Intramolecular & Intermolecular Forces Liquids, Solids, and Phase changes

- An Overview of Physical Changes and Phase Changes
- > Quantitative Aspects of Phase Changes
  - Heat Involved in Phase Changes
  - Equilibrium Nature of Phase Changes
  - Phase Diagrams
- > Types of Intermolecular Forces
  - Ion-Dipole Forces
  - Dipole-Dipole Forces
  - The Hydrogen Bond
  - Charge-Induced Dipole Forces
  - Dispersion (London) Forces

States of Matter Properties of the Liquid State Surface Tension Capillarity Viscosity The Uniqueness of Water Solvent Properties Thermal Properties Surface Properties Density of Solid and Liquid Water

> Solid State: Structure, Properties, and Bonding Structural Features of Solids Crystalline Solids Amorphous Solids Bonding in Solids > Advanced Materials Electronic Materials Liquid Crystals Ceramic Materials • Polymers Nanotechnology

Physical States of Matter – any physically distinct, homogenous part of a system

- Phases Types of Physical State
  - Gases
  - Liquids
  - Solids
  - Plasma

#### Intermolecular and Intramolecular Forces

- In all of the 1<sup>st</sup> 3 phases, Electrostatic Forces among (between) the particles combine with the Kinetic Energy of the particle to create the properties of each phase as well as phase changes
  - Vapor Pressure
  - Boiling Point
  - Melting Point

- Comparison of gases, liquids, and solids
  - > Gases
    - Compressible fluids conforming to the shape and volume of container
    - Molecules are widely separated

> Liquids

- Relatively incompressible fluids
- Conform to shape of container, volume limited by surface
- Molecules are more tightly packed
- Solids
  - Nearly incompressible and rigid, maintaining their own shape and volume
     Molecules or ions are in close contact and do not move

Representation of the States of Matter



Condensation – Process by which a gas changes to a liquid
 Vaporization – Process by which a liquid changes to a gas
 Heat of Vaporization (ΔH<sub>vap</sub>) – Endothermic Enthalpy Changes

Freezing – Process by which a liquid changes to a solid

- Melting (Fusion) Process by which a solid changes to a liquid
  - > Heat of Fusion ( $\Delta H_{fus}$ ) Endothermic Enthalpy Change
- Sublimation Process by which a solid changes directly to a gas
  - Heat of Sublimation ( $\Delta H_{sub}$ ) Endothermic Enthalpy Change

Deposition – Process by which a gas changes directly to a solid

#### **Changes of State**

A <u>change of state</u> or <u>phase transition</u> is a change of a substance from one state to another



- A phase diagram is a graphical way to summarize the conditions under which the different states of a substance are stable
  - The diagram is divided into three areas representing each state of the substance
    - Gas
    - Liquid
    - Solid

The curves separating each area represent the boundaries of phase changes

Typical phase diagram

Consists of three curves that divide the diagram into regions labeled:

Solid Liquid Gas



Curve AB, dividing the solid region from the liquid region, represents the conditions under which the solid and liquid are in equilibrium



Usually, the melting point is only slightly affected by pressure. For this reason, the melting point curve, AB, is nearly vertical



If a liquid is more dense than its solid, the curve leans slightly to the left, causing the melting point to decrease with pressure



If a liquid is <u>less</u> dense than its solid, the curve leans slightly to the right, causing the melting point to increase with pressure



Curve AC, which divides the liquid region from the gaseous region, represents the boiling points of the liquid for various pressures



Curve AD, which divides the solid region from the gaseous region, represents the vapor pressures of the solid at various temperatures

The Phase change of a solid directly to a gas is referred to as "<u>Sublimation</u>"



The curves intersect at A, the triple point, which is the temperature and pressure where three phases of a substance exist in equilibrium



The temperature above which the liquid state of a substance no longer exists regardless of pressure is called the critical temperature



## **Practice Problem**

Shown here is the phase diagram for compound X. The triple point of X is  $-25.1^{\circ}$ C at 0.50 atm and the critical point is 22°C and 21.3 atm.



- a. What is the state of X at position A?
- b. If we decrease the temperature from the compound at position A to  $-28.2^{\circ}$ C while holding the pressure constant, what is the state of X?
- c. If we take the compound starting under the conditions of part b and increase the temperature to 15.3°C and decrease the pressure to 0.002 atm, what is the state of X?
- d. Would it be possible to make the compound starting under the conditions of part c a solid by increasing just the pressure?

a. Position A – Gas b. Position B – Solid c. Position C – Gas d. Position D – Since the solid – liquid line angles to the right, eventually the compound would form a solid (high pressure)

#### Bonding Forces vs. Non-Bonding Forces

Intramolecular Forces (Bonding within molecules)

- Relatively strong because charges are closer together
- > Attractions between:
  - Anions & Cations (Ionic Bonding within molecules)
  - Nuclei & Electron pairs (Covalent Bonding)
  - Metal cations and Delocalized electrons (Metallic)
- Intermolecular Forces (Non-Bonding <u>between</u> molecules)
  - Relatively Weak because charges are smaller and farther apart
  - Phase and phase changes (solid, liquid, gas) are a function of the Intermolecular forces
  - > Attractions between:
    - Molecules with partial charges or
    - Molecules and Ions

#### Bonding Forces vs. Non-Bonding Forces

#### Intramolecular (Bonding Forces within molecules)

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation-anion	400-4000	NaCl
Covalent	0,0	Nuclei-shared e pair	150-1100	н—н
Metallic		Cations-delocalized electrons	75–1000	Fe

