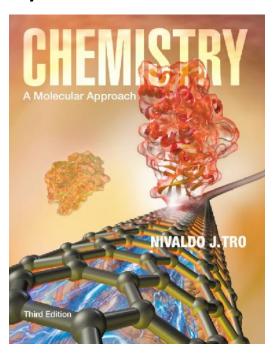
#### Course Introduction

- Instructor Dr. Cheng-Yu Lai SCS300
- CHEM 102- 3 Credits Lecture and/or 1 credit Lab.
- Textbook
- Evaluation and Assessment

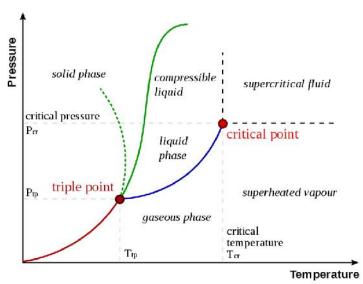


Attendance and performance + Quizzes /Homework (30%); 3 Exams (50%) + 1ACS Test (20%)= 100%

Any Question?

# Chapter 11 Liquids, Solids and Intermolecular Forces

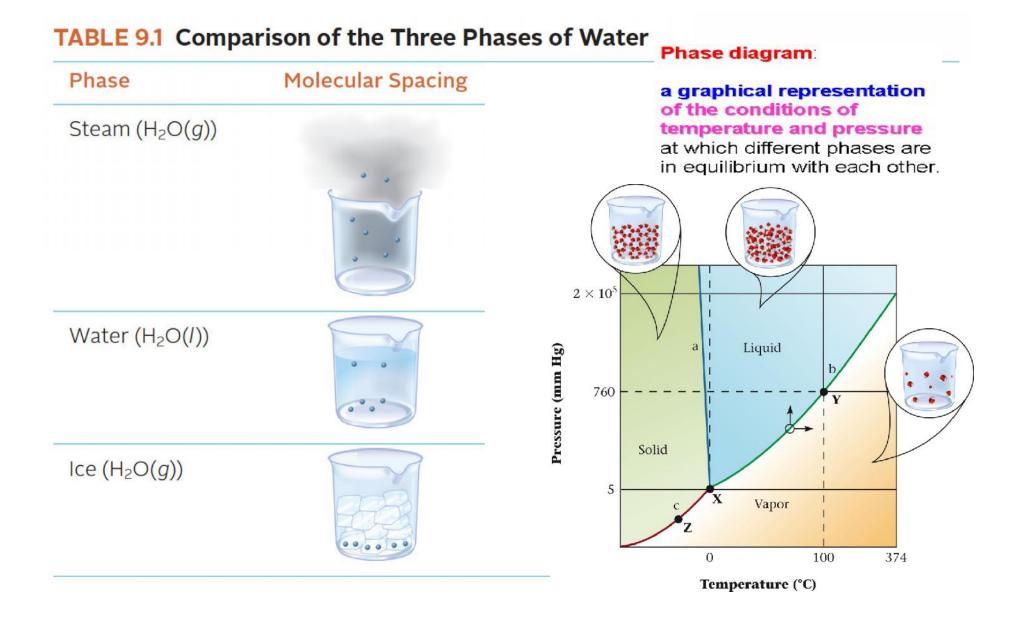
- Phase Diagrams
- Intermolecular Forces
- Types of Substances
  - Molecular, Covalent,
     ionic and metallic Solids
- Crystal Structures
- Vapor Pressure and Phase Equilibrium



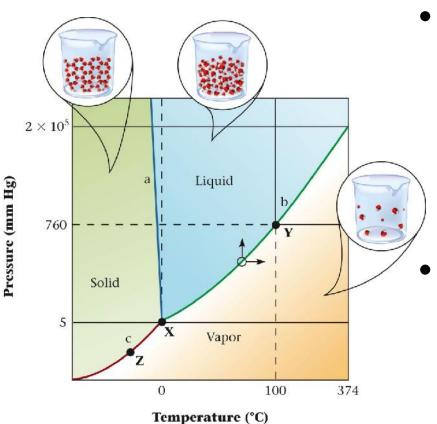


Modified by Dr. Cheng-Yu Lai

## 3 Phases of water-Phase Transition

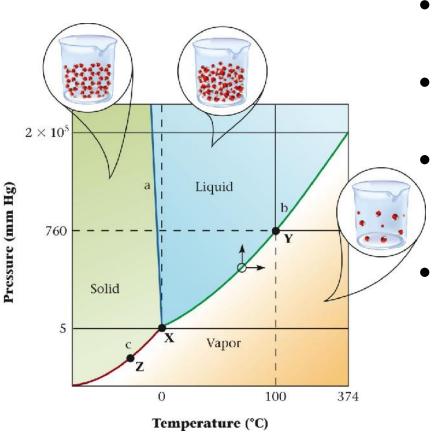


# What is Phase Diagram?



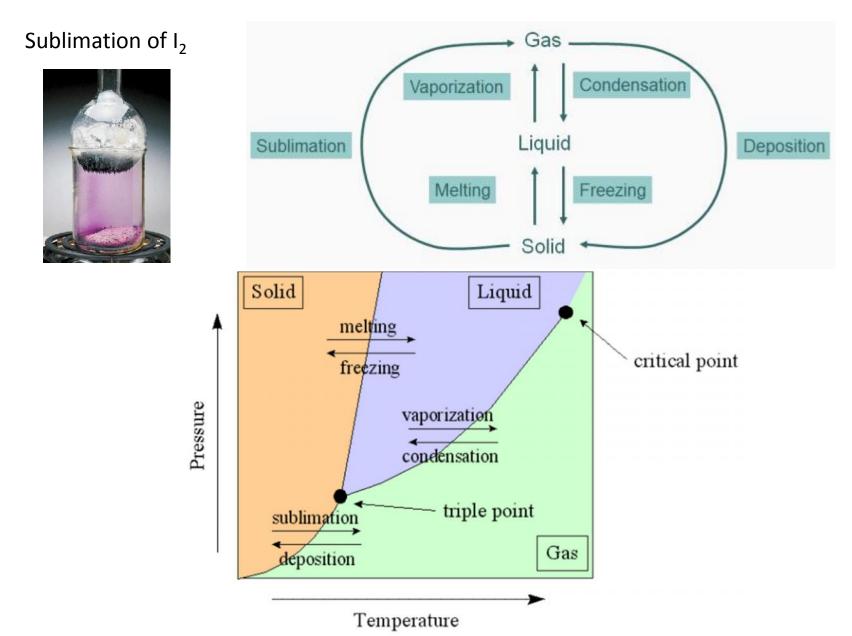
- Phase diagrams are graphical representations of the pressure and temperature dependence of a pure substance
  - Pressure on the y-axis
  - Temperature on the x-axis
  - Three places to consider
    - In a region, one phase exists
    - On a line, two phases exist in equilibrium
    - At a point, three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

