Chapter 10

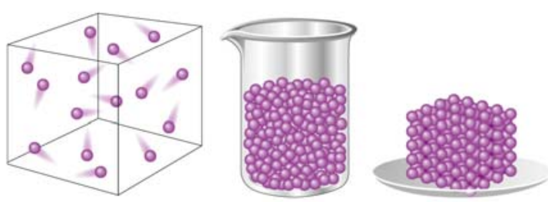
Liquids & Solids

Table 11.1
Kinds of Phase Transitions

Phase Transition	Name	Examples
Solid ⟶ liquid	Melting, fusion	Melting of snow and ice
Solid ⟶ gas	Sublimation	Sublimation of dry ice, freeze-drying of coffee
Liquid ⟶ solid	Freezing	Freezing of water or a liquid metal
Liquid ⟶ gas	Vaporization	Evaporation of water or refrigerant
Gas ⟶ liquid	Condensation, liquefaction	Formation of dew, liquefaction of carbon dioxide
Gas ⟶ solid	Condensation, deposition	Formation of frost and snow

Return to Slide 3

Representation of the states of matter.

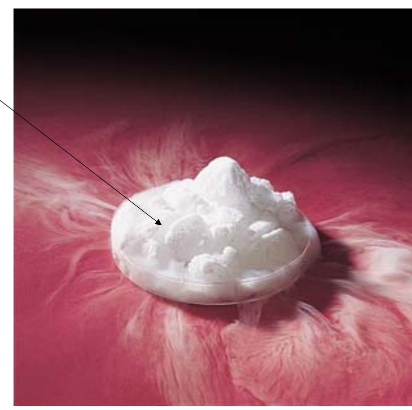


Sublimation

Dry ice (solid CO_2).

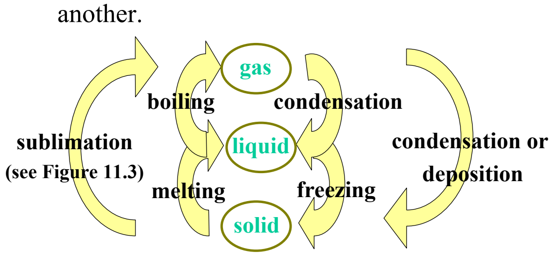
Photo courtesy of

American Color.



Changes of State

- A change of state or phase transition is a change of a substance from one state to another.



Intermolecular Forces

Forces between (rather than within) molecules.

- dipole-dipole attraction: molecules with dipoles orient themselves so that “+” and “–” ends of the dipoles are close to each other.
- hydrogen bonds: dipole-dipole attraction in which hydrogen is bound to a highly electronegative atom. (F, O, N)

Table 11.4
Types of Intermolecular and Chemical Bonding Interactions

Type of Interaction	Approximate Energy (kJ/mol)
Intermolecular	
Van der Waals (dipole–dipole, London)	0.1 to 10
Hydrogen bonding	10 to 40
Chemical bonding	
Ionic	100 to 1000
Covalent	100 to 1000

Hydrogen Bonding

- **Hydrogen bonding** is a force that exists between a hydrogen atom covalently bonded to a very electronegative atom, X, and a lone pair of electrons on a very electronegative atom, Y.
  - To exhibit hydrogen bonding, one of the following three structures must be present.

H—N̈   **H—Ö**   **H—F̈**

  - Only N, O, and F are electronegative enough to leave the hydrogen nucleus exposed.

Dipole-Dipole Forces

- Polar molecules can attract one another through **dipole-dipole forces**.
  - The **dipole-dipole force** is an attractive intermolecular force resulting from the tendency of **polar molecules** to align themselves positive end to negative end.

δ^+ **H—Cl** δ^- δ^+ **H—Cl** δ^-

Figure 11.21 shows the alignment of polar molecules.

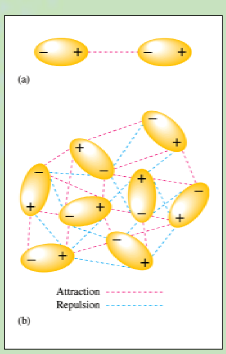
Figure 11.23: Fluoromethane

and methanol.

CH_3F

CH_3OH

Figure 10.2:
(a) The electrostatic interaction of two polar molecules.
(b) The interaction of many dipoles in a condensed state.



Hydrogen Bonding

- A hydrogen atom bonded to an electronegative atom appears to be special.
  - The electrons in the O-H bond are drawn to the O atom, leaving the dense positive charge of the hydrogen nucleus exposed.
  - It's the strong attraction of this exposed nucleus for the lone pair on an adjacent molecule that accounts for the strong attraction.
  - A similar mechanism explains the attractions in HF and NH_3.