#### Intermolecular (Non- Bonding Forces <u>between</u> molecules)

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Int	termolecular)			L
Ion-dipole	••••••	Ion charge– dipole charge	40-600	Na+O
H bond	δ- δ+ δ- −A−H······:B−	Polar bond to H– dipole charge (high EN of N, O, F	10-40 )	ю́—н…ю́—н 
Dipole-dipole	<b>↔ ↔</b>	Dipole charges	5-25	I-CI-CI
lon-induced dipole	••••••	Ion charge– polarizable e <sup>–</sup> cloud	3-15	Fe <sup>2+</sup> O <sub>2</sub>
Dipole-induced dipole	<b>↔</b> ( <del>)</del>	Dipole charge- polarizable e <sup>-</sup> cloud	2-10	H—CI····CI—CI
Dispersion (London)	0	Polarizable e <sup>-</sup> clouds	0.05-40	F-F···F-F

## **Intermolecular Forces**

Many of the physical properties of liquids (and certain solids) can be explained in terms of the <u>forces of attraction between molecules</u>, that is, the

#### **Intermolecular Forces**

Three types of forces are known to exist between neutral molecules

 London (or dispersion) forces – weakest (non-polar molecules)

 Dipole-Dipole forces – stronger (polar molecules)

Hydrogen bonding

strongest

(in substances where Hydrogen is directly bonded to either <u>Oxygen</u>, <u>Nitrogen</u> or <u>Fluorine</u>)

#### London Forces

London forces are the weak attractive forces resulting from instantaneous dipoles that occur due to the distortion of the electron cloud surrounding a molecule

London forces:

#### increase with molecular weight

The larger a molecule, the more easily the electron clould can be distorted to give an instantaneous dipole

All covalent molecules exhibit some London force

#### **Intermolecular Forces**

Van der Waals (VDW) forces – general term that includes

#### London and Dipole-Dipole forces

- Van der Waals forces are the weak attractive forces in a large number of substances
  - The distance between two non-bonded atoms in "adjacent" molecules
  - London forces are <u>dispersion forces</u> and are the <u>weakest</u> of the intermolecular forces



#### **Intermolecular Forces**

#### Van der Waals (vdw) Forces

- Dipole Dipole
  - An external electric field orients gaseous polar molecules
  - The polar molecules in liquids and solids lie near each other and their partial charges act as tiny electric fields and give rise to

#### "Dipole-Dipole" forces

- Dipole-Dipole forces slightly stronger than the London forces, but less than Hydrogen Bonding
- Magnitude of the Dipole-Dipole force depends on the magnitude of the molecular dipole moment

## 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

Polar molecules arise from the differences in the <u>electronegativity</u> of atoms within a molecule



# Origin of the London Force At <u>any instant</u> there are more e<sup>-</sup> on one side of the Neon (Ne) atom than the other (A)



Opposite ends of instantaneous dipoles attract (B)
 Electrons on adjacent atoms tend to move together to create new instantaneous dipoles (C)
 All molecular compounds have London attractive forces

#### **Intermolecular Forces**

- Polarizability and Induced Dipole Forces
  - A nearby electric field can "induce" a distortion in the electron cloud:
    - Pulling electron density toward a positive pole of the field or
    - Pushing it away from a negative pole
  - For a "nonpolar" molecule the distortion induces a temporary dipole moment
  - For a "polar" molecular, the distortion <u>enhances</u> the dipole moment already present
  - Polarizability increases "Down" a group as size increases (electron cloud is easier to distort)
  - Polarizability decreases across a period because increasing Z<sub>eff</sub> makes the atoms smaller holding electrons closer

## Hydrogen Bonding

- Hydrogen Bonding is a special dipole-dipole force that exists between a Hydrogen atom covalently bonded to a very electronegative atom with a lone pair of electrons
  - Only N, O, and F are electronegative enough to leave the Hydrogen nucleus exposed
  - To exhibit Hydrogen Bonding, one of the following three structures must be present

     H-O
     H-F

 Hydrogen Bonding between molecules
 Note: Hydrogen Bonding between molecules is indicated by dotted line • • • •

## Sample Problem

Which of the following substances exhibits Hydrogen Bonding?

For those that do, draw two molecules of the substance with the H bond(s) between them

a.  $C_2H_6$  b.  $CH_3OH$  c.  $CH_3C - NH_2$ 

Ans: a. C<sub>2</sub>H<sub>6</sub> does not form any Hydrogen Bonds

b. For CH<sub>3</sub>OH. The H covalently bonded to the O in one molecule forms an H-Bond to the lone pair of electrons on the O of an adjacent molecule

c. For CH<sub>3</sub>C – NH<sub>2</sub>. Two of these molecules can form one H bond between an H bonded to N and the O, or they can form two such bonds



## Hydrogen Bonding

Hydrogen Bonding and Boiling Point

> Boiling points rise as molar mass increases in Group 4A Hydrides

#### $(CH_4, SiH_4, GeH_4, SnH_4)$

- > In the other groups, the first member of each series
  - NH<sub>3</sub>, HF, H<sub>2</sub>O deviates considerably The H bonds in these substances require additional energy to
  - break before the molecules can separate and enter the gas phase



## Hydrogen Bonding in Water



## 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<sub>3</sub> Hydrogen Bonding Water (H<sub>2</sub>O) Molecule



## **Intermolecular Forces**

#### Summary of Intermolecular Forces

> Ions

- Ionic Bonding (strongest)
- Polar Molecules
- Ion-Dipole; Dipole-Dipole, Hydrogen Bonding
- Polar & Non-Polar Dipole-Induced Dipole
- > Non-Polar

- (London) Dispersion (weakest)

Note: Dispersion forces are present in <u>ALL</u> molecules



## Sample Problem

The forces of attraction between molecules of I<sub>2</sub> are
a. induced dipole–dipole attractions
b. dipole–dipole attractions
c. covalent bonds
d. London forces
e. dipole-induced dipole attractions

Ans: d The I<sub>2</sub> molecule is non-polar no dipole-dipole no Hydrogen bonding

The forces of attractions between molecules of  ${\rm I_2}$  are mostly dispersive (London forces)
How many of the following compounds will exhibit Hydrogen Bonding?