## Phase Diagram of Water

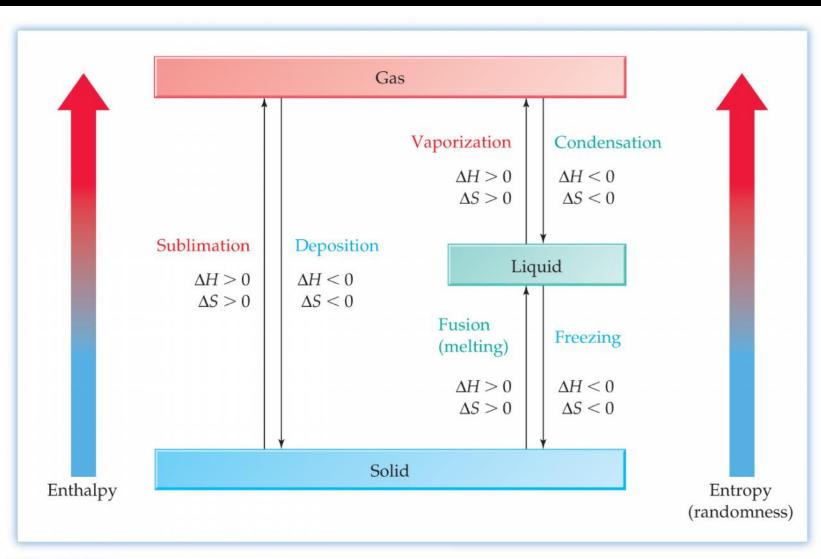


- Curve b (green) is the vapor pressuretemperature curve of liquid water
- Curve c (red) is the vapor pressure curve of ice
  - Line a (blue) gives the temperaturepressure dependence for ice in equilibrium with water
  - Point X is the *triple point* 
    - All three phases are in equilibrium
    - There is only one triple point for a pure substance
    - For water, the triple point is at 0.01
       °C and 4.56 mmHg

## **Definition of Phase Conversion**



# **Phase Changes**

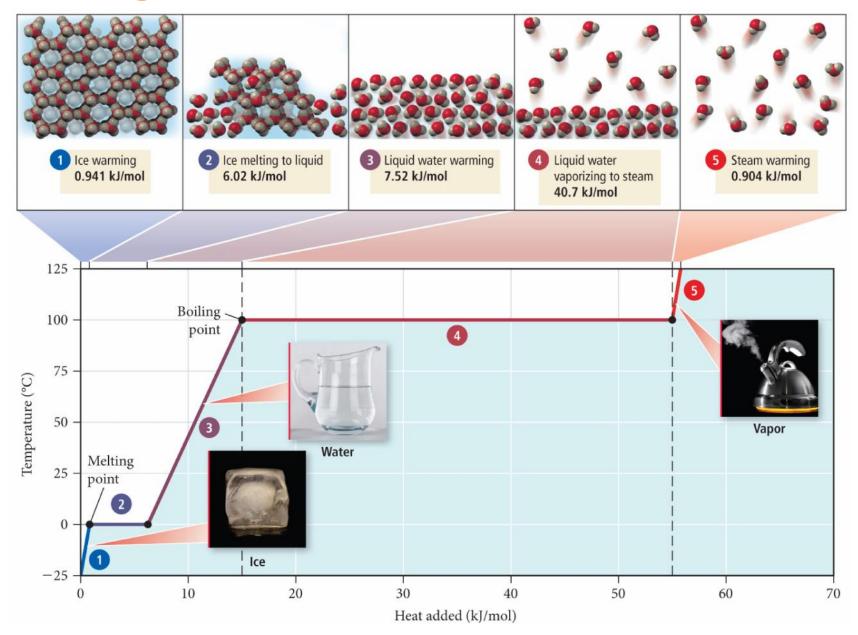


# **Phase Changes**

**Heat (Enthalpy) of Fusion (DH**<sub>fusion</sub>): The amount of energy required to overcome enough intermolecular forces to convert a solid to a liquid

Heat (Enthalpy) of Vaporization (D $H_{\text{vap}}$ ): The amount of energy required to overcome enough intermolecular forces to convert a liquid to a gas

## **Heating Curve of Water**



- Heating 1.00 mole of ice at -25.0 ° C up to the melting point, 0.0 ° C
- $q = \text{mass} \times C_s \times \Delta T$ 
  - Mass of 1.00 mole of ice = 18.0 g
  - $-C_s = 2.09 \text{ J/mol} \cdot ^{\circ} \text{ C}$

$$q = (18.0 \text{ g}) \times (2.09 \frac{\text{J}}{\text{g.°C}}) \times (0.0 \text{°C} - (-25.0 \text{°C}))$$
  
 $q = 941 \text{ J} = 0.941 \text{ kJ}$ 

- Melting 1.00 mole of ice at the melting point, 0.0 ° C
- $q = n \cdot \Delta H_{\text{fus}}$ 
  - -n = 1.00 mole of ice
  - $-\Delta H_{fus} = 6.02 \text{ kJ/mol}$

$$q = (1.00 \text{ mol}) \times (6.02 \frac{\text{kJ}}{\text{mol}})$$
  
 $q = 6.02 \text{ kJ}$ 

- Heating 1.00 mole of water at 0.0 ° C up to the boiling point, 100.0 ° C
- $q = \text{mass} \times C_s \times \Delta T$ 
  - Mass of 1.00 mole of water = 18.0 g
  - $-C_s = 2.09 \text{ J/mol} \cdot ^{\circ} \text{ C}$

$$q = (18.0 \text{ g}) \times (4.18 \frac{J}{g \cdot C}) \times (100.0 \text{ °C} - (0.0 \text{ °C}))$$
  
 $q = 7.52 \times 10^3 \text{ J} = 7.52 \text{ kJ}$ 

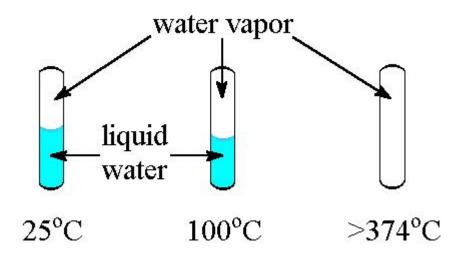
- Boiling 1.00 mole of water at the boiling point, 100.0 ° C
- $q = n \cdot \Delta H_{\text{vap}}$ 
  - -n = 1.00 mole of ice
  - $-\Delta H_{fus} = 40.7 \text{ kJ/mol}$

$$q = (1.00 \text{ mol}) \times (40.7 \frac{\text{kJ}}{\text{mol}})$$
  
 $q = 40.7 \text{ kJ}$ 

- Heating 1.00 mole of steam at 100.0 ° C up to 125.0 ° C
- $q = \text{mass} \times C_s \times \Delta T$ 
  - Mass of 1.00 mole of water = 18.0 g
  - $-C_s = 2.01 \text{ J/mol} \cdot ^{\circ} \text{ C}$

$$q = (18.0 \text{ g}) \times (2.01 \frac{\text{J}}{\text{g} \cdot \text{°C}}) \times (125.0 \text{°C} - (100.0 \text{°C}))$$
  
 $q = 904 \text{ J} = 0.904 \text{ kJ}$ 

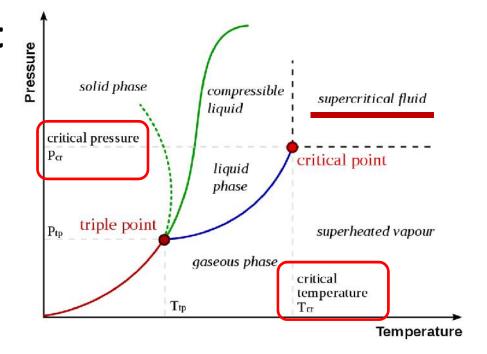
#### Critical Temp and Pressure



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

Tubes containing water at several temperatures.

Note that at or above 374°C (the critical temperature for water), only water vapor exists in the tube.



