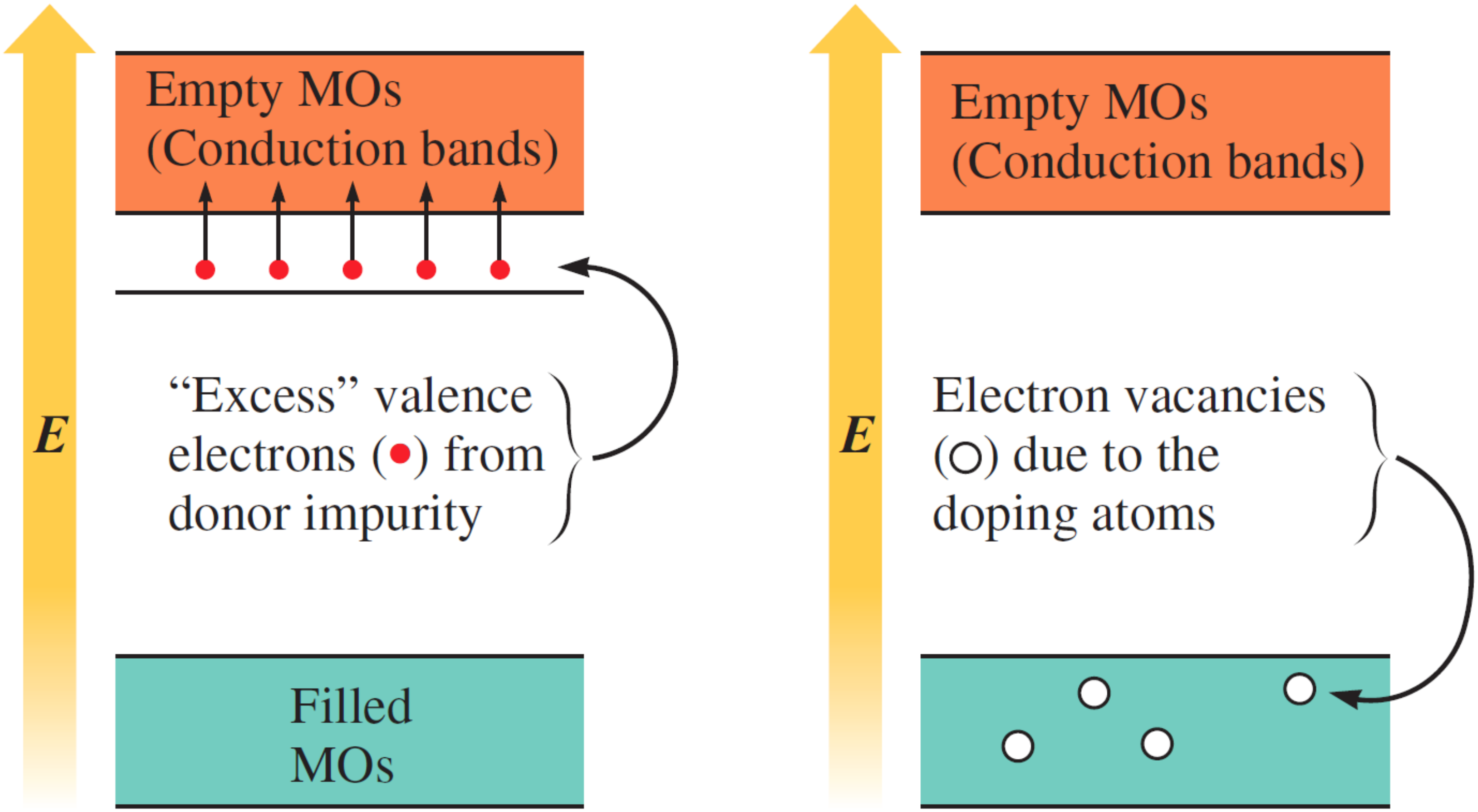
Semiconductors

- Conduct only a slight electric current at room temperature
  - Show increased conductivity at higher temperatures
- Types
  - **n-type semiconductor**
    - Substance whose conductivity is increased by doping the element with atoms that have more valence electrons than the atoms in the host crystal

Semiconductors (Continued)

  - **p-type semiconductor**: Semiconductors are doped with atoms that have fewer valence electrons than the atoms in the host crystal
    - Substance becomes a better conductor
- A p-type and an n-type semiconductor can be connected to form a **p–n junction**
  - Makes an excellent rectifier
    - Rectifier - Device that produces a pulsating direct current from alternating current

Figure 10.30 - Energy-Level Diagrams for an N-Type and a P-Type Semiconductor



P–N Junction

- A small number of electrons migrate from the n-type region into the p-type region
  - The migrations place a negative charge on the p-type region and a positive charge on the n-type region
  - Contact potential prevents further migration
    - Contact potential - Charge buildup

Figure 10.31 (a) - Charge Carriers in the P-Type and N-Type Regions

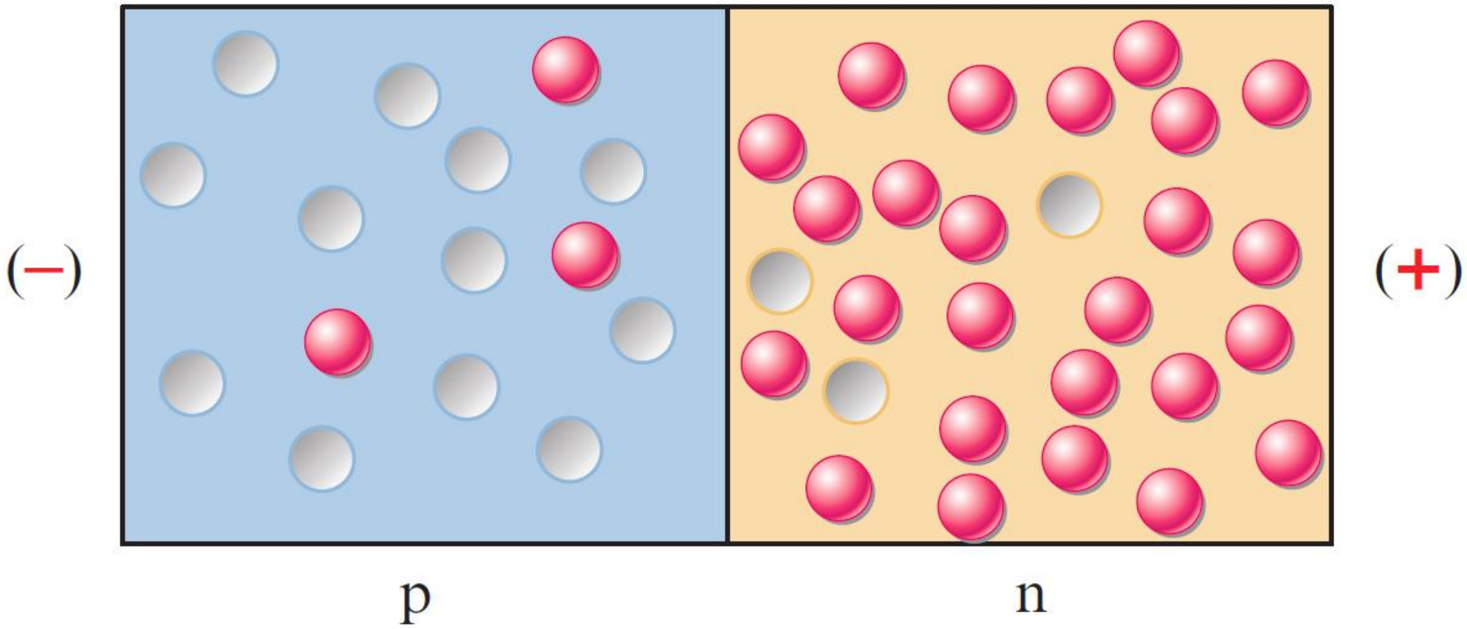
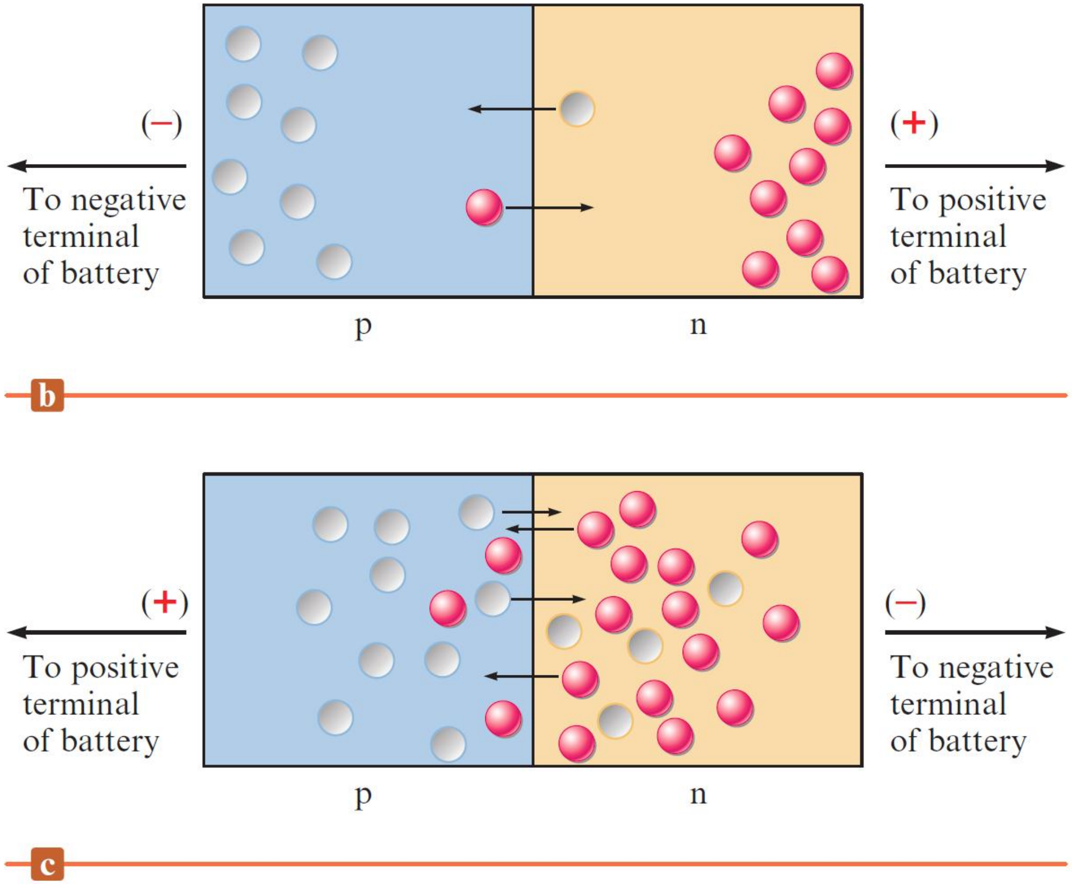
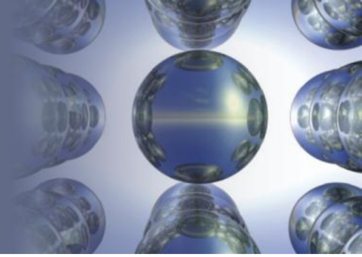