 $H_2NNH_2$  $CH_3CI$  $HNF_2$  $CH_3OCH_3$  $H_2CO$ a. 1b. 2c. 3d. 4e. 5

Ans: 2

H<sub>2</sub>NNH<sub>2</sub> & HNF<sub>2</sub>

H bonded to Nitrogen (N) & Fluorine (F)

What is the strongest inter-particle force in each substance?

a.  $CH_3OH$  b.  $CCl_4$  c.  $Cl_2$ 

#### Ans: a. Hydrogen Bonding

- b. Non-polar compound Dispersion forces (The 4 Cl atoms are positioned symmetrically around the Carbon atom)
- c. Non-polar compound Dispersion forces

What is the strongest inter-particle force in each substance?

a.  $H_3PO_4$  b.  $SO_2$ 

Ans: a. Hydrogen Bonding

- b. Dipole-Dipole(Covalent Molecule)
- c. Ionic Bond (Metal/nonmetal forms ionic compound)



MgCl<sub>2</sub>

С.

Which member of each pair of compounds forms intermolecular hydrogen bonds?

- a. CH<sub>3</sub>CHOHCH<sub>3</sub> or b. CH<sub>3</sub>SCH<sub>3</sub>
  - Ans: a The presence of OH group leads to formation of Hydrogen bonds
- a. HF or b. HBr
  - Ans: a The presence of H attached to highly electronegative F sets up hydrogen bonds

The H in HBr does not form Hydrogen bonds (Br not electronegative enough)

#### Van der Waals Forces and the Properties of Liquids

In summary, Van der Waals intermolecular forces:

- > London (or dispersion) forces (weakest)
- > Dipole-dipole forces

play a large role in many of the physical properties of liquids and gases. These include:

vapor pressure surface tension boiling point viscosity

# Vapor Pressure

#### Liquids are continuously vaporizing

- If a liquid is in a closed vessel with space above it, a partial pressure of the vapor state builds up in this space
- The vapor pressure of a liquid is the partial pressure of the vapor over the liquid, measured at equilibrium at a given temperature
- Raising the temperature of a liquid increases the fraction of molecules moving fast enough to escape the liquid and decreases the fraction moving slowly enough to be recaptured.
  The higher the temperature, the

higher the vapor pressure

#### Rates of Vaporization and Condensation of a Liquid Over Time



In C, system comes to equilibrium where rate of condensation = rate of vaporization At this point the vapor pressure is reached

## Vapor Pressure

The vapor pressure of a liquid depends on its temperature

As the temperature increases, the kinetic energy of the molecular motion becomes greater, and vapor pressure increases

Liquids and solids with relatively high vapor pressures at normal temperatures are said to be volatile

# **Boiling Point**

The temperature at which the vapor pressure of a liquid equals the pressure exerted on the liquid is called the boiling point

As the temperature of a liquid increases, the vapor pressure increases until it reaches external pressure (usually atmospheric pressure)

> At this point, stable bubbles of vapor form within the liquid. This is called boiling

Normal Boiling Point is the boiling point at

1 atmosphere (atm) = 760 torr = 760 mm Hg

# **Boiling Point**

#### A liquid boils when the VP inside a bubble equals the external P



#### Heat of Phase Transition Heat of Vaporization

To boil a pure substance from its melting point requires an extra boost of energy to overcome intermolecular forces

The heat needed to boil 1 mol of a pure liquid substance is called the Heat of Vaporization and denoted by AH<sub>vap</sub>

For ice at the melting point, the heat of vaporization of water is 40.66 kJ/mol

 $H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{vap} = +40.66 \text{ kJ / mol}$ 

Endothermic reaction requiring energy input

#### Heat of Vaporization (vapor pressure & boiling point)

The heat of vaporization (AH<sub>vap</sub>) is inversely proportional to the vapor pressure

 $\Delta H_{vap} \propto \frac{1}{Vapor Pressure}$ 

The higher the vapor pressure (low boiling point) the lower the heat of vaporization

■ The heat of vaporization (△H<sub>vap</sub>) is proportional to the boiling point

 $\Delta H_{vap} \infty$  Boiling Point  $\infty$ 

Vapor Pressure

Liquids with low vapor pressure require more energy to invoke boiling, i.e., they have higher boiling points

Which compound should have the lowest heat of vaporization?

a.  $C_5H_{12}$  b.  $C_6H_{14}$  c.  $C_7H_{16}$ d.  $C_8H_{18}$  e.  $C_8H_{16}$ 

Ans: a

 $C_5H_{12}$  has the lowest molecular weight and should have the highest vapor pressure and, thus, the lowest boiling point

Therefore, the Heat of Vaporization ( $\triangle$ H) should be the lowest

## Heating Curve for Water



## **Clausius-Clapeyron Equation**

Recall: <u>Vapor Pressure is a function of Temperature</u>

- Vapor Pressure also depends on the Intermolecular Forces present
- At a given temperature molecules with weaker intermolecular forces have a higher vapor pressure and vaporize more easily
- The weaker the intermolecular forces the higher the vapor pressure

# **Clausius-Clapeyron Equation**

The impact of the intermolecular forces produces a <u>non-linear</u> relationship between Vapor Pressure and Temperature





# Clausius – Clapeyron Equation Clausius – Clapeyron Equation

The non-linear relationship, as shown in the diagrams, can be expressed as a <u>linear</u> relationship by plotting the natural logarithm of Vapor Pressure (In P) versus the reciprocal of the absolute temperature (°K)

Clausius - Clapeyron Equation  $ln P = \left(\frac{-\Delta H_{vap}}{R}\right) \left(\frac{1}{T}\right) + C$  y = m \* x + b  $slope \qquad intercept$ 