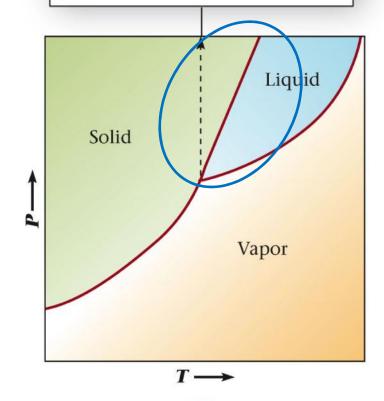
#### The slope of the solid-liquid line depicts the behavior of the freezing

**point** as pressure is increased or decreased

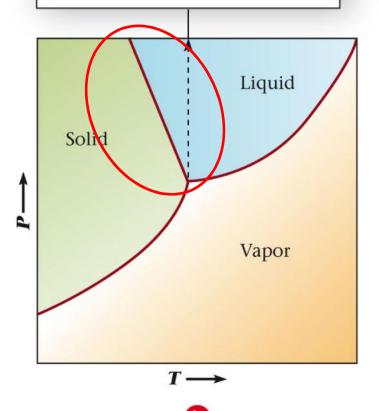
Positive slope: solid is denser than liquid

Negative slope: liquid is denser than solid – water due to *H bonding* 

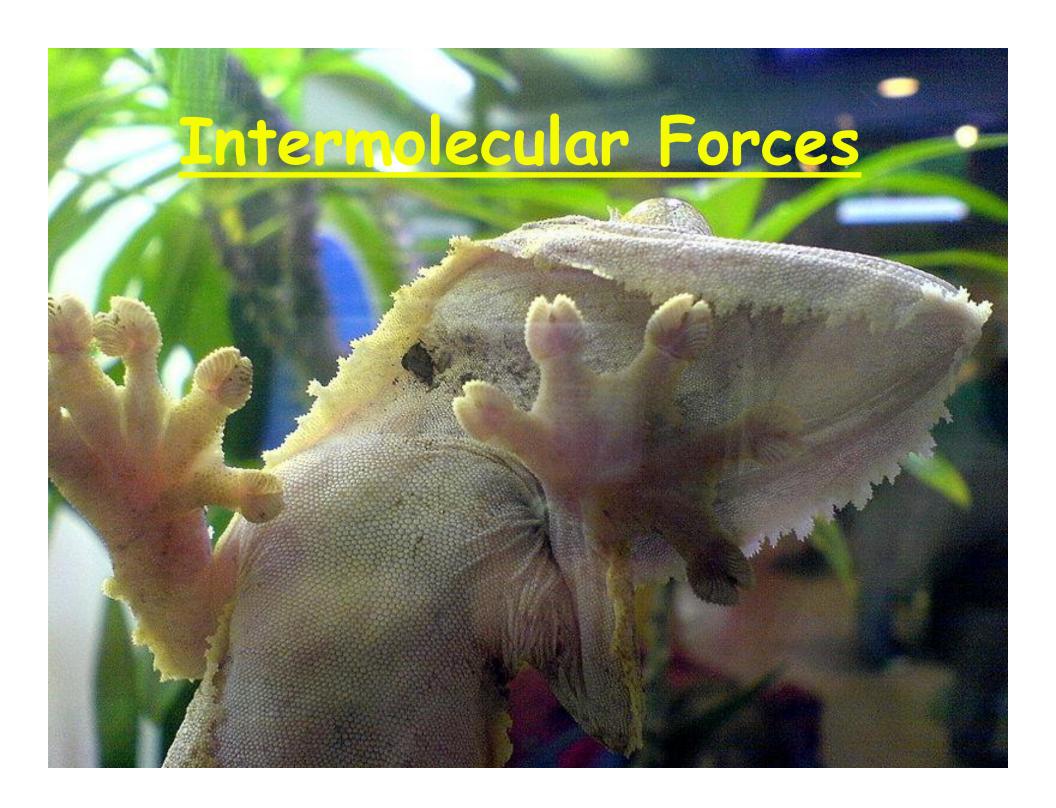
When the solid is the more dense phase, an increase in pressure converts liquid to solid; the melting point increases.



If the liquid is the more dense phase, an increase in pressure converts solid to liquid and the melting point decreases.







#### Intermolecular Forces – Among Molecules

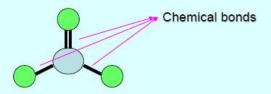
One could explain the observed **phase-change behavior of different materials.** For example, water (18 g/mol) is a liquid at ambient conditions but methane (16 g/mol) is a gas. The explanation requires an understanding of the intermolecular forces that are involved

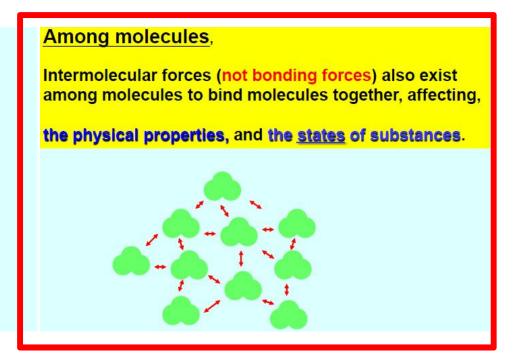
#### Inside a molecule,

bonding forces exist inside of a molecule to bind atoms together, affecting,

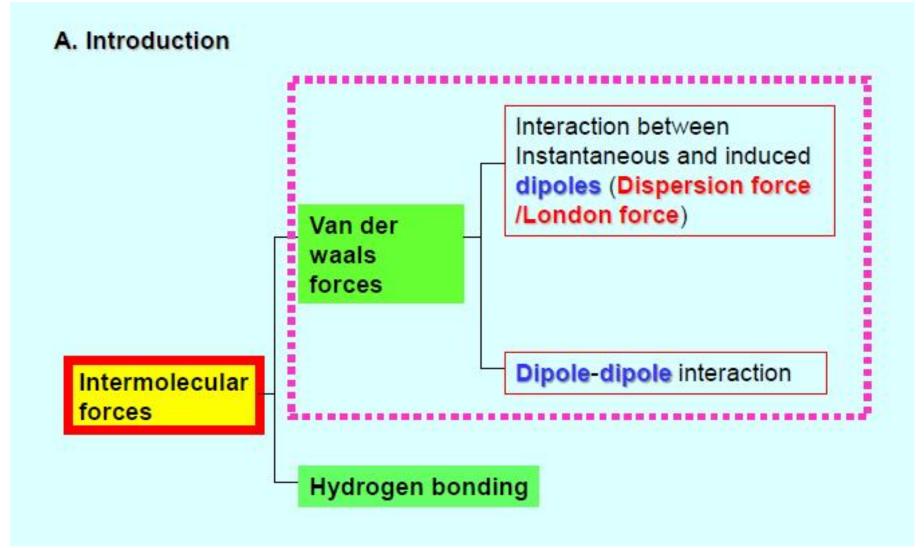
the chemical properties, and

the <u>stability</u> of substances.