Hydrogen Bonding

- Molecules exhibiting hydrogen bonding have **abnormally high boiling points** compared to molecules with similar van der Waals forces.
  - For example, water has the highest boiling point of the Group VI hydrides. (see Figure 11.24A)
  - Similar trends are seen in the Group V and VII hydrides. (see Figure 11.24B)

Figure 10.3: (a) The polar water molecule.
(b) Hydrogen bonding among water molecules.

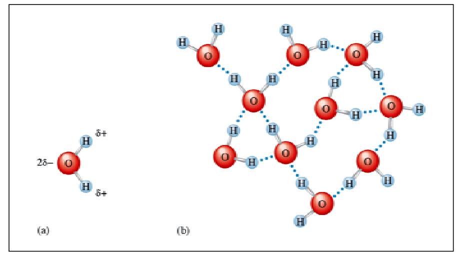
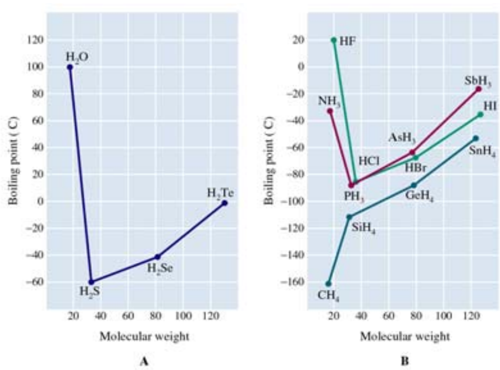
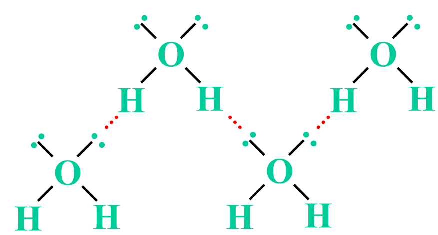


Figure 11.24: Boiling point versus molecular weight for hydrides.



Return to Slide 41

Hydrogen Bonding



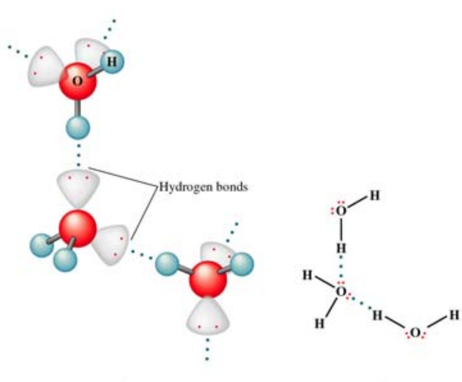


Figure 11.25: Hydrogen bonding in water.

TABLE 10.1
Densities of the Three States of Water

State	Density (g/cm^3)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

Figure 11.26: Hydrogen bonding between two biologically important molecules.
Journal of Chemical Education, Vol. 74, No. 7, 1997, cover;

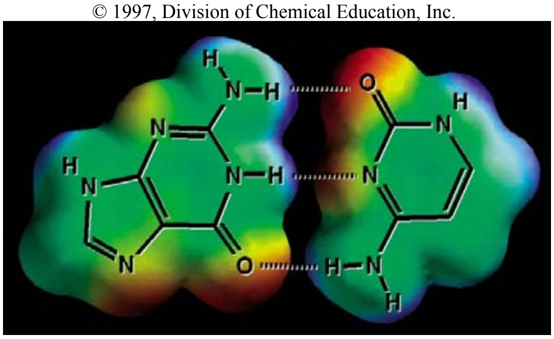


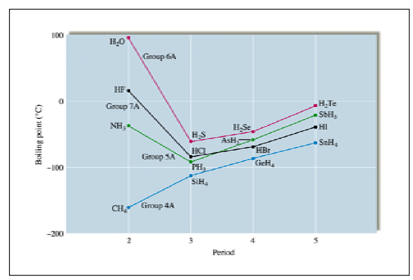
TABLE 10.2 The Freezing Points of the Group 8A Elements

Element	Freezing Point (°C)
Helium*	−269.7
Neon	−248.6
Argon	−189.4
Krypton	−157.3
Xenon	−111.9

London Dispersion Forces

- relatively weak forces that exist among noble gas atoms and nonpolar molecules. (Ar, C_8H_{18})
- caused by instantaneous dipole, in which electron distribution becomes asymmetrical.
- the ease with which electron "cloud" of an atom can be distorted is called polarizability. Atoms with larger electron clouds are more "polarizable" and exhibit stronger LD forces.