## **Clausius-Clapeyron Equation**

A modification of the Clausius-Clapeyron equation, the two point version, allows for the description of the vapor pressure of a liquid at two different temperatures and pressures

$$\ln \frac{P}{\frac{2}{P_{1}}} = \frac{-\Delta H}{R} \left( \frac{1}{T_{2}} - \frac{1}{T_{1}} \right) = \frac{-\Delta H}{R} \left( \frac{T_{1}}{\frac{1}{2}} - \frac{T_{1}}{T_{2}} \right)$$

Note: R can be expressed in 2 different sets of units  $R = 8.31447 \text{ J/mol} \bullet \text{K}$  $R = 0.0821 (L \bullet \text{atm})/(\text{mol} \bullet \text{K})$ 

#### Note: 1 L • atm = 101.3 J Units for Heat of Vaporization - kJ/mol

The compound Methylchloride,  $CH_3Cl$ , has a vapor pressure of 100 mm Hg at 210 K and 10 mm Hg a 181 K. Calculate the Heat of Vaporization ( $\Delta H_{vap}$ ) of  $CH_3Cl$ .



Carbon Disulfide,  $CS_2$ , has a heat of vaporization of 29.2 kJ/mol. At 268 K it has a vapor pressure of 100 mmHg. What is its vapor pressure at 301 K?

$$\ln \frac{P_{2}}{P_{1}} = \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T_{2}} \cdot \frac{1}{T_{1}} \right) = \frac{-\Delta H_{vap}}{R} \left( \frac{T_{1} - T_{2}}{T_{2} \times T_{1}} \right)$$

$$P_{1} = 100 \text{ nm Hg}$$

$$T_{1} = 268^{\circ} \text{ K}$$

$$P_{2} = ?$$

$$InP_{2} \cdot InP_{1} = \left( \frac{-\Delta H_{vap}}{R} \right) \left( \frac{T_{1} \cdot T_{2}}{T_{2} \times T_{1}} \right)$$

$$InP_{2} = \left( \frac{-\Delta H_{vap}}{R} \right) \left( \frac{T_{1} \cdot T_{2}}{T_{2} \times T_{1}} \right) + InP_{1}$$

$$P_{1} = 100 \text{ nm Hg}$$

$$T_{1} = 268^{\circ} \text{ K}$$

$$P_{2} = ?$$

$$T_{2} = 301^{\circ} \text{ K}$$

$$\Delta H_{vap} = 29.2 \text{ kJ / mol} = 29,200 \text{ J / mol}$$

$$R = 8.31447 \text{ J / mol} \circ \text{ K}$$

$$\ln P_{2} = \left(\frac{-29,200 \frac{J}{mol}}{8.31447 \frac{J}{mol \cdot K}}\right) \left(\frac{268 - 301}{301 \times 268} K\right) + \ln(100) \, \text{mmH}$$

$$\ln P_{2} = 1.43668 + 4.60517 = 6.04185$$
$$P_{2}^{2} = 421 \text{ mm Hg}$$

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#### Trouton's Rule (Heat of Vaporization – Organic liquids)

■ The Heat of Vaporization (△H<sub>vap</sub>) of an organic liquid can be estimated using <u>Trouton's Rule</u>:

$$\Delta H_{vap} = 88 \frac{\text{Joules}}{\text{mol} \bullet^{o} K} \times T_{b}(K) \qquad [T_{b} = \text{Boiling Point}(^{o} K)]$$

#### **Practice Problem**

The liquid Tribromomethane, CHBr<sub>3</sub>, has a vapor pressure of 751 Pa at 25 °C and its Boiling Point is 149.5°C.

What is  $\Delta H_{vap}$  of CHBr<sub>3</sub>?

a. 13.2 kJ/mol b. 29.4 kJ/mol c. 37.2 kJ/mol

d. 59.1 kJ/mol e. 70.8 kJ/mol

$$\Delta H_{vap} = 88 \left( \frac{J}{mol \cdot K} \right) \times T_b = 88 \left( \frac{J}{mol \cdot K} \right) \times \left( (149.5^{\circ} C + 273.15) \right)$$

$$\Delta \mathbf{H}_{vap} = 3.7 \times 10^4 \, \mathrm{J} \, / \, \mathrm{mol} \left( \frac{1 \, \mathrm{kJ}}{1000 \, \mathrm{J}} \right)$$

 $\Delta H_{vap} = 37.2 \text{ kJ} / \text{mol}$ 

#### **Practice Problem**

The liquid Tribromomethane, CHBr<sub>3</sub>, has a vapor pressure of 751 Pa at 25 °C and its Boiling Point is 149.5°C.

What is the vapor pressure in Pa of CHBr<sub>3</sub> at 10 °C?

a. 2,190 b. 974 c. 698 d. 339 e. 119  $\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T_1} \cdot \frac{1}{T_2} \right) = \frac{-\Delta H_{vap}}{R} \left( \frac{T_1 \cdot T_2}{T_2 \times T_1} \right) \qquad \ln P_2 = \left( \frac{-\Delta H_{vap}}{R} \right) \left( \frac{T_1 \cdot T_2}{T \times T} \right) + \ln P_1$  $\ln P_{2} = \left(-\frac{37.2 \text{ kJ/mol} \frac{1000 \text{ J}}{1 \text{ kJ}}}{8.31447 - \frac{\text{J}}{1 \text{ c}}} \right) \left(\frac{(25 + 273.15) \cdot (10 + 273.15)}{(10 + 273.15) \times (25 + 273.15)K}\right) + \ln(751 \text{ Pa})$  $\ln P_{2} = \left[ -\frac{37,200 \text{ J}}{8.31447 - \frac{\text{J}}{100 \text{ J}}} \left( \frac{15}{84,421 \text{ K}} \right) + 6.6214 \right]$ Note:  $\triangle H_{vap} = 37.2 \text{ kJ/mol}$ from previous example  $\ln P = -0.79497 + 6.6214 = 5.8264$  $\frac{P_2 = 339 Pa}{4/28/2019}$ 