## 2 Categories/3 Types Intermolecular Forces



London Force, Dipole-Dipole Interaction and Hydrogen Bond

#### 1. London Dispersion Forces



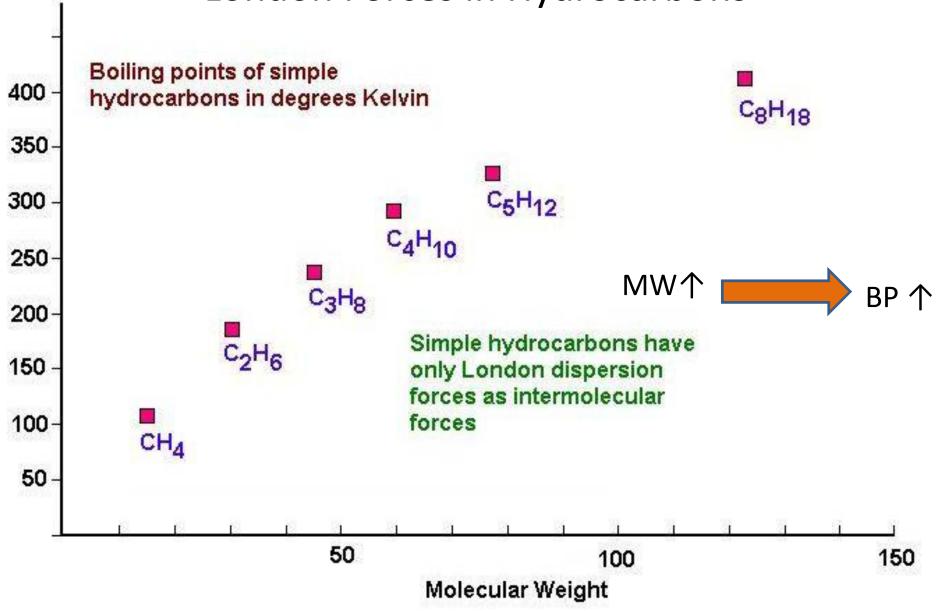
Fritz London 1900-1954

- 1. All substances have dispersion forces.
  Also called <u>London or Van Der Waals forces</u>
  Stem from induced dipoles in molecules
- 2. Motion of <u>electrons</u> in the molecule causes transient dipoles to form As molar mass increases, dispersion forces become stronger,

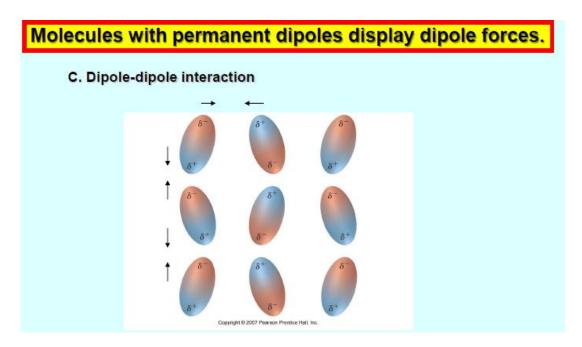
London forces increase with the size of the molecules.

Synonyms: "London forces", "dispersion forces", and "dispersion-interaction forces"

#### London Forces in Hydrocarbons



#### 2. Dipole-Dipole Interaction



- 1. Molecules with permanent dipoles display dipole forces Dispersion forces are also present but are much weaker
- 2. Adjacent molecules line up so that the negative pole of one molecule is as close as possible to the positive pole of another molecule
- ⇒ A molecule has dipole–dipole forces if it is polar.

#### **Example 11.1 Dipole-Dipole Forces**

Which of these molecules have dipole-dipole forces?

 $a. CO_2$ 

- **b.**  $CH_2CI_2$
- $\mathbf{c.}$  CH<sub>4</sub>

#### **Solution**

A molecule has dipole—dipole forces if it is polar. To determine if a molecule is polar, (1) *determine if the molecule contains polar bonds* and (2) *determine if the polar bonds add together to form a net dipole moment* (Section 9.6).

Trends in Electronegativity

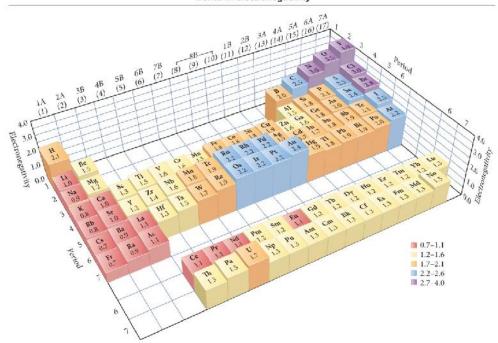
- (a)  $CO_2$ 
  - (1) Since the electronegativity of carbon is 2.5 and that of oxygen is 3.5 (Figure 9.8), CO<sub>2</sub> has polar bonds.
  - (2) The geometry of CO<sub>2</sub> is linear.

    Consequently, the dipoles of the polar bonds cancel, so the molecule is *not polar* and does not have dipole–dipole forces.

$$0 = C = 0$$



No dipole forces present

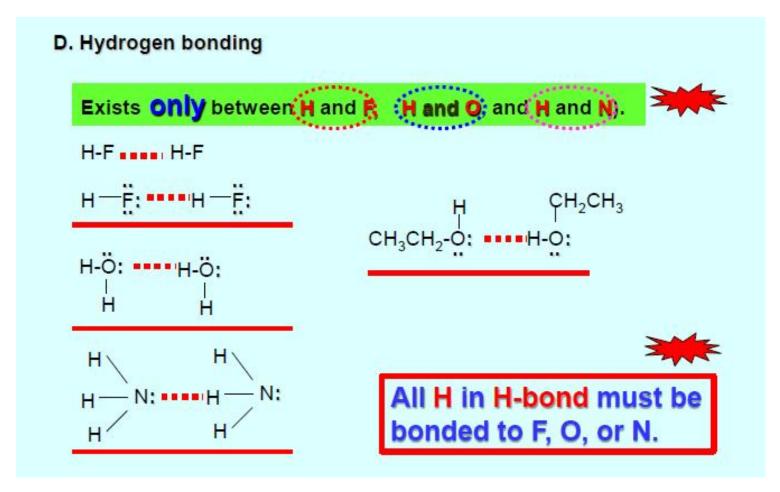


**FIGURE 9.8 Electronegativities of the Elements** Electronegativity generally increases as we move across a row in the periodic table and decreases as we move down a column.

## 3. Hydrogen Bonding

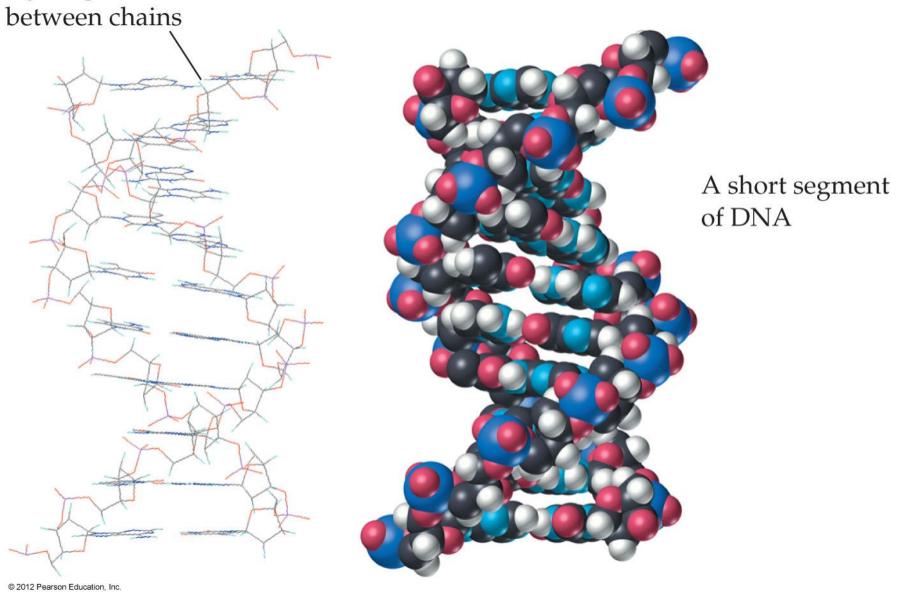
Unusually strong type of dipole force H attached to a(n) N,