Figure 10.31 (b) and (c) - Reverse and Forward Bias



Reverse bias

Forward bias



Molecular Solids

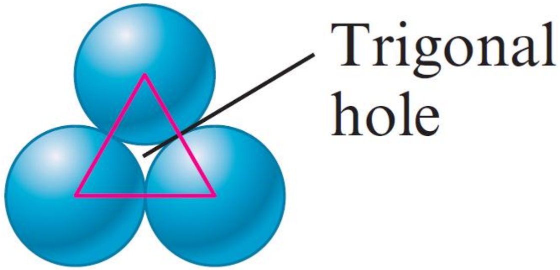
- Characterized by strong covalent bonding within molecules and weak bonding between molecules
- Intermolecular forces depend on the nature of the molecules
  - Molecules that do not have a dipole moment possess London dispersion forces
  - Molecules with dipole moments have greater intermolecular forces when hydrogen bonding is possible

Ionic Solids

- Stable, high-melting substances held together by the strong electrostatic forces that exist between oppositely charged ions
- Structure of binary ionic solids can be explained by closest packing of spheres
    - Spheres are packed to:
        - Maximize electrostatic attractions among oppositely charged ions
        - Minimize repulsions among ions with like charges

Types of Holes in Closest Packed Structures

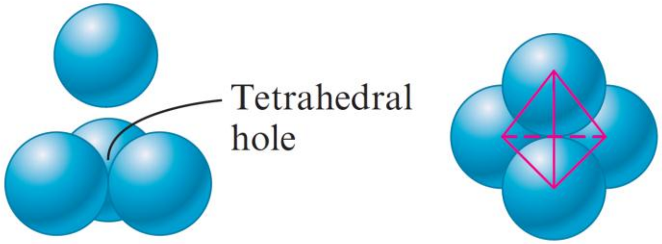
- Trigonal holes - Formed by three spheres in the same layer
  - Never occupied in binary ionic compounds



- Tetrahedral holes
  - Formed when a sphere is located in the dimple of three spheres in an adjacent layer

Types of Holes in Closest Packed Structures (Continued)

  - There are twice as many tetrahedral holes as packed anions in a closest packed structure



- Octahedral holes
  - Formed between two sets of three spheres in adjoining layers of the closest packed structures
  - Closest packed structures contain the same number of octahedral holes as packed spheres

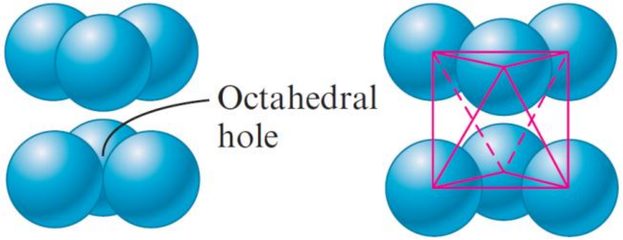
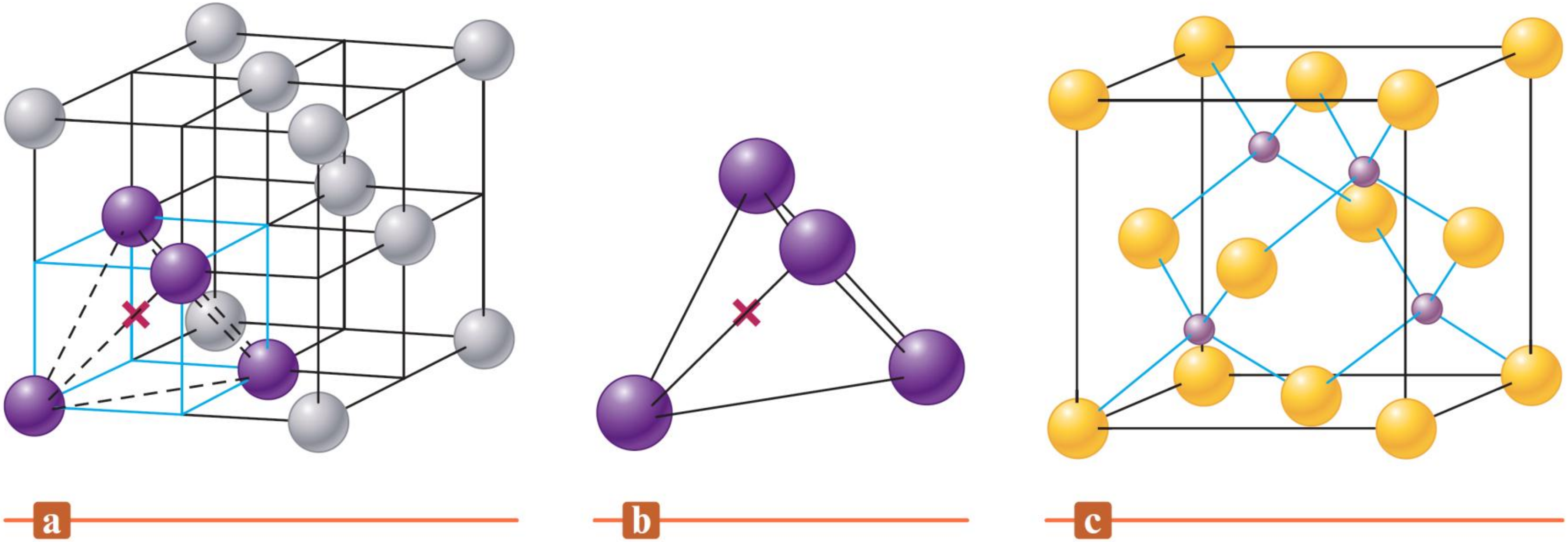