# Freezing (Melting) Point

The temperature at which a pure liquid changes to a crystalline solid, or freezes, is called the freezing point

The Melting Point is identical to the Freezing Point and is defined as the temperature at which a solid becomes a liquid

Unlike boiling points, melting points are affected significantly by only large pressure changes

#### Freezing (Melting) Point Heat of Phase Transition

To melt a pure substance at its melting point requires an extra boost of energy to overcome lattice energies

The heat needed to melt 1 mol of a pure substance is called the heat of fusion, AH<sub>fus</sub>

For ice, the heat of fusion is 6.01 kJ/mol

 $H_2O(s) \rightarrow H_2O(l)$   $\Delta H_{fus} = 6.01 \text{ kJ/mol}$ 

How much energy in Joules (J) does it take to melt 1.0 kg of ice at  $0^{\circ}C$ ? ( $\Delta H^{\circ}_{fus} = 6.01 \text{ kJ/mol}$ )

$$1 \text{ kg}_{(\text{ics})} \frac{1000 \text{ g}_{(\text{ice})}}{\text{ kg}_{(\text{ice})}} \left( \frac{1 \text{ mol}_{(\text{ice})}}{18.016 \text{ g}_{(\text{ice})}} \right) = 55.506 \text{ mol}_{(\text{ice})}$$
$$\Delta H = 55.506 \text{ mol}_{(\text{ice})} \times \left( \frac{6.01 \text{ kJ}}{\text{mol}_{(\text{ice})}} \right) \left( \frac{1000 \text{ J}}{\text{kJ}} \right) = 3.34 \times 10^5 \text{ J}$$

The heat of combustion of Methane ( $CH_4$ ) is shown below. How many grams of Methane does it take to melt 1.0 kg of ice?

 $\begin{array}{rcl} \mathsf{CH}_4(\mathsf{g}) &+& 2 \ \mathsf{O}_2(\mathsf{g}) &\to& \mathsf{CO}_2(\mathsf{g}) &+& 2 \ \mathsf{H}_2\mathsf{O}(\mathsf{I}) \\ & & \Delta\mathsf{H}=-890.0 \ \mathsf{kJ}/\mathsf{mol}_{\mathsf{CH4}} \end{array}$ 

 $\Delta H(1kg)_{(ice)} = 3.34 \times 10^5 \text{ J} / kg\left(\frac{1kJ}{1000J}\right) = 334 \text{ kJ} / kg_{(ice)}$ 

 $\left| \frac{-890.0 \text{ kJ}}{\text{mol}_{\text{CH}_4} \times \frac{16.042 \text{ g}}{\text{mol}_{\text{CH}_4}}} \right| = -55.478 \text{ kJ / g}_{\text{CH}_4} \qquad \begin{array}{c} \text{Convert } \Delta \text{H for 1 mol CH}_4 \text{ to} \\ \text{kJ/g of CH}_4 \end{array} \right|$   $\left| \frac{334 \text{ kJ}}{\text{kg}_{(\text{ice})}} \right|$   $55.479 \text{ kJ / g}_{(\text{CH}_4)} = 6.02 \text{ g}_{(\text{CH}_4)} / \text{ kg}_{(\text{ice})}$ 

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#### Properties of Liquids Surface Tension

- Surface tension is the energy required to increase the surface area of a liquid by a unit amount
  - Surface tension is a contractive tendency of the surface of a liquid that allows it to resist an external force
  - For example, some objects float on the surface of water, even though they are denser than water, e.g. water striders to run on the water surface
  - This property is caused by cohesion of similar molecules, and is responsible for many of the behaviors of liquids

## Surface Tension

- A molecule within the bulk of a liquid is pulled equally in all directions by neighboring liquid molecules (cohesion), resulting in a net force of zero
- At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside the liquid but are not attracted as intensely by the molecules in the neighboring medium (be it vacuum, air or another liquid)
- As a result, there is a tendency for the surface area of the liquid to be minimized, i.e. downward pointing meniscus
- This also explains why falling raindrops are nearly spherical, minimizing surface area

# **Explaining Surface Tension**

- Molecule on a liquid surface experiences a net force toward the interior while a molecule in the interior experiences no net force
- The <u>stronger</u> the forces are between the particles in a liquid, the <u>greater</u> the surface tension
- Surfactants (surface-active agents), such as soap and fat emulsifiers, decrease the surface tension of water by congregating at the surface and disrupting the H bonds



#### Properties of Liquids Capillarity

- Capillarity The rising of a liquid through a narrow space against the pull of gravity
- Water
  - In a glass capillary tube (SiO<sub>2</sub>), the water molecules form Hydrogen Bonds to the Oxygen atoms of the inner wall of the glass tubes
  - Water will move up the wall of the tube because the <u>adhesive</u> forces from the H-Bonding between the water and the wall are <u>stronger</u> that the cohesive forces (H-bonding) within the water
  - At the same time, the cohesive forces that give rise to surface tension pull the liquid surface taut
  - These adhesive and cohesive forces combine to raise the water level and produces the familiar <u>concave meniscus</u>
  - The liquid rises until gravity pulling down is balanced by the adhesive forces pulling up

#### Capillarity

#### Mercury

- The <u>Mercury</u> level in a glass tube immersed in a bowl of Mercury will drop <u>below</u> the level in the bowl
- Mercury has a higher surface tension than water because of the stronger cohesive forces from metallic bonding
- The cohesive forces among the Mercury atoms are much stronger than the adhesive forces (mostly dispersion) between Mercury and glass, thus the Mercury atoms tend to pull away from the walls of the glass tube
- At the same time, the surface atoms near the glass wall are being pulled toward the interior of the Mercury by its high surface tension forcing the overall level to drop forming a convex (upward pointing) meniscus

#### Properties of Liquids Capillarity

#### Water displays a <u>concave</u> meniscus in a glass tube

- > Adhesive (H-Bond) forces between H<sub>2</sub>O and O-Si-O groups of the glass are stronger than the cohesive forces (H-Bond) within the water
- Mercury displays a <u>convex</u> meniscus in a glass tube
  - The cohesive (metallic bond) forces within mercury are stronger than the adhesive (dispersion) forces between the mercury and the glass



In a glass tube, water molecules are pulled toward the glass surface creeping up the tube, but the surface molecules are being pulled down; combined forces form a downward concave meniscus. Mercury molecules are pulled away from the glass forming an upward (convex) surface curve. The surface atoms are pulled downward dropping the level below the dish level.