O, or F



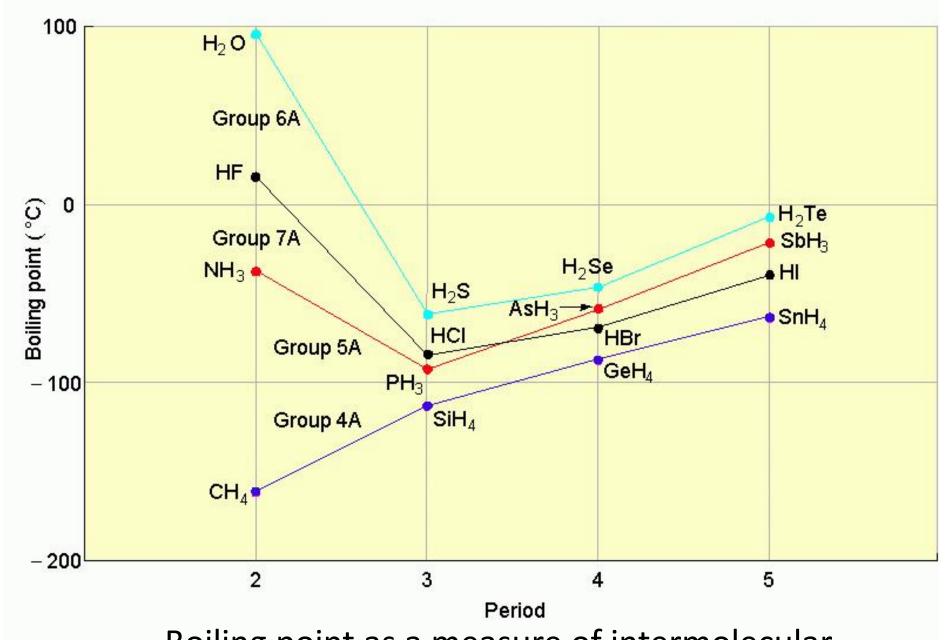
HF, H<sub>2</sub>O and NH<sub>3</sub>: unusually high boiling points as a result of hydrogen bonding

Hydrogen bond



Chapter 10/25

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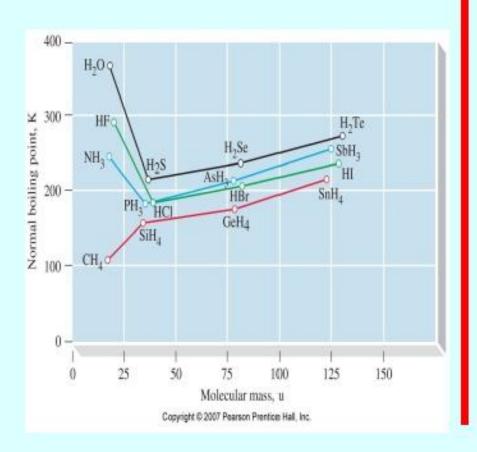


Boiling point as a measure of intermolecular attractive forces

#### Effect of H-bond



#### C. Effect of hydrogen bonding



H-bond leads to

Increasing boiling point

Increasing viscosity

Decreasing vapor pressure

## Intermolecular Forces

TABLE 10.5 A Comparison of Intermolecular Forces		
Force	Strength	Characteristics
Ion-dipole	Moderate (10–50 kJ/mol)	Occurs between ions and polar solvents
Dipole-dipole	Weak (3–4 kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1–10 kJ/mol)	Occurs between all molecules; strength depends on size, polarizability
Hydrogen bond	Moderate (10–40 kJ/mol)	Occurs between molecules with O—H, N—H, and F—H bonds

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## **Kinds of Solids**

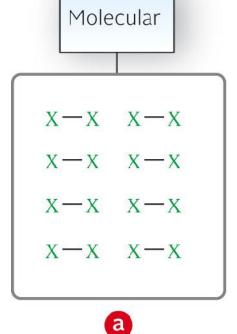
**Amorphous Solids**: Particles are randomly arranged and have no ordered long-range structure. Example - rubber

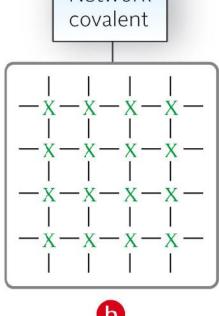
Crystalline Solids: Particles have an ordered arrangement extending over a long range.

- Ionic solids
- Molecular solids
- Covalent network solids
- Metallic solids

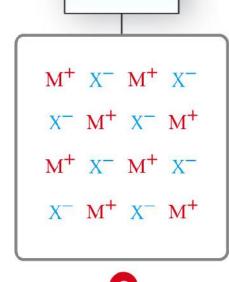
#### 4 Types of Solid Interaction



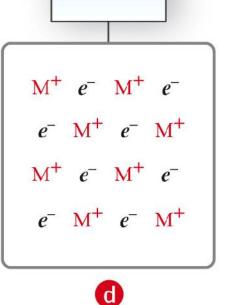




Network



Ionic



Metallic

Examples: Ice (H<sub>2</sub>O); dry ice (CO<sub>2</sub>); **b** SiO2

Examples: NaCl, KCl, MgO.

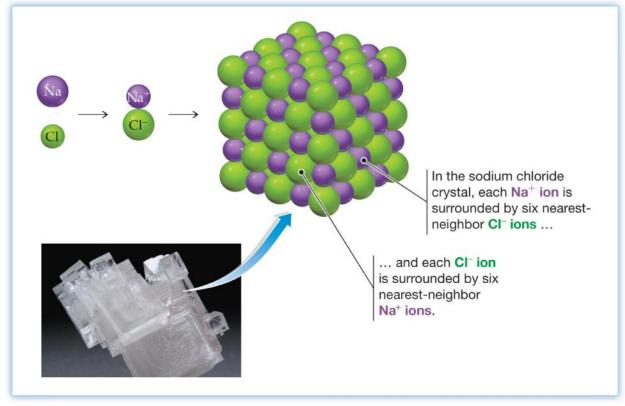
Diamond (C), graphite (C), quartz (SiO<sub>2</sub>),

Silver (Ag), iron (Fe), copper (Cu),

Diamond (C), graphite (C), quartz (SiO<sub>2</sub>), silicon (Si), germanium (Ge), silicon carbide (SiC), and boron nitride (BN).

#### Kinds of Solids

1. Ionic Solids: Particles are ions ordered in a regular three-dimensional arrangement and held together by ionic bonds. Example - sodium chloride.

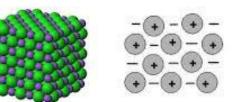


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# Ionic Solids-Oppositely-charged ions held together by strong electrical forces

Characteristics

- Ionic and Metallic Bonding
- 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

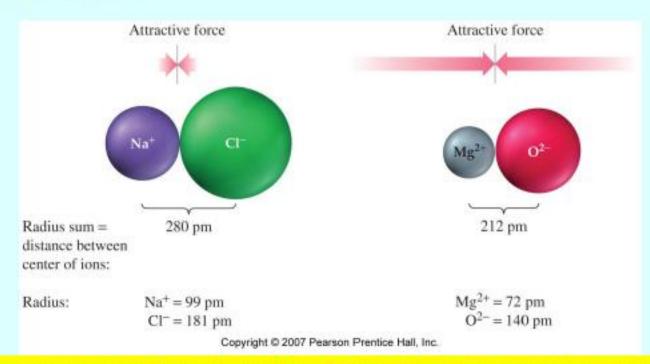
$$E = \frac{k \times Q_1 \times Q_2}{d}$$
$$d = r_{cation} + r_{anion}$$

Strength of ionic bond depends on

- 1. Charges of the ions (higher charges produce stronger bonds); Q
- 2. Sizes of the ions (smaller internuclear distances result in stronger bonds); d

## Strength of ionic bond

#### D. Ionic solids



The more charges and smaller size of ions, the stronger the attractive force.