Figure 10.34 (a), (b), and (c) - Tetrahedral Holes

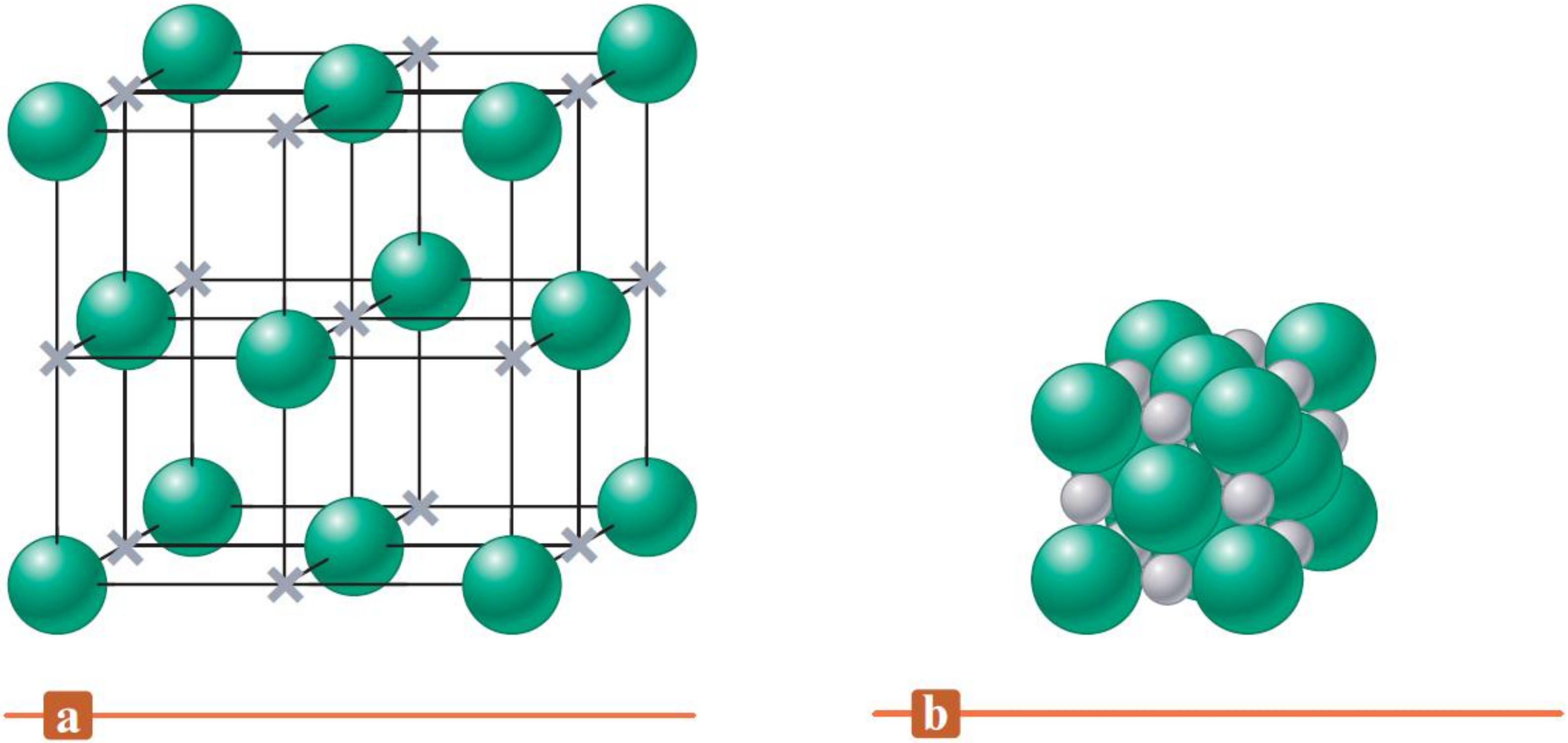


The location (red X) of a tetrahedral hole

One of the tetrahedral holes

ZnS

Figure 10.35 - Octahedral Holes



The locations (gray X) of the octahedral holes

Representation of the unit cell for solid NaCl

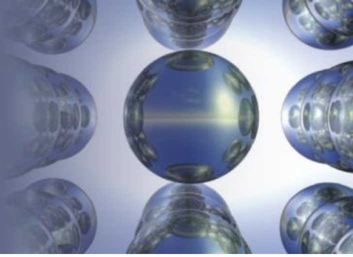
Interactive Example 10.3 - Determining the Number of Ions in a Unit Cell

- Determine the net number of Na^+ and Cl^- ions in the sodium chloride unit cell

Interactive Example 10.3 - Solution

- The Cl^- ions are cubic closest packed and thus form a face-centered cubic unit cell
- There is a Cl^- ion on each corner and one at the center of each face of the cube
    - The net number of Cl^- ions present in a unit cell is

$$8\left(\frac{1}{8}\right)+6\left(\frac{1}{2}\right)=4$$



Interactive Example 10.3 - Solution (Continued 1)

- The Na^+ ions occupy the octahedral holes located in the center of the cube and midway along each edge
    - The Na^+ ion in the center of the cube is contained entirely in the unit cell, whereas those on the edges are shared by four unit cells

Interactive Example 10.3 - Solution (Continued 2)

  - Since the number of edges in a cube is 12, the net number of Na^+ ions present is:

$$1(1)+12\left(\frac{1}{4}\right)=4$$

- We have shown that the net number of ions in a unit cell is 4 Na^+ ions and 4 Cl^- ions
  - Agrees with the 1:1 stoichiometry of sodium chloride

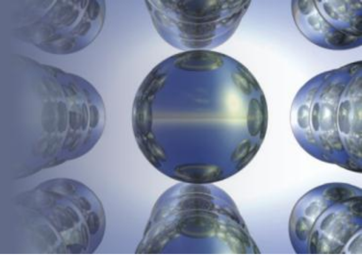


Table 10.7 - Types and Properties of Solids

Type of Solid	**Atomic**			**Molecular**	**Ionic**
	Network	**Metallic**	**Group 8A**		
Structural Unit	Atom	Atom	Atom	Molecule	Ion
Type of Bonding	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties	Hard	Wide range of hardness		Soft	Hard
	High melting point	Wide range of melting points	Very low melting point	Low melting point	High melting point
	Insulator	Conductor		Insulator	Insulator
Examples	Diamond	Silver Iron Brass	Argon(*s*)	Ice (solid H_2O) Dry ice (solid CO_2)	Sodium chloride Calcium fluoride

Interactive Example 10.4 - Types of Solids

- Using the Table 10.7, classify each of the following substances according to the type of solid it forms
  a. Gold
  b. Carbon dioxide
  c. Lithium fluoride
  d. Krypton

Interactive Example 10.4 - Solution

a. Solid gold is an atomic solid with metallic properties

b. Solid carbon dioxide contains nonpolar carbon dioxide molecules and is a molecular solid

c. Solid lithium fluoride contains Li^+ and F^- ions and is a binary ionic solid

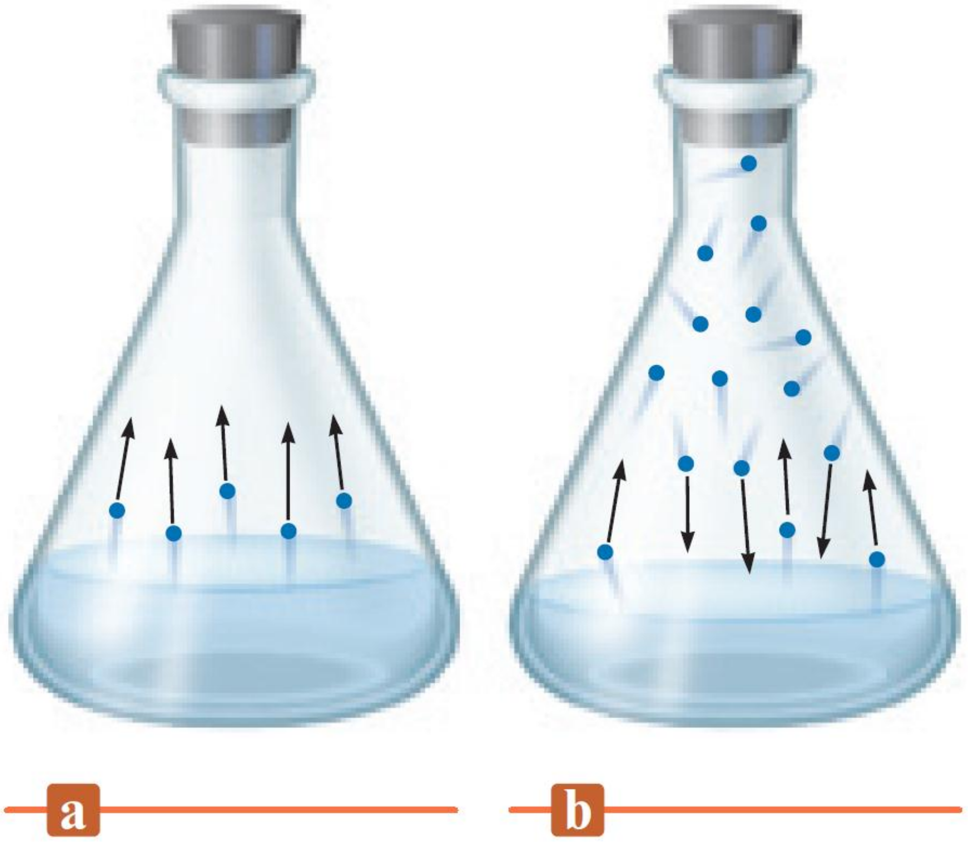
Interactive Example 10.4 - Solution (Continued)

d. Solid krypton contains krypton atoms that can interact only through London dispersion forces
    - It is an atomic solid but has properties characteristic of a molecular solid with nonpolar molecules