#### Properties of Liquids Viscosity

- Viscosity is a measure of the resistance to flow (units of kg/m•s) exhibited by all liquids and gases being deformed by either shear stress or extensional stress
  - Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction
  - Viscosity decreases with increase temperature
  - Viscosity can be illustrated by measuring the time required for a steel ball to fall through a column of the liquid
  - Even without such measurements, you know that syrup has a greater viscosity than water

#### Van der Waals Forces and the Properties of Liquids

The <u>molecular structure</u> of a substance defines the intermolecular forces holding it together

Many physical properties of substances are attributed to their intermolecular forces

> These properties include:

Vapor Pressure

**Boiling Point** 

Surface Tension

Viscosity

#### Van der Waals Forces and the Properties of Liquids

- Vapor pressure (also known as equilibrium vapor pressure), is the pressure of a vapor in equilibrium with its non-vapor phases
- The atmospheric pressure boiling point of a liquid (also known as the normal boiling point is the temperature where the vapor pressure equals the ambient atmospheric pressure
- The vapor pressure of a liquid depends on intermolecular forces
- When the intermolecular forces in a liquid are strong, you expect the vapor pressure to be low
- The normal boiling point is related to vapor pressure and is lowest for liquids with the weakest intermolecular forces
#### Van der Waals Forces and the Properties of Liquids

Vapor Pressure Summary:

- The vapor pressure of any substance increases non-linearly with temperature according to the Clausius-Clapeyron relation
- The higher the vapor pressure of a liquid at a given temperature, the lower the normal boiling point (i.e., the boiling point at atmospheric pressure) of the liquid

High VP – Weak IM Forces Low Boiling Point Low VP – Strong IM Forces

#### Van der Waals Forces and the Properties of Liquids

#### Surface tension

- Intermolecular forces produce attractions between the molecules of a liquid
- Intermolecular forces exert different effects on a molecule at the surface of the liquid than on a molecule in the interior (bulk) of the liquid
- There is a net attraction downward and move toward the interior to increase attractions and become more stable
- As intermolecular forces between molecules increase, the apparent surface tension <u>also</u> increases
- The liquid surface tends to have the smallest possible area (sphere-like)

#### Van der Waals Forces and the Properties of Liquids

#### Viscosity

- A liquid's viscosity (resistance to flow) results from intermolecular attractions that impede the ability of the molecules to slide around each other
- Both gases and liquids flow, but liquid viscosities are much higher because intermolecular forces operate over much shorter distances
- When molecules move faster at higher temperatures, they can overcome (reduce the effect of) intermolecular forces more easily, thus reducing the resistance to flow
- As intermolecular forces <u>increase</u>, the resistance to flow (<u>viscosity</u>) usually <u>increases</u>

# Intermolecular vs Chemical Bonding

**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	

# **Properties of Liquids**

#### Properties of Some Liquids at 20°C

Substance	Molecular Weight (amu)	Vapor Pressure (mmHg)	Surface Tension (J/m <sup>2</sup> )	Viscosity (kg/m · s)
Water, H <sub>2</sub> O	18	$1.8  imes 10^1$	$7.3 \times 10^{-2}$	$1.0 \times 10^{-3}$
Carbon dioxide, CO <sub>2</sub>	44	$4.3 \times 10^{4}$	$1.2 \times 10^{-3}$	$7.1 \times 10^{-5}$
Pentane, C <sub>5</sub> H <sub>12</sub>	72	$4.4 \times 10^{2}$	$1.6 \times 10^{-2}$	$2.4 \times 10^{-4}$
Glycerol, C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	92	$1.6 \times 10^{-4}$	$6.3 \times 10^{-2}$	$1.5  imes 10^{\circ}$
Chloroform, CHCl <sub>3</sub>	119	$1.7 \times 10^{2}$	$2.7 \times 10^{-2}$	$5.8 \times 10^{-4}$
Carbon tetrachloride, CCl4	154	$8.7 imes10^1$	$2.7 \times 10^{-2}$	$9.7 \times 10^{-4}$
Bromoform, CHBr <sub>3</sub>	253	$3.9  imes 10^{0}$	$4.2  imes 10^{-2}$	$2.0 \times 10^{-3}$

**Conceptual Problem** Consider two flasks that each contains different pure liquids at 20°C.



The liquid in one flask, substance A, has a molar mass of 100 g/mol and has hydrogen bonding. The liquid in the other flask, substance B, has a molar mass of 105 g/mol and has dipole–dipole interactions.

- a. If the molecular structures of the compounds are very similar, which flask likely contains substance A?
- b. If you were to increase the temperature of each of the flasks by 15°C, how would the pictures change (assume that you stay below the boiling points of the liquids)?

 a. The flask with the red molecules has a lower Vapor Pressure; thus a higher boiling point due to "strong" intermolecular forces", probably Hydrogen Bonding.