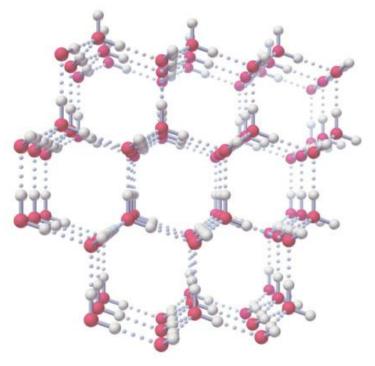
NaCl melting point: 801 °C

MgO melting point: 2852 °C

## **Kinds of Solids**

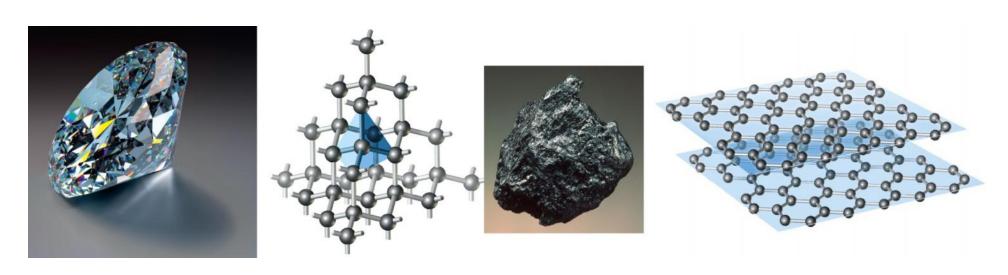
# 2. Molecular Solids: Particles are molecules held together by intermolecular forces. Example - ice

(a) Ice consists of individual H<sub>2</sub>O molecules held together in a regular manner by hydrogen bonds.



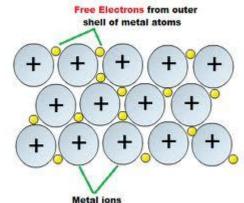
#### 3. Network Covalent Solids

- 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



# 4. Metallic Solids - Structural unit are +1, +2 and +3 metals with associated electrons

- 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



# Example

### **EXAMPLE 9.7 CONCEPTUAL**

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

A B

(a) CO<sub>2</sub> (e) ionic, high-melting

(b) CuSO<sub>4</sub> (f) liquid metal, good conductor

(c) SiO<sub>2</sub> (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

- 1. Characterize each species with respect to type, forces within and between particles, and if necessary, physical properties.
- 2. Find the appropriate matches.

SO		Ш	T	10	N
20	-	U	S 100	10	EN

(a)	$CO_2$	molecul	le, nonpolar
, ,	- 4		· 1

Only match is (j) even if you did not know that CO<sub>2</sub> is a gas at 25°C.

(b) CuSO<sub>4</sub> ionic, water soluble

Only match is (e) even if you did not know that CuSO<sub>4</sub> has a high melting point.

(c) SiO<sub>2</sub> network covalent

Only match is (i).

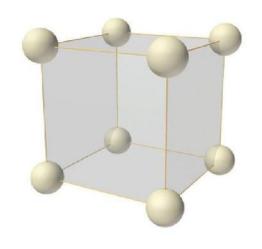
(d) Hg metal, liquid at room temperature

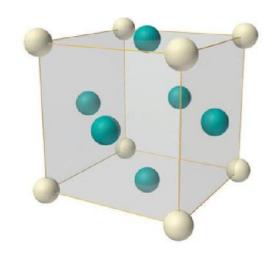
Only match is (f).

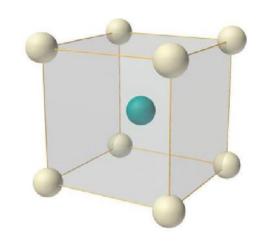
### Crystal Building Blocks- atoms/ ions arrangements

- 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

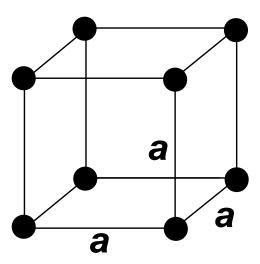
# Crystal Structures – <u>Cubic Unit Cells</u>