Vaporization (Evaporation)

- Molecules of a liquid escape the liquid's surface to form a gas
- **Heat of vaporization (ΔH_{vap})**: Energy required to vaporize 1 mole of a liquid at a pressure of 1 atm
- Endothermic in nature

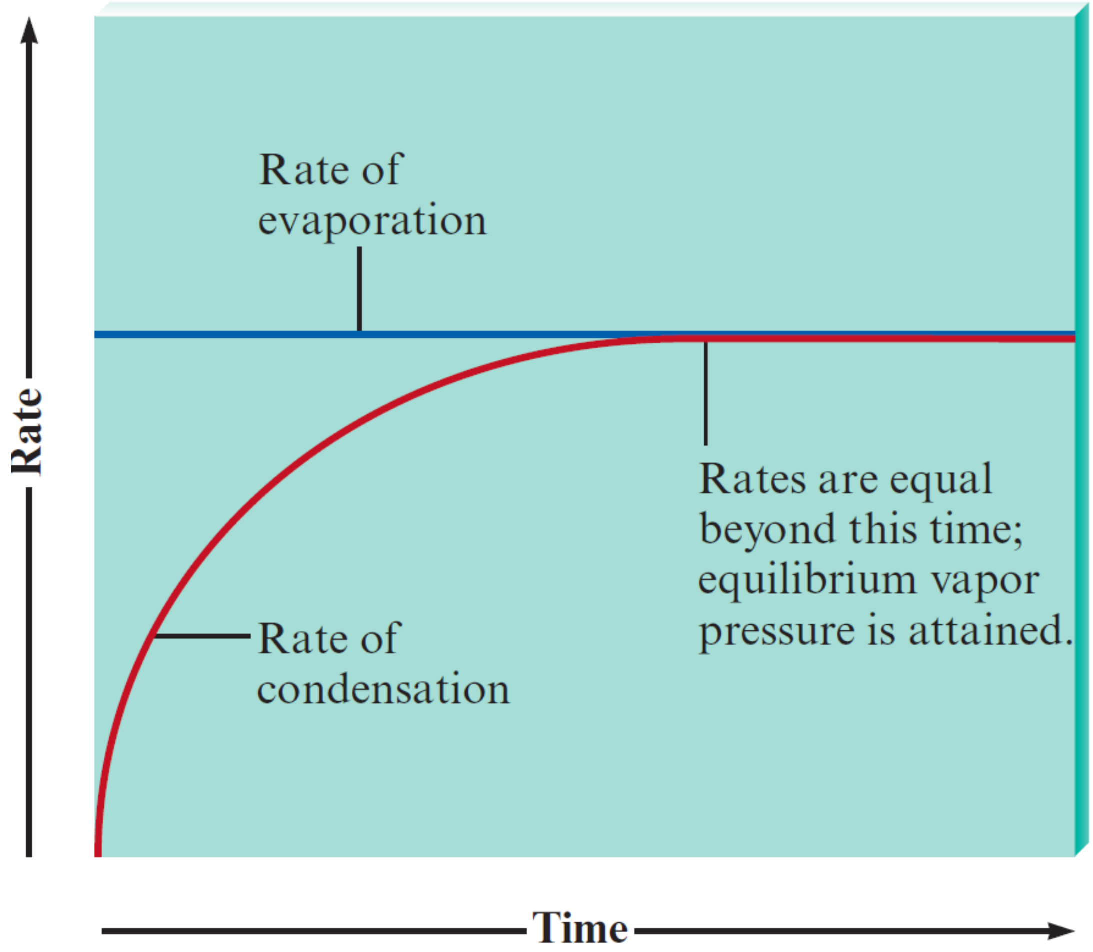
Figure 10.36 (a) and (b) - Behavior of a Liquid in a Closed Container



Vapor Pressure

- **Equilibrium**: The point at which no further net change occurs in the amount of liquid or vapor
    - Rate of condensation equals rate of evaporation
        - **Condensation**: Process by which gases become liquids
    - **Equilibrium vapor pressure**: Pressure of vapor at equilibrium

Figure 10.37 - Rates of Condensation and Evaporation

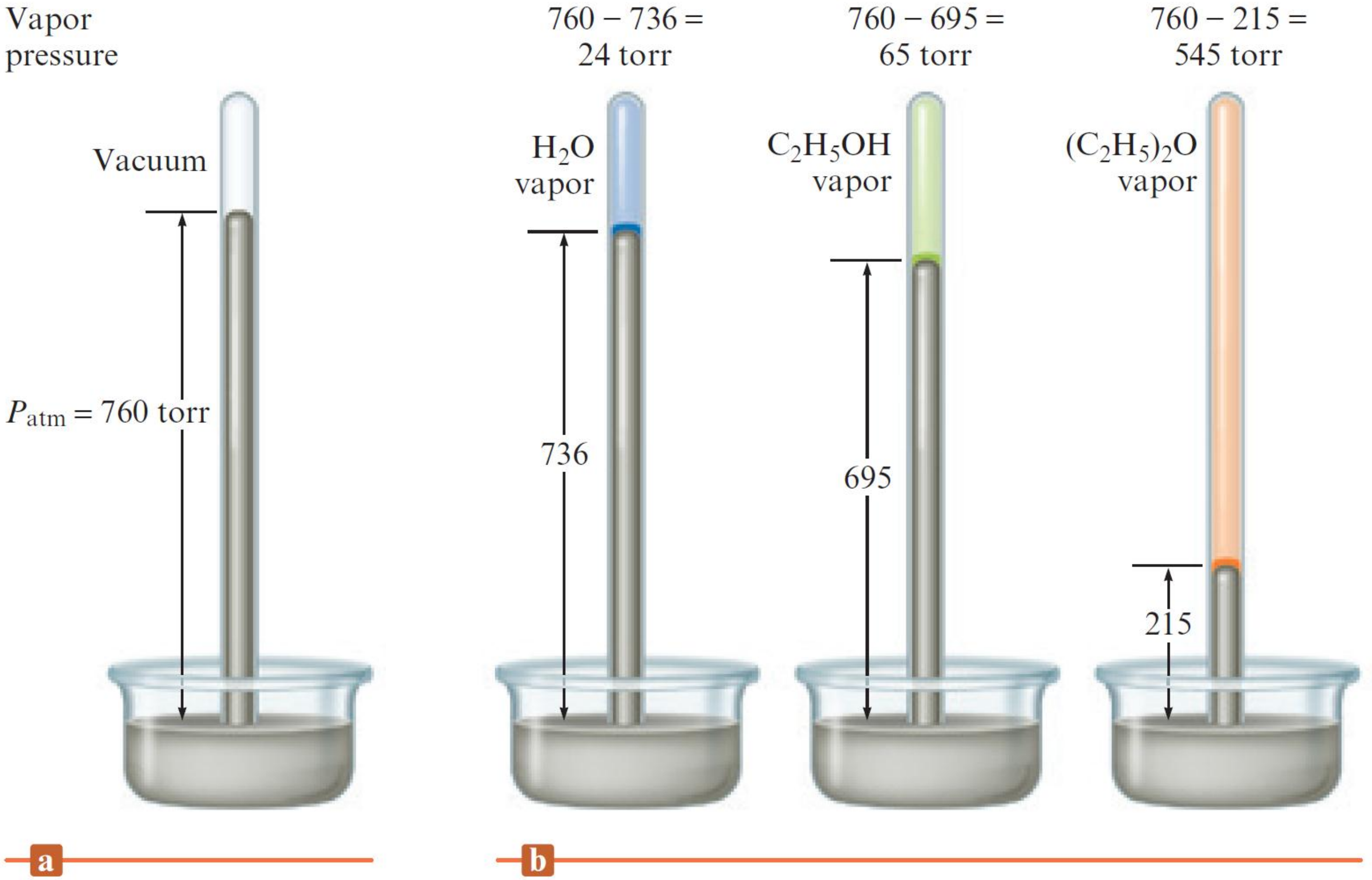


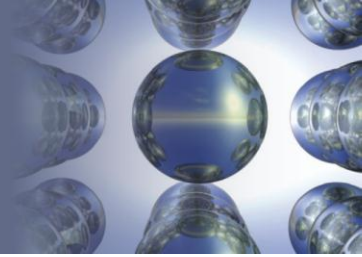
Measurement of Vapor Pressure

- Vapor pressure can be measured using a simple barometer
    - When the system reaches equilibrium, the vapor pressure can be determined from the change in the height of the mercury column

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$$

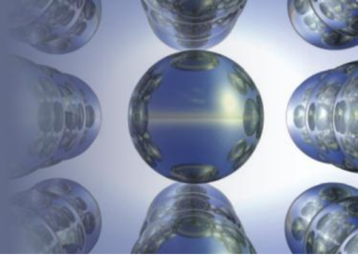
Figure 10.38 - Measuring Vapor Pressure





Critical Thinking

- You have seen that the water molecule has a bent shape and therefore is a polar molecule
  - This accounts for many of water’s interesting properties
  - What if the water molecule was linear?
    - How would this affect the properties of water, such as its surface tension, heat of vaporization, and vapor pressure?
    - How would life be different?