Figure 10.4: The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.



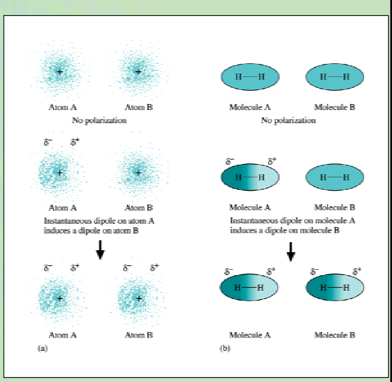


Figure 10.5: (a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B. (b) Nonpolar molecules such as H_2 also can develop instantaneous and induced dipoles.

CONCEPT CHECK 11.3

A common misconception is that the following chemical reaction occurs when boiling water:

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

instead of

$$H_2O(l) \longrightarrow H_2O(g)$$

a. What evidence do you have that the second reaction is correct?

b. How would the enthalpy of the wrong reaction compare with that of the correct reaction?

c. How could you calculate the enthalpy change for the wrong reaction (Chapter 6)?

Properties of Liquids

The particles in the gas phase (whether they are atoms, molecules, or ions) have sufficient kinetic energy to overcome their intermolecular forces and move freely within their container.

Particles in the liquid phase have sufficient kinetic energy to move past one another but lack enough kinetic energy to completely escape from their intermolecular forces.

Properties of Liquids; Surface Tension and Viscosity

- **Surface tension** is the energy required to increase the surface area of a liquid by a unit amount.
  - This explains why falling raindrops are nearly spherical, minimizing surface area.
  - In comparisons of substances, **as intermolecular forces between molecules increase, the apparent surface tension also increases**.

Some Properties of a Liquid

Surface Tension: The resistance to an increase in its surface area (strongest in polar molecules).

Capillary Action: Spontaneous rising of a liquid in a narrow tube.

Viscosity: Resistance to flow (molecules or atoms with large intermolecular forces). Molecules which can hydrogen-bond tend to be more viscous than those which cannot (exception: Hg - it is highly polarizable.)

Figure 11.18: A steel pin floating on the surface of water. Photo courtesy of American Color.

Figure 10.6: A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.

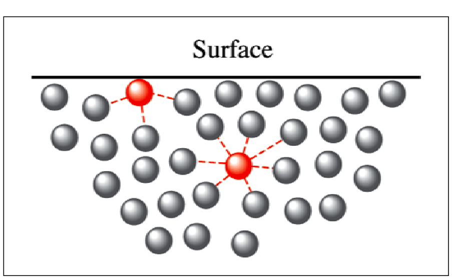


Figure 11.18: The water surface is depressed and stretched by the pin.

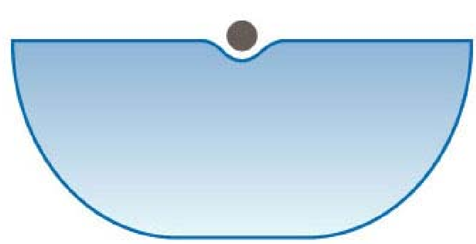
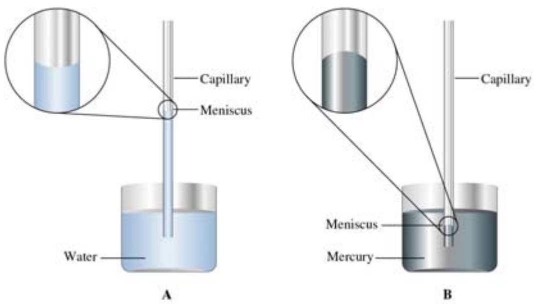


Figure 11.19: Liquid levels in capillaries.



Van der Waals Forces and the Properties of Liquids

- The **normal boiling point** is related to vapor pressure and is lowest for liquids with the weakest intermolecular forces. The same is true of melting point - lower melting points are found for liquids with weak intermolecular forces.

Problem 30, p. 500.