The flask with the blue molecules has a higher vapor pressure and lower boiling point due to weak intermolecular forces – dispersion & dipoledipole

 b. Increasing the temperature will increase the vapor pressure of both liquids, but would not change the relative vapor pressures

For each of the following substances, List the kinds of intermolecular forces expected



- b. isopropyl alcohol, CH<sub>3</sub>CHOHCH<sub>3</sub>
  c. hydrogen iodide, HI
- d. krypton, Kr

- a. Molecule is non-polar with mostly dispersion forces
- b. Isopropyl Alcohol is Polar with some dispersion, but mostly Hydrogen Bonding
- c. Iodine is not electronegative enough to support Hydrogen bonding ∴ dipole-dipole
- d. Krypton is a monatomic element ∴ dispersive forces

List the following substances in order of increasing boiling point





#### **Increasing Boiling Pt**

- D methane -161 °C
- C ethane - 88.6°C
- A methanol 64.7°C
- B ethylene glycol 197.2°C

Methane & Ethane are non-polar with dispersion forces. Increasing Mol Wgt increases Boiling Point.

Methanol and Ethylene Glycol both have hydrogen bonding

Ethylene glycol has more Hydrogen bonding than Methanol

Which of the following compounds is expected to have the **HIGHEST boiling point?** 

a.  $CH_3OCH_3$  b.  $CH_3CH_2OH$  c.  $CH_3CH_2CH_2CH_3$ d.  $CH_3CH_2CH_3$  e.  $CH_3CI$ 

Ans: b (Ethyl Alcohol (CH<sub>3</sub>CH<sub>2</sub>OH) – 78.29 °C) Ethanol has Hydrogen Bonding



Which of the following compounds is expected to have the **HIGHEST vapor pressure? Lowest VP?** 

- a.  $CH_3CH_2CH_3$  b.  $CH_3OCH_3$  c.  $CH_3CH_2OH$
- Highest Vapor Pressure (lowest boiling point) (intermolecular dipole-dipole)
  - Ans: b. Dimethyl Ether (CH<sub>3</sub>OCH<sub>3</sub> bp -24.8°C

Lowest Vapor Pressure (highest boiling point) (Hydrogen Bonding)

Ans: c Ethyl Alcohol ( $CH_3CH_2OH$ ) bp 78.29°C

#### Solid State

- A solid is a nearly incompressible state of matter with a well-defined shape
- The units making up the solid are in close contact and in fixed positions
- Solids are characterized by the type of force holding the structural units together
- In some cases, these forces are intermolecular, but in others they are chemical bonds (metallic, ionic, or covalent)

#### Solid State

From this point of view, there are four types of solids **Relative Bond** Energy Molecular (Van der Waals forces) 0.01 – 660 kj/mol 75 – 1000 kJ/mol > Metallic (Metallic bond) Covalent (Covalent bond) 150 – 1100 kJ/mol 400 – 4000 kJ/mol > Ionic (Ionic bond)

# Types of Solids

- A molecular solid is a solid that consists of atoms or molecules held together by intermolecular forces.
- A metallic solid is a solid that consists of positive cores of atoms held together by a surrounding "sea" of electrons (metallic bonding)
- An ionic solid is a solid that consists of cations and anions held together by electrical attraction of opposite charges (ionic bond)
- A covalent network solid is a solid that consists of atoms held together in large networks or chains by covalent bonds

Many physical properties of a solid can be attributed to its structure

#### **Melting Point and Structure**

- For a solid to melt, the forces holding the structural units together must be overcome
- For a molecular solid, these are weak intermolecular attractions
- > Thus, molecular solids tend to have low melting points (below 300 °C)

 Many physical properties of a solid can be attributed to its structure (con't)
 Melting Point and Structure

- For ionic solids and covalent network solids to melt, chemical bonds must be broken
- For that reason, their melting points are relatively high
  - Note that for ionic solids, melting points increase with the strength of the ionic bond
  - Ionic bonds are stronger when:
    - The magnitude of charge is high
    - The ions are small (higher charge density)

#### Melting Point and Structure

- Metals often have high melting points, but there is considerable variability
- Melting points are low for Groups IA and IIA but increase as you move into the transition metals
- The elements in the middle of the transition metals have the highest melting points

c.  $NO_2$ 

Which of the following compounds would be expected to have the highest melting point?

- a.  $CO_2$  b.  $SiO_2$
- d.  $P_4O_{10}$  e.  $N_2O_5$

#### Ans: b

CO<sub>2</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> are covalent gases P<sub>4</sub>O<sub>10</sub> (mp 560°C) is a crystalline covalent solid SiO<sub>2</sub> (mp 1650°C) molecules have stronger dipole-dipole intermolecular than P<sub>4</sub>O<sub>10</sub>

#### Hardness and Structure

- Hardness depends on how easily structural units can be moved relative to one another
- Molecular solids with weak intermolecular attractions are rather soft compared with ionic compounds, where forces are much stronger
- Covalent network solids are quite hard because of the rigidity of the covalent network structure
- Molecular and ionic crystals are generally brittle because they fracture easily along crystal plane

Metallic solids, by contrast, are malleable

Physical Properties

Electrical Conductivity and Structure

- Molecular and ionic solids are generally considered nonconductors
- Ionic compounds conduct in their molten state, as ions are then free to move
- Metals are all considered conductors
- > Of the covalent network solids, only graphite conducts electricity
  - This is due to the delocalization of the resonant p electrons in graphite's sp<sup>2</sup> hybridization

#### Crystalline Solids Crystal Lattices and Unit Cells

Solids can be crystalline or amorphous

- A crystalline solid is composed of one or more crystals; each crystal has a well-defined, ordered structure in three dimensions
  - Examples include sodium chloride and sucrose

An amorphous solid has a disordered structure. It lacks the well-defined arrangement of basic units found in a crystal

Glass is an amorphous solid

### **Crystal Lattices**

- A crystal lattice is the geometric arrangement of lattice points in a crystal
  - A unit cell is the smallest boxlike unit from which you can construct a crystal by stacking the units in three dimensions
  - There are seven (7) basic shapes possible for unit cells, which give rise to seven crystal systems used to classify crystals