Vapor Pressure and Liquids

- Liquids with high vapor pressures are volatile
    - Evaporation occurs rapidly in an open environment
- The size of the intermolecular forces in a liquid determines its vapor pressure
    - Substances with large molar masses have relatively low vapor pressures

Vapor Pressure and Liquids (Continued)

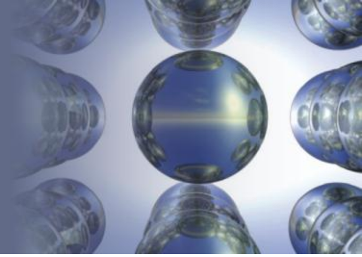
- Vapor pressure increases significantly with temperature
  - A molecule must have sufficient kinetic energy to overcome intermolecular forces

Vapor Pressure versus Temperature

- Produces a straight line when plotted on a graph

$$\ln\left(P_{\text{vap}}\right) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}\right) + C \qquad (10.4)$$

  - T - Temperature in Kelvin
  - ΔH_{vap} - Enthalpy of vaporization
  - R - Universal gas constant
  - C - Constant characteristic of a given liquid
  - ln - Natural logarithm of the vapor pressure



Vapor Pressure versus Temperature (Continued)

- Equation 10.4 is the equation for a straight line of the form *y* = *mx* + *b*

$$y = \ln(P_{\text{vap}})$$

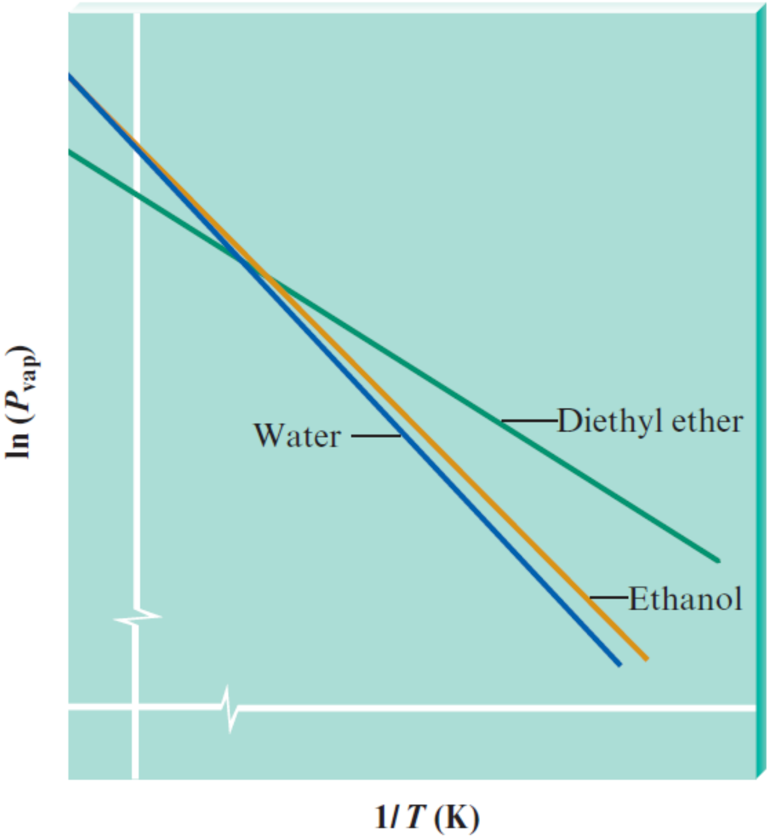
$$\text{x} = \frac{1}{T}$$

$$m = \text{slope} = -\frac{\Delta H_{\text{vap}}}{R}$$

$$b = \text{intercept} = \text{C}$$

Example 10.5 - Determining Enthalpies of Vaporization

- Using the plots in the figure determine whether water or diethyl ether has the larger enthalpy of vaporization



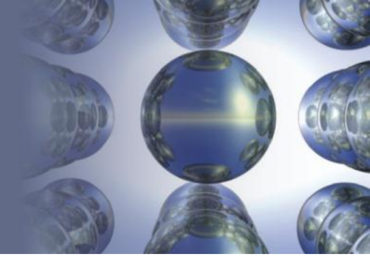
Example 10.5 - Solution

- When ln(P_{vap}) is plotted versus 1/T, the slope of the resulting straight line is $-\dfrac{\Delta H_{\text{vap}}}{R}$
- The slopes of the lines for water and diethyl ether are both negative, as expected, and that the line for ether has the smaller slope
    - Ether has the smaller value of ΔH_{vap}
        - This makes sense because the hydrogen bonding in water causes it to have a relatively large enthalpy of vaporization

The Clausius–Clapeyron Equation

- When the values of ΔH_{vap} and P_{vap} at one temperature are known, it is possible to calculate the value of P_{vap} at another temperature
    - Assume that C does not depend on temperature
    - At temperatures T_1 and T_2

$$\ln(P_{\mathrm{vap},\mathrm{T}_1}) + \frac{\Delta H_{\mathrm{vap}}}{RT_1} = C = \ln(P_{\mathrm{vap},\mathrm{T}_2}) + \frac{\Delta H_{\mathrm{vap}}}{RT_2}$$



The Clausius–Clapeyron Equation (Continued)

- Rearranging the equation gives

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

  - P_{vap} = vapor pressure
  - ΔH_{vap} = enthalpy of vaporization
  - R = Universal gas constant
  - T = temperature (in Kelvin)

Interactive Example 10.6 - Calculating Vapor Pressure

- The vapor pressure of water at 25° C is 23.8 torr, and the heat of vaporization of water at 25° C is 43.9 kJ/mol
  - Calculate the vapor pressure of water at 50° C

Interactive Example 10.6 - Solution

- We will use the following equation:

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- For water we have
  - P_{vap,T_1} = 23.8 torr
  - T_1 = 25 + 273 = 298 K T_2 = 50 + 273 = 323 K
  - ΔH_{vap} = 43.9 kJ/mol = 43,900 J/mol
  - R = 8.3145 J/K · mol

Interactive Example 10.6 - Solution (Continued)

$$\ln\left(\frac{23.8\ \text{torr}}{P_{\text{vap},T_2}\ (\text{torr})}\right) = \frac{43{,}900\ \text{J/mol}}{8.3145\ \text{J/K}\cdot\text{mol}}\left(\frac{1}{323\ \text{K}} - \frac{1}{298\ \text{K}}\right)$$

$$\ln\left(\frac{23.8}{P_{\text{vap},T_2}}\right) = -1.37$$

- Taking the antilog of both sides gives

$$\frac{23.8}{P_{\text{vap},T_2}} = 0.254$$

$$P_{\text{vap},T_2} = 93.7\ \text{torr}$$

Sublimation

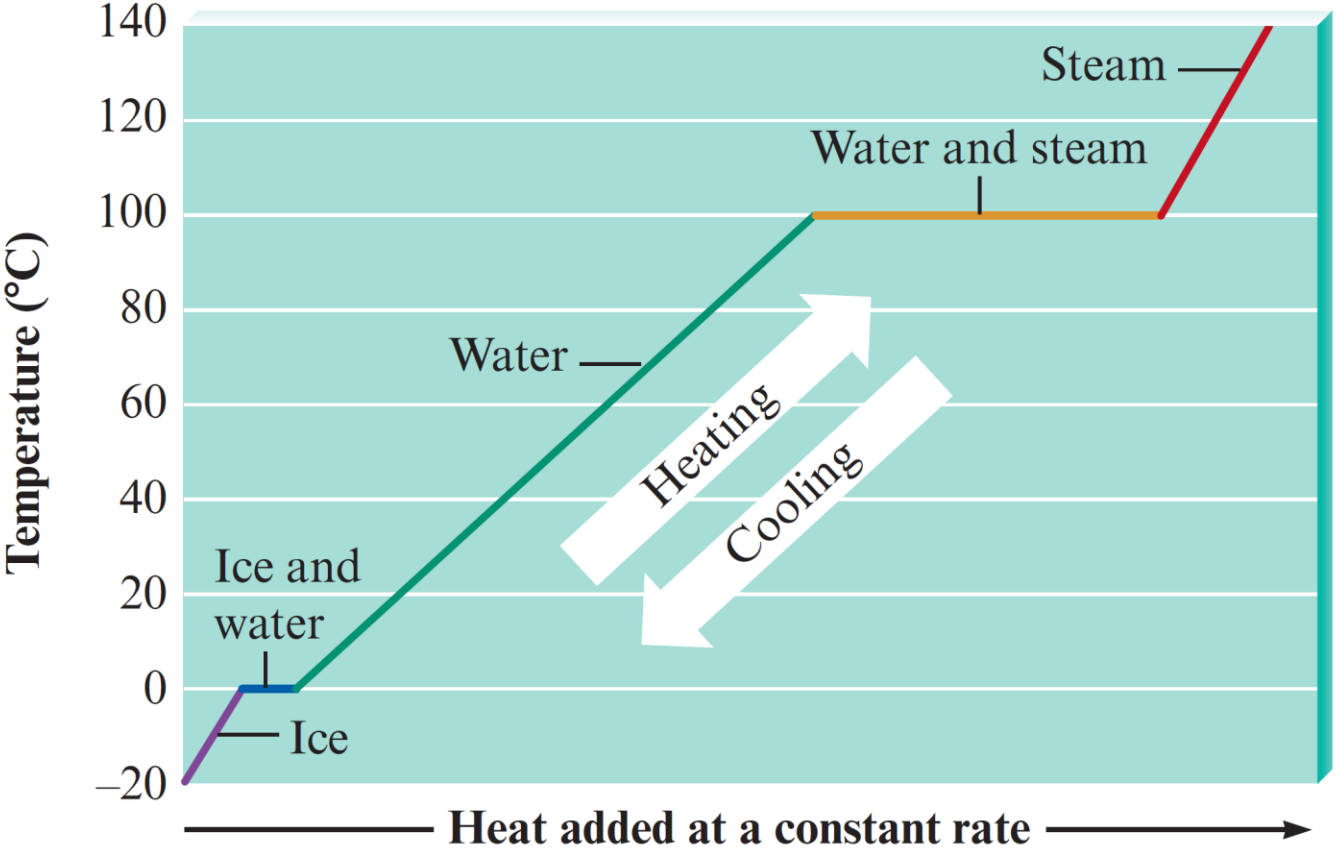
- Process in which solids change to gases without passing through the liquid state
- Occurs with dry ice and iodine