Intermolecular Forces; Explaining Liquid Properties

- **Viscosity** is the resistance to flow exhibited by all liquids and gases.
  - Viscosity can be illustrated by measuring the time required for a steel ball to fall through a column of the liquid. (see Figures 11.19 and 11.20)
  - Even without such measurements, you know that syrup has a greater viscosity than water.
  - In comparisons of substances, **as intermolecular forces increase, viscosity usually increases.**

Bonding in Solids

Bonding in solids may be described as "bands" of molecular orbitals

In metals – conduction "bands" are partially vacant orbitals which allow electrons to flow

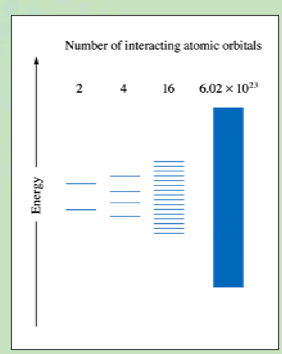
In insulators – the valence orbitals or bands are "full" there is a large energy difference (gap) between the valence band and lowest band of empty orbitals (conduction band)

In semiconductors – there is a small gap between between the valence band and conduction band

Van der Waals Forces and the Properties of Liquids

- **Viscosity** increases with increasing intermolecular forces because increasing these forces increases the resistance to flow.
  - Other factors, such as the possibility of molecules tangling together, affect viscosity.
  - Liquids with long molecules that tangle together are expected to have high viscosities.

Figure 10.19: The molecular orbital energy levels produced when various numbers of atomic orbitals interact.

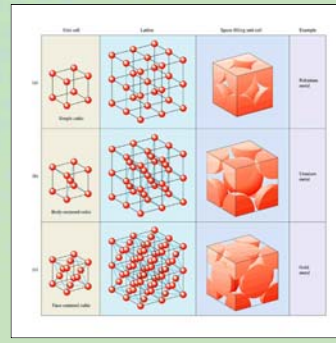


Types of Solids

Crystalline Solids: highly regular arrangement of their components [table salt (NaCl), pyrite (FeS_2)].

Amorphous solids: considerable disorder in their structures (glass).

Figure 10.9: Three cubic unit cells and the corresponding lattices.



Representation of Components in a Crystalline Solid

Lattice: A 3-dimensional system of points designating the centers of components (atoms, ions, or molecules) that make up the substance.

Bragg Equation

Used for analysis of crystal structures.

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

d = distance between atoms

n = an integer

λ = wavelength of the x-rays

Representation of Components in a Crystalline Solid

Unit Cell: The smallest repeating unit of the lattice.

- simple cubic
- body-centered cubic
- face-centered cubic

Types of Crystalline Solids

Ionic Solid: contains ions at the points of the lattice that describe the structure of the solid (NaCl).

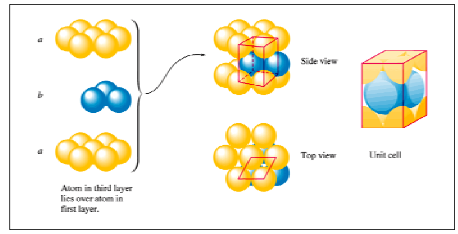
Molecular Solid: discrete covalently bonded molecules at each of its lattice points (sucrose, ice).

Atomic Solid: atoms occupy lattice points (carbon, metal) of the solid

TABLE 10.3 Classification of Solids

	Atomic Solids				
	Metallic	*Network*	*Group 8A*	*Molecular Solids*	*Ionic Solids*
Components That Occupy the Lattice Points:	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding:	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

Figure 10.14: When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (aba), the unit cell is the hexagonal prism illustrated here in red.



Packing in Metals

Model: Packing uniform, hard spheres to best use available space. This is called closest packing. Each atom has 12 nearest neighbors.

- hexagonal closest packed ("aba")
- cubic closest packed ("abc")

Figure 10.15: When spheres are packed in the abc arrangement, the unit cell is face-centered cubic.

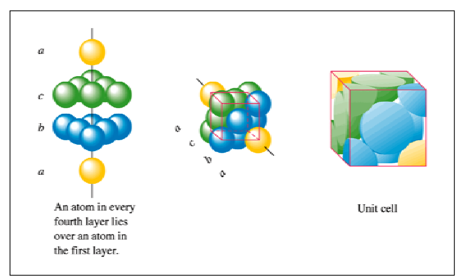


Figure 10.13: The closest packing arrangement of uniform spheres, (a) aba packing (b) abc packing.

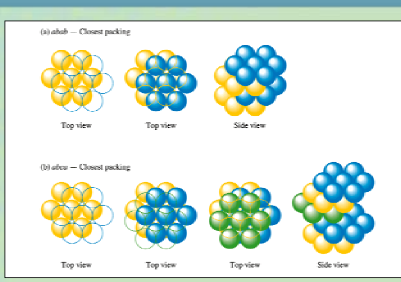


Figure 10.16: The indicated sphere has 12 nearest neighbors.