# Crystal Lattices

Crystal Lattice (Con't)

These seven systems can have more than one possible crystal lattice

> A "primitive" lattice has lattice points only at the corners of each cell

Other lattices in the same crystal may have lattice points on the "faces" of the unit cell

## **Crystal Lattices**

#### Crystal Lattice

#### Unit-Cell Shapes of the 7 Different Crystal Systems



## **Cubic Unit Cells**

- A simple cubic unit cell is a cubic cell in which the lattice points are situated only at the corners
- A body-centered cubic unit cell is one in which there is a lattice point in the center of the cell as well as at the corners
- A face-centered cubic unit cell is one in which there are lattice points at the center of each face of the cell as well as at the corners

## Cubic Unit Cells





# Cubic Unit Cells Space-filling representation of cubic unit cells



Shown here is a representation of a unit cell for a crystal. The orange balls are atom A, and the grey ball are atom B.

- a. What is the chemical formula of the compound that has this unit cell  $(A_2B_2)$ ?
- b. Consider the configuration of the A atoms. Is this a cubic unit cell? If so, which type?



a.  $A_9B_6$ 

**b. Body Center Cubic** 

Decide which substance in each of the following pairs has the lower melting point

Explain how you made each choice

a. potassium chloride, KCl; or calcium oxide, CaO





c. zinc, Zn; or chromium, Cr d. acetic acid, CH<sub>3</sub>COOH; or ethyl chloride,  $C_2H_5Cl$ 

- a. KCl (775°C) vs CaO (2572°C), both ionic but calcium oxide is smaller and has a higher charge magnitude requiring more energy to overcome forces holding molecules together
- b. Carbon tetrachloride (mp -19°C) would have a lower melting point than hexachloroethane (mp-tp 187) because it has a lower molecular weight and less intermolecular forces to overcome
- c. Chromium (mp 1857°C) has a much high melting point than Zinc (mp 419°C) because of its higher ionic charges and smaller radius
- d. Acetic acid (mp 16.5oC) has a high mp than Ethyl chloride (mp -139°C) because hydrogen bonds require more energy to overcome the forces holding the molecules together

### **Crystal Defects**

There are principally two kinds of defects that occur in crystalline substances

Chemical impurities, such as in rubies, where the crystal is mainly aluminum oxide with an occasional Al<sup>3+</sup> ion replaced with Cr<sup>3+</sup>, which gives a red color

Defects in the formation of the lattice. Crystal planes may be misaligned, or sites in the crystal lattice may remain vacant

#### Calculations Involving Unit Cell Dimensions

- X-ray diffraction is a method for determining the structure and dimensions of a unit cell in a crystalline compound
  - Once the dimensions and structure are known, the volume and mass of a single atom in the crystal can be calculated
  - The determination of the mass of a single atom gave us one of the first accurate determinations of Avogadro's number

LiCl crystallizes in a face-centered cubic structure. The unit cell length is  $5.14 \times 10^{-8}$  cm. The chloride ions are touching each other along the face diagonal of the unit cell. The Li<sup>+</sup> ions fit into the holes between the chloride ions.

How many Li<sup>+</sup> ions are there in this unit cell?

Each cell contains 12  $\frac{1}{4}$  Li<sup>+</sup> ions plus 1 whole Li<sup>+</sup> ion 12 x 1/4 + 1 = 4 (total)

How many Cl<sup>-</sup> ions are there in the cell?  $c_{l-}$  Li Each cell contain 8 1/8 Cl<sup>-</sup> ions and 6 1/2 Cl<sup>-</sup> ions 8 x 1/8 + 6 x 1/2 = 4 (total)



LiCl crystallizes in a face-centered cubic structure. The unit cell length is  $5.14 \times 10^{-8}$  cm. The chloride ions are touching each other along the face diagonal of the unit cell. The Li<sup>+</sup> ions fit into the holes between the chloride ions.

What is the mass of the LiCl cell?

Mass Cl =  $35.45 \frac{g}{mol} / (6.02214 \times 10^{23} / mol) \times 4 \text{ atoms / cell} = <math>2.355 \times 10^{-22} \text{g / cell}$ Mass Li =  $6.940 \frac{g}{mol} / (6.02214 \times 10^{23} / mol) \times 4 \text{ atoms / cell} = <math>4.610 \times 10^{-23} \text{g / cell}$ 

Total Mass of Cell =  $2.355 \times 10^{-22}$ g +  $4.610 \times 10^{-23}$ g =  $2.816 \times 10^{-22}$ g

LiCl crystallizes in a face-centered cubic structure. The unit cell length is  $5.14 \times 10^{-8}$  cm. The chloride ions are touching each other along the face diagonal of the unit cell. The Li<sup>+</sup> ions fit into the holes between the chloride ions.

What is the density of LiCl?

Volume of Cell =  $(5.14 \times 10^{-8})^3$  =  $1.36 \times 10^{-22}$  cm<sup>3</sup>

Total Mass of Cell =  $2.816 \times 10^{-22}$  g

**Density** = mass / volume

Density =  $\frac{2.816 \times 10^{-22} \text{ g}}{1.36 \times 10^{-22} \text{ cm}^3}$  = 2.07 g/cm<sup>3</sup> (Actual Density - 2.07 g/cm<sup>3</sup>)

LiCl crystallizes in a face-centered cubic structure The unit cell length is  $5.14 \times 10^{-8}$  cm The Chloride ions are touching each other along the face diagonal of the unit cell The Li<sup>+</sup> ions fit into the holes between the Chloride ions What is the radius of the Cl<sup>-</sup> ion in meters? (hint: in a square, Diagonal = cell length (S) x  $\sqrt{2}$ 



Diagonal (C) =  $A\sqrt{2}$  = 5.14×10<sup>-8</sup> × 1.4142 = 7.269×10<sup>-8</sup> cm