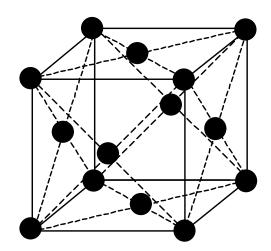




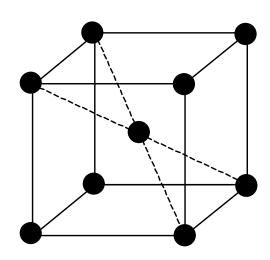
Simple



Face-Centered

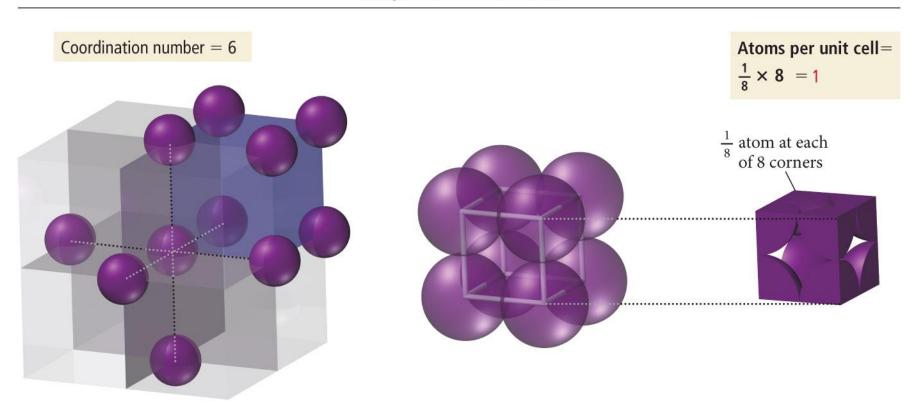


**Body-Centered** 



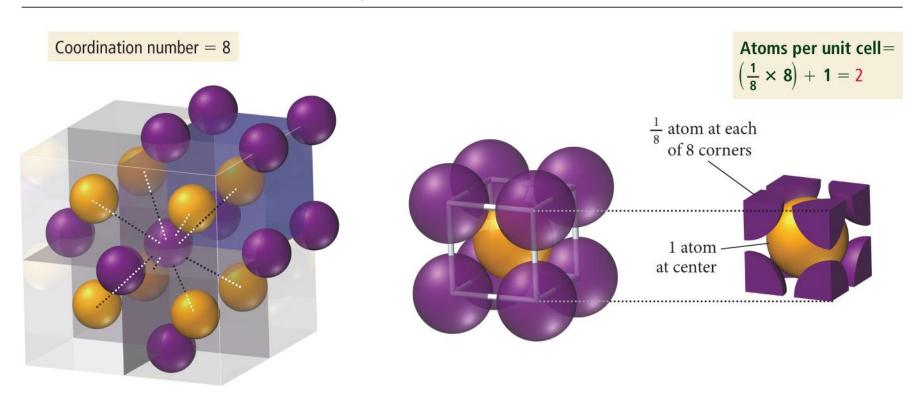
# Simple Cubic

### **Simple Cubic Unit Cell**



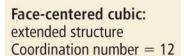
# **Body-Centered Cubic**

### **Body-Centered Cubic Unit Cell**

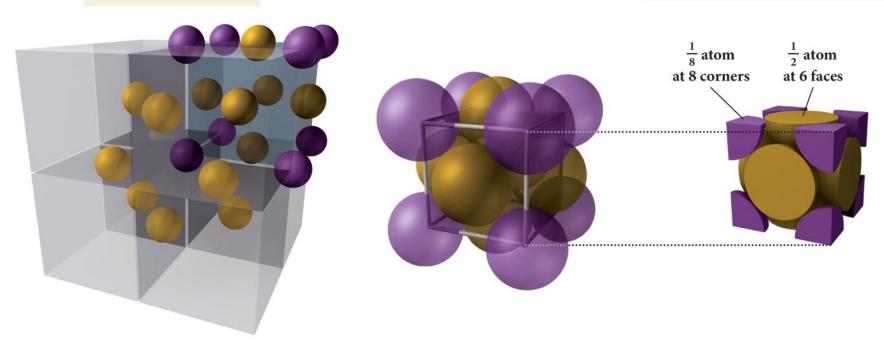


### Face-Centered Cubic

### **Face-Centered Cubic Unit Cell**



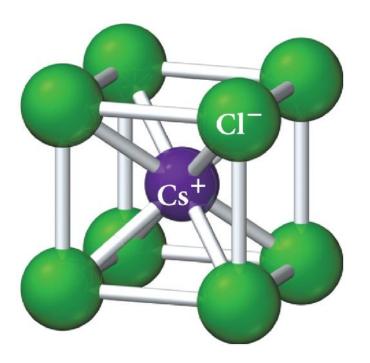
Face-centered cubic: unit cell Atoms/unit =  $\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 4$ 



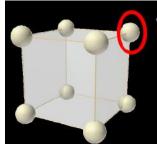
### **Cesium Chloride Structures**

- Coordination number = 8
- of each Cl (184 pm) inside the unit cell
- Whole Cs<sup>+</sup> (167 pm) inside the unit cell
  - Cubic hole = hole in simple cubic arrangement of Cl ions
- Cs:Cl = 1: (8 × ); therefore the formula is CsCl.

Cesium chloride (CsCl)

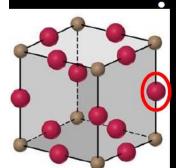


### Atom Numbers Per Unit- Empirical Formula



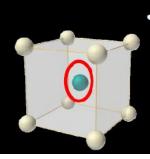
Types of spheres:

a. COrner sphere – shared by 8 adjacent unit cells, thus each counts as 1/8 atom.



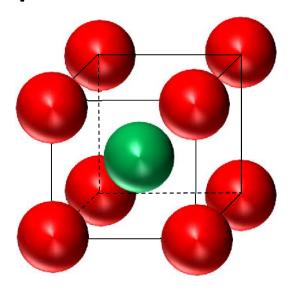
Types of spheres:

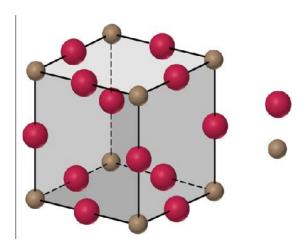
d. edge sphere – shared by 4 unit cells; each counts as 1/4 atom.



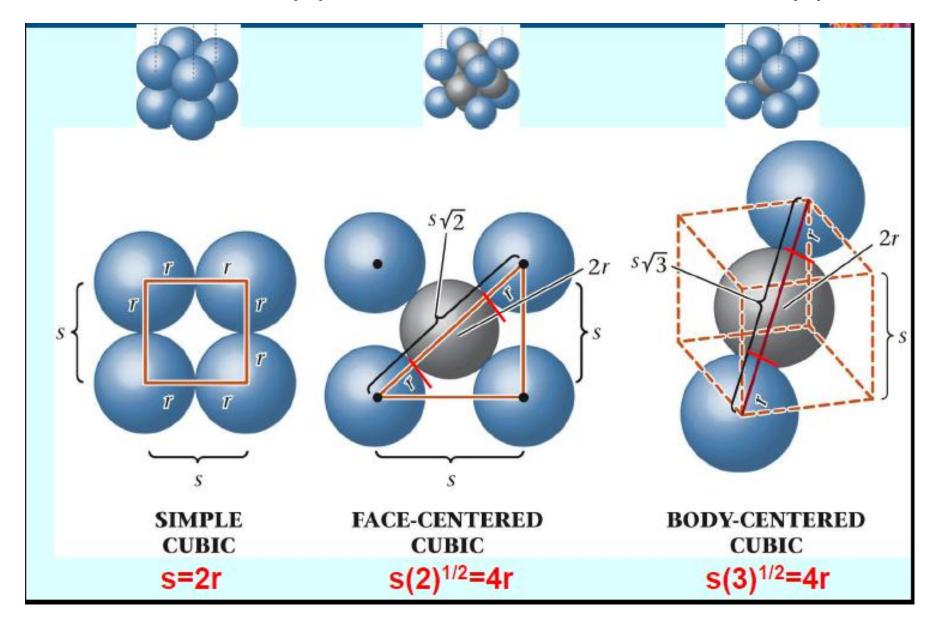
Types of spheres:

b. body-centered sphere - belongs exclusively to the unit cell; each counts as 1 atom.





### Side of cell (s) and radius of atom or ion (r)



### Property of Cubic Unit Cells

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

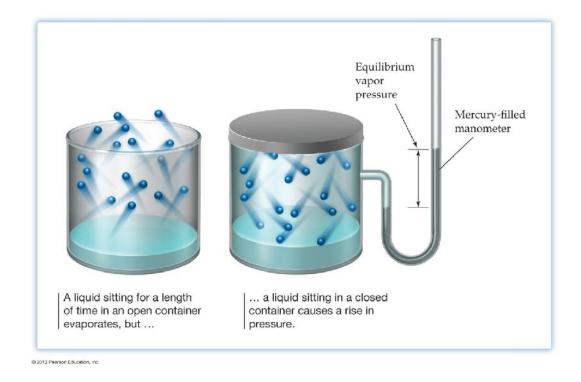
### **TABLE 9.7** Properties of Cubic Unit Cells

	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

# **Vapor Pressure**

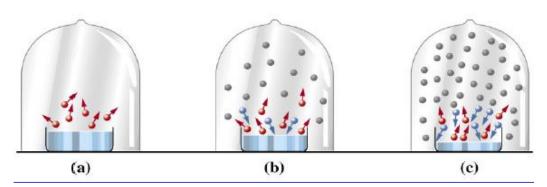
# Vapor Pressure: The partial pressure of a gas in equilibrium with liquid at a constant temperature





### Vapor Pressure and Phase Equilibrium

- Molecules in vapor state
- Molecules undergoing vaporization
- -- Molecules undergoing condensation



Molecules are entering the vapor phase from the liquid and condensing from the vapor phase to the liquid at the same rate



### 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:

    - The double arrow indicates a dynamic equilibrium.