Richard Megna/Fundamental Photographs

Changes of State

- **Heating curve**: Plot of temperature versus time for a process where energy is added at a constant rate
  - When a solid is heated, it melts to form a liquid
    - If the heating continues, it will eventually form the vapor phase
- **Heat of fusion (enthalpy of fusion)**: Change in enthalpy at the melting point of a solid

Figure 10.42 - Heating Curve for a Specific Quantity of Water



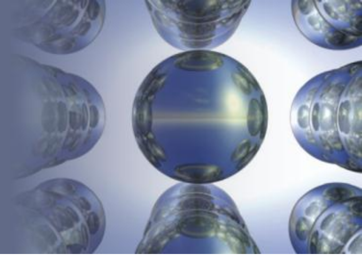
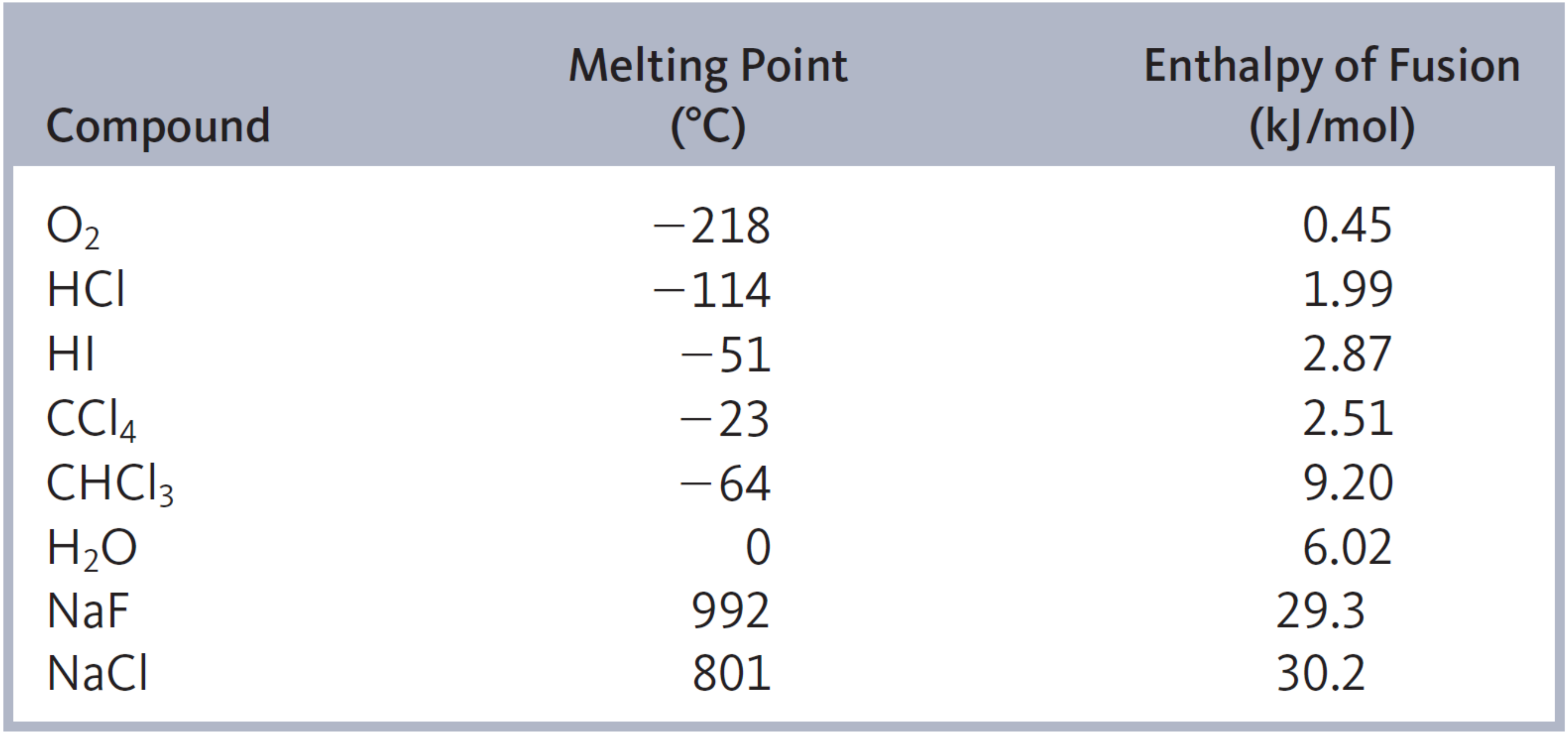


Table 10.9 - Melting Points and Enthalpies of Fusion for Several Representative Solids



Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O_2	−218	0.45
HCl	−114	1.99
HI	−51	2.87
CCl_4	−23	2.51
$CHCl_3$	−64	9.20
H_2O	0	6.02
NaF	992	29.3
$NaCl$	801	30.2

Melting Point

- The temperature at which the solid and liquid have identical vapor pressures

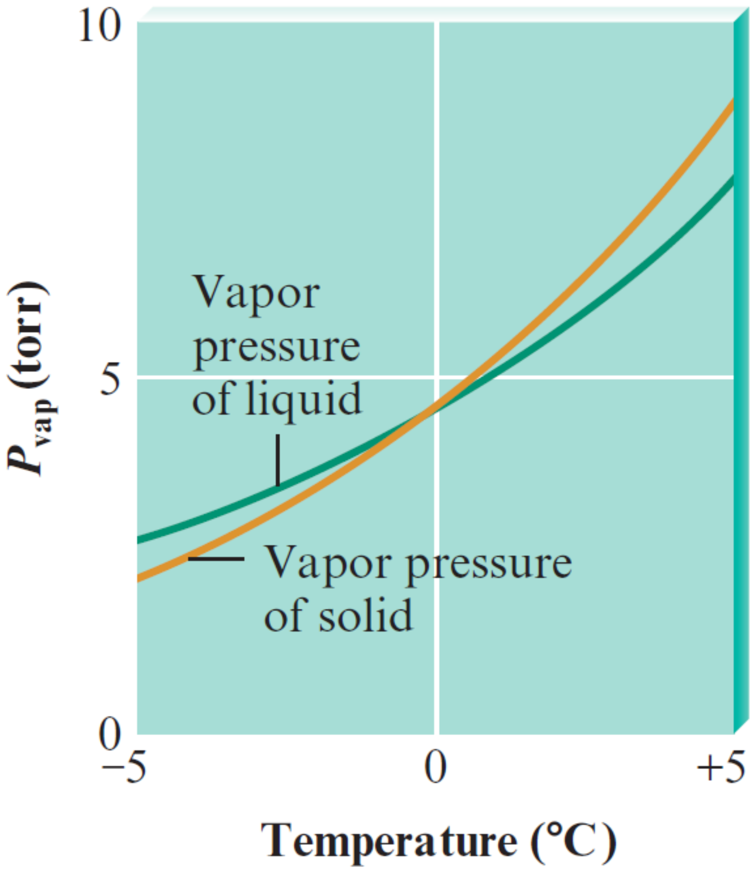
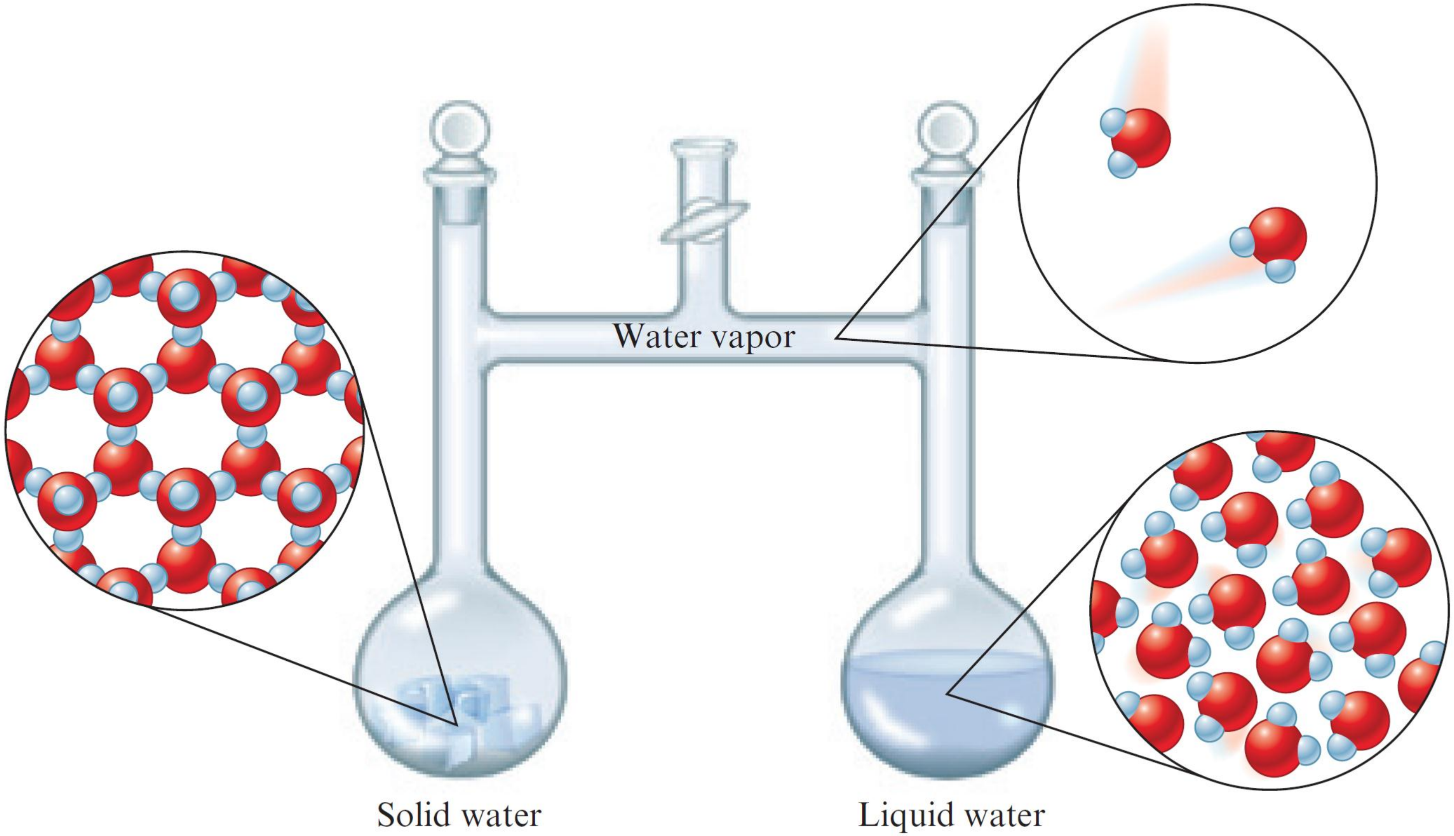


Figure 10.44 - Interaction of Solid and Liquid Water in the Vapor State

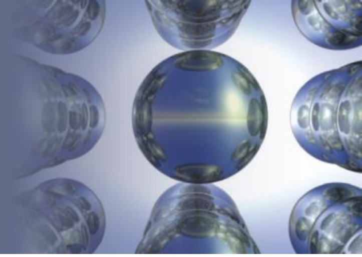


Temperature and Vapor Pressure - Case 1

- Temperature at which the vapor pressure of the solid is greater than that of the liquid
    - The solid releases vapor, attempting to achieve equilibrium
    - The liquid attempts to achieve equilibrium by absorbing vapor
    - Net effect - Conversion from solid to liquid through the vapor phase
        - Temperature would be above the melting point of ice

Temperature and Vapor Pressure - Case 2

- Temperature at which vapor pressure of the solid is less than that of the liquid
  - Liquid will disappear, and the amount of ice will increase
  - Solid will achieve equilibrium with the vapor
    - Temperature should be below the melting point of ice

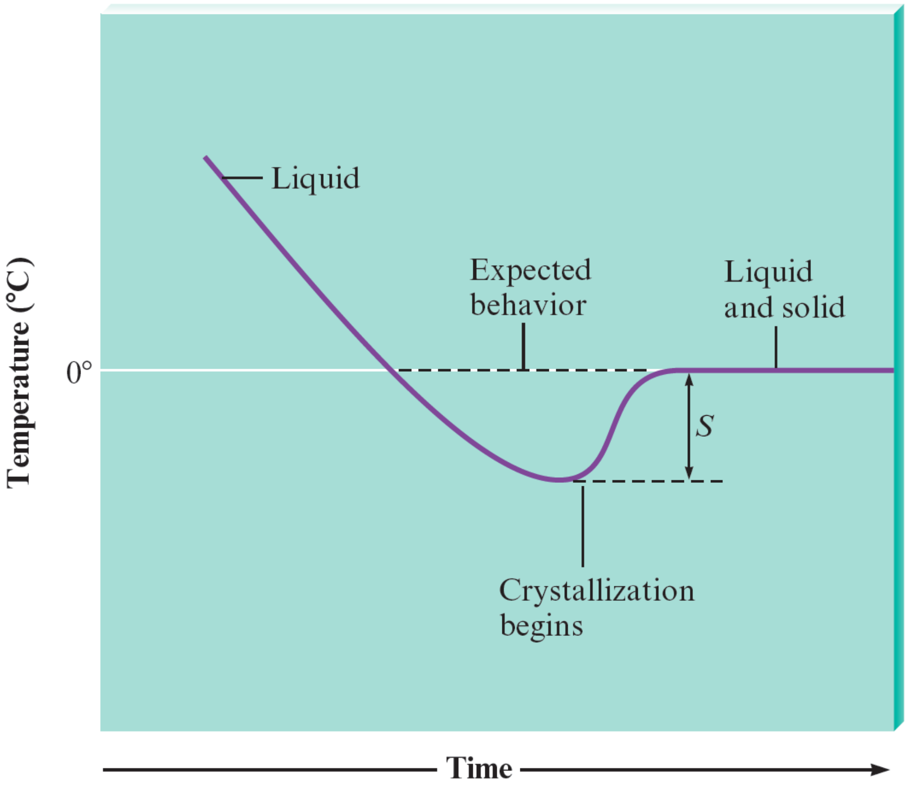


Temperature and Vapor Pressure - Case 3

- Temperature at which the vapor pressures of the solid and liquid are identical
  - Coexist in the apparatus at equilibrium with the vapor
  - **Normal melting point**: Temperature at which the vapor pressures of the solid and liquid states are identical at 1 atmosphere of pressure
    - Represents the freezing point that enables existence of solid and liquid states

Temperature and Vapor Pressure - Case 3 (Continued 1)

- **Normal boiling point**
  - Temperature at which the vapor pressure of the liquid is 1 atmosphere
- Changes of state do not always occur at the boiling or melting point

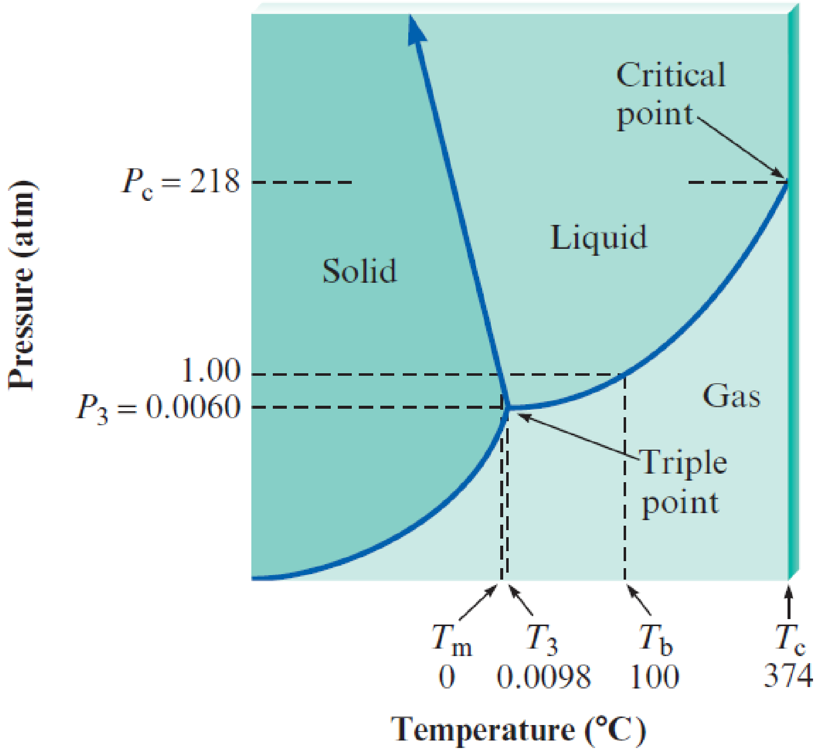


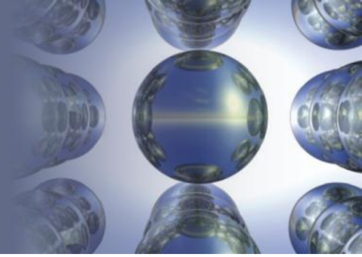
Temperature and Vapor Pressure - Case 3 (Continued 2)

- **Supercooled** water remains in the liquid state below 0° C and 1 atm of pressure
- Water can be **superheated** if it is heated rapidly
    - Vapor pressure in the liquid is greater than atmospheric pressure
    - Bubbles formed burst before reaching the surface, resulting in bumping

Phase Diagram

- Convenient method of representing the phases of a substance as a function of temperature and pressure
- Phase diagram of water
  - T_m - Normal melting point
  - T_3 and P_3 - Triple point
  - T_b - Normal boiling point
  - T_c - Critical temperature
  - P_c - Critical pressure



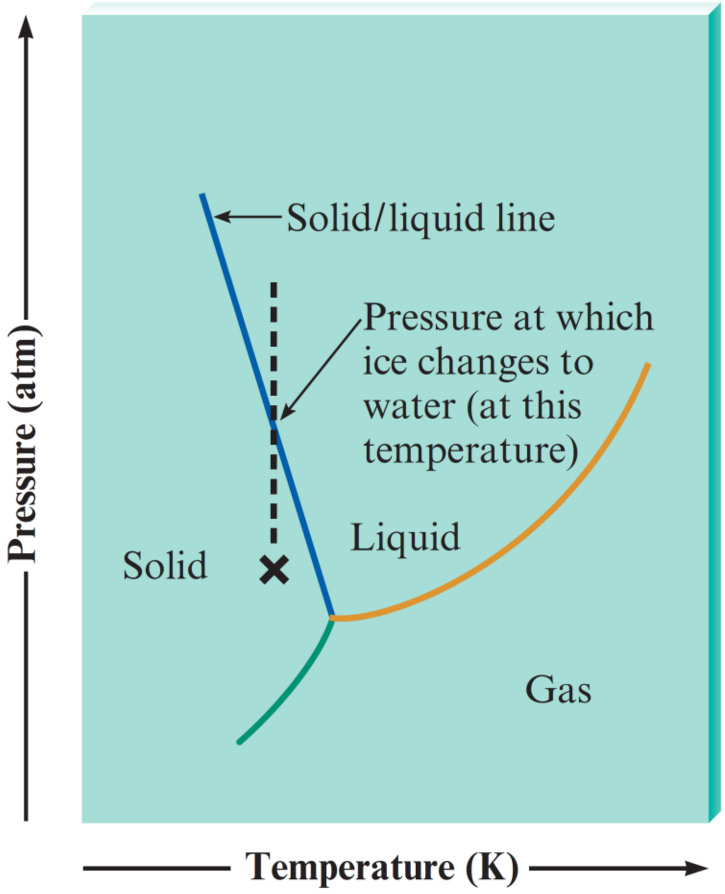


Phase Diagram (Continued)

- **Triple point**: Temperature at which all three phases exist simultaneously
- **Critical point**: Defined by critical pressure and temperature
    - **Critical pressure**: Pressure required to produce liquefaction at the critical temperature
    - **Critical temperature**: The temperature above which vapor cannot be liquefied, irrespective of the pressure applied

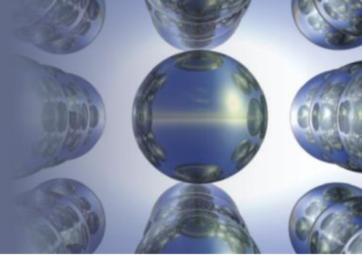
Phase Diagram for Water

- Describes a closed system
- At point *X*, ice is subjected to increased pressure at constant temperature
    - Solid/liquid line is crossed as the pressure is increased



Phase Diagram for Water - Observations

- The solid/liquid boundary line has a negative slope
- At the melting point, liquid and solid are in dynamic equilibrium
  - When pressure is applied, the volume is reduced
  - A given mass of ice has more volume at 0° C than the same mass of water in liquid state
  - Freezing point of water is less than 0° C when external pressure is greater than 1 atm



Phase Diagram for Water - Applications

- Ice skating
    - Narrow blades of skates exert a large amount of pressure
    - Frictional heat caused when skates moves over ice contributes to further melting of ice
    - As the blades pass by, the liquid refreezes
- Low density of ice
    - Causes ice formed on rivers and lakes to float, and this helps prevent water bodies from freezing in the winter

Table 10.10 - Boiling Point of Water at Various Locations

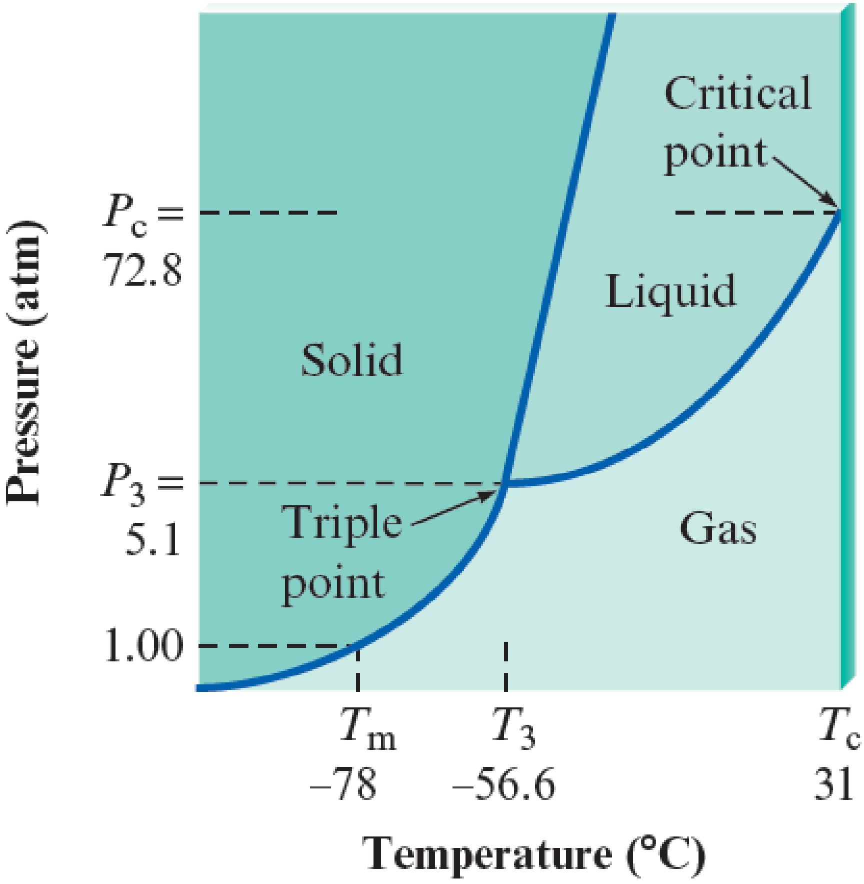
Location	Feet Above Sea Level	P_{atm} (torr)	Boiling Point (°C)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6293	590	93
Boulder, Colo.	5430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	−282	770	100.3

Critical Thinking

- Ice is less dense than liquid water, as evidenced by the fact that ice floats in a glass of water
  - What if ice was more dense than liquid water?
    - How would this affect the phase diagram for water?

Figure 9.49 - Phase Diagram for Carbon Dioxide

- The liquid state does not exist at a pressure of 1 atm
- Solid/liquid line has a positive slope
    - Density of solid carbon dioxide is greater than that of liquid carbon dioxide



Phase Diagram for Carbon Dioxide - Applications

- Carbon dioxide is used in fire extinguishers
    - Liquid released from the extinguisher into the environment at 1 atm immediately changes to a vapor
- Dry ice
    - A convenient refrigerant as it does not undergo the liquid phase under normal atmospheric conditions