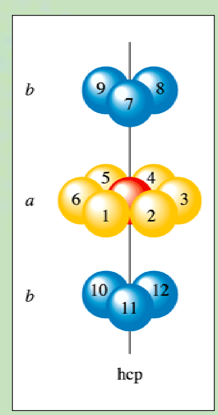
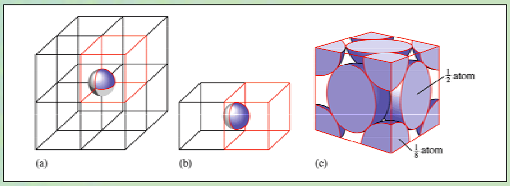


Figure 10.17: The net number of spheres in a face-centered cubic unit cell.



Problem 59, p. 502

Basic Equation for Unit Cell Calculations

Density (g/cm^3) =

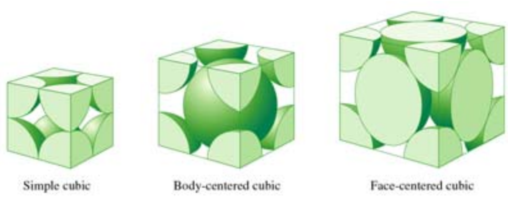
$$\frac{\text{(Molar mass of substance, g/mol)(\# atoms/unit cell)}}{\text{(Unit cell volume, cm}^3\text{)(6.02 x }10^{23}\text{ atoms/mol)}}$$

Unit cell volume = (edge, cm)^3

By definition: 1 mL = 1 cm^3

1.00 pm^3 (1.00 x 10^{-10} cm/pm)^3 = 1.00 x 10^{-30} cm^3

Figure 11.33: Space-filling representation of cubic unit cells.



Bonding Models for Metals

Electron Sea Model: A regular array of metals in a “sea” of electrons.

Band (Molecular Orbital) Model: Electrons assumed to travel around metal crystal in MOs formed from valence atomic orbitals of metal atoms.

Figure 11.40: Crystal structures of metals.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA
Li bcc	Be hcp													
Na bcc	Mg hcp											Al ccp		
K bcc	Ca ccp	Sc hcp	Ti hcp	V bcc	Cr bcc	Mn bcc	Fe bcc	Co hcp	Ni ccp	Cu ccp	Zn hcp	Ga or		
Rb bcc	Sr ccp	Y hcp	Zr hcp	Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh ccp	Pd ccp	Ag ccp	Cd hcp	In bct	Sn bct	
Cs bcc	Ba bcc	La hcp	Hf hcp	Ta bcc	W bcc	Re hcp	Os hcp	Ir ccp	Pt ccp	Au ccp	Hg rh	Tl hcp	Pb ccp	Bi rh

Figure 10.18: The electron sea model for metals postulates a regular array of cations in a "sea" of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.

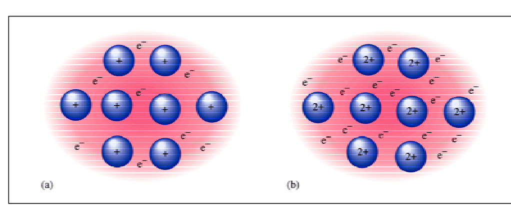


Figure 10.20: (left) A representation of the energy levels (bands) in a magnesium crystal. (right) Crystals of magnesium grown from a vapor.

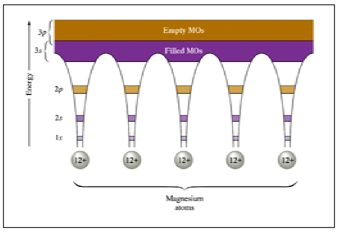
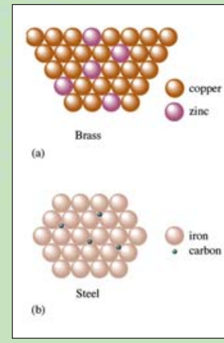


Figure 10.21: Two types of alloys.



Metal Alloys

Substances that have a mixture of elements and metallic properties.

1. Substitutional Alloy: some metal atoms replaced by others of similar size.

brass = Cu/Zn

Network Solids

Composed of strong directional covalent bonds that are best viewed as a "giant molecule".

- brittle
- do not conduct heat or electricity
- carbon, silicon-based

graphite, diamond, ceramics, glass

Metal Alloys

(continued)

2. Interstitial Alloy: Interstices (holes) in closest packed metal structure are occupied by small atoms.

   steel = iron + carbon

3. Both types: Alloy steels contain a mix of substitutional (carbon) and interstitial (Cr, Mo) alloys.

Figure 10.22: The structures of diamond and graphite. In each case only a small part of the entire structure is shown.