### Vapor Pressure and Volume / Temperature

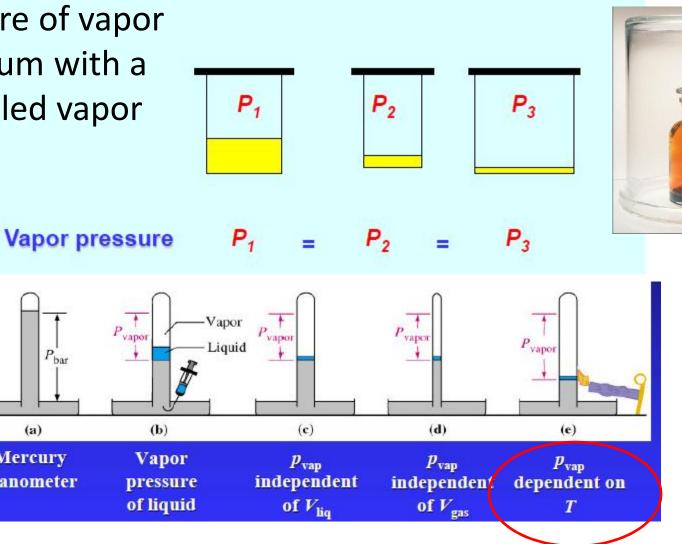
As long as both liquid and vapor are present, the vapor pressure is independent of the volume of the container.

The pressure of vapor in equilibrium with a liquid is called vapor pressure.

(a)

Mercury

manometer



### Vapor Pressure Versus Temperature

The vapor pressure of a liquid increases as the temperature rises

Increase in P is not linear with

temperature

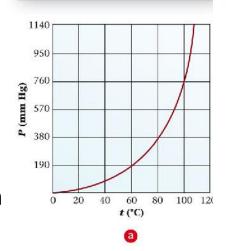
Water

VP is 24 mmHg at 25 °C

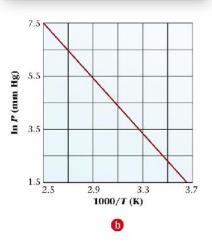
VP is 92 mmHg at 50 °C

To make a linear plot, the natural logarithm is required

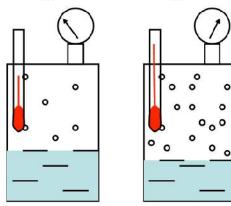
A plot of vapor pressure vs. temperature (in °C) for a liquid is an exponentially increasing curve.



A plot of the logarithm of the vapor pressure vs. 1/T (in K) is a straight line. (To provide larger numbers, we have plotted 1000/T.)



The quantity of vapor above a liquid in a closed system increases with the temperature of the system. The quantity of vapor can be measured as the vapor pressure of the system. This relationship is pictorially shown in **Figure 1**.



$$\ln(P) = \frac{-\Delta H_{\text{vap}}}{R} \frac{1}{T} + \ln(A)$$

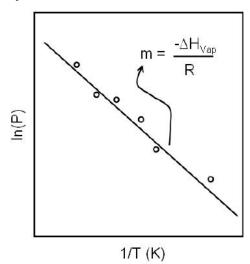
$$\uparrow \qquad \uparrow \qquad \uparrow$$

$$y = m \qquad x + b$$

Clausius-Clapeyron Equation

# The Clausius-Clapeyron Equation

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



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

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

- Notes:
  - Temperatures must be in Kelvin
    - $R = 8.31 \text{ J/mol} \cdot \text{K}$
    - H<sub>vap</sub> must be in J for use with this value for R

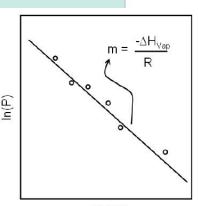
## The Clausius-Clapeyron Equation

#### **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.

AA	IA	LA	10	100
AN	NA	L	5	5

Information given:	vapor pressure at 40°C (183 mm Hg) temperature (25°C) $\Delta H_{\rm vap}$ (30.8 kJ/mol)
Information implied:	R value with energy units
Asked for:	pressure at 25°C
	· ·



1/T (K)

#### STRATEGY

- 1. Use subscript 2 for the higher temperature, pressure pair:  $P_2 = 183$  mm Hg;  $T_2 = 40$ °C
- 2. Substitute into Equation 9.1 using the appropriate R value and T in K.

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

#### SOLUTION

Substitute into Equation 9.1 
$$\ln 183 - \ln P_1 = \frac{30.8 \text{ kJ/mol}}{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}} \left[ \frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}} \right]$$
$$\ln 183 = 5.209$$
$$\frac{30.8 \text{ kJ/mol}}{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}} \left[ \frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}} \right] = 0.596$$
$$P_1$$
$$5.209 - \ln P_1 = 0.596; \ln P_1 = 4.613; P_1 = 101 \text{ mm Hg}$$

#### **END POINT**

This value is reasonable. Lowering the temperature (40°C to 25°C) should decrease the pressure. The answer shows that it does (183 mm Hg to 101 mm Hg)!

# Example

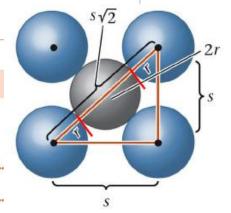
### **EXAMPLE 9.8 GRADED**

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  $V = \frac{4}{3}\pi r^3$ .)
- What is the density of a single silver atom?

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	ANALYSIS
Information given:	type of cubic cell (face-centered) length of side, $s(0.407 \text{ nm})$ nm to cm conversion (1 nm = $1 \times 10^{-7} \text{ cm}$ )
Information implied:	side and atomic radius relationship in a face-centered cubic cell
Asked for:	atomic radius of silver in cm



### FACE-CENTERED CUBIC

s(2)1/2=4r

#### STRATEGY

- 1. Relate the atomic radius, r, to the side of the cube, s, in a face-centered cubic cell (FCC). See Table 9.7.
- 2. Substitute into the equation  $4r = s\sqrt{2}$ .
- 3. Convert nm to cm.

#### SOLUTION

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

# Example 9.8, (Cont'd)

<b>(b)</b>		
	ANALYSIS	
Information given:	from part (a); atomic radius, $r$ (1.44 $\times$ 10 <sup>-8</sup> cm) formula for the volume of a sphere ( $V = \frac{4}{3}\pi r^3$ )	
Asked for:	volume of a single Ag atom	continued

### STRATEGY

Assume that the atom is a perfect sphere and substitute into the formula for the volume of a sphere.

### SOLUTION

V

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

# Example 9.8, (Cont'd)

C	
	ANALYSIS
Information given:	from part (b): atomic volume, $V(1.25 \times 10^{-23} \text{ cm}^3)$ formula for the volume of a sphere $(V = \frac{4}{3}\pi r^3)$
Information implied:	molar mass of Ag Avogadro's number
Asked for:	density of a single Ag atom

#### STRATEGY

- 1. Recall that density = mass/volume.
- 2. Find the mass of a single Ag atom. Recall that there are  $6.022 \times 10^{23}$  atoms of silver in one molar mass of silver (107.9 g/mol). Use that as a conversion factor.

#### SOLUTION

mass of 1 Ag atom	1 Ag atom $\times \frac{107.9 \text{ g}}{6.022 \times 10^{23} \text{ atoms}} = 1.792 \times 10^{-22} \text{ g}$
density	density = $\frac{\text{mass}}{\text{volume}} = \frac{1.792 \times 10^{-22} \text{g}}{1.25 \times 10^{-23} \text{cm}^3} = 14.3 \text{g/cm}^3$

#### **END POINTS**

- 1. In face-centered cubic cells, the fraction of empty space is 0.26.
- 2. The calculated density in part (c) assumes no empty space. If empty space is factored in, [(0.26)(14.3) = 3.7], then  $3.7 \text{ g/cm}^3$  has to be subtracted from the density obtained in part (c). The calculated density is therefore  $[14.3 3.7] = 10.6 \text{ g/cm}^3$ . The experimentally obtained value is  $10.5 \text{ g/cm}^3$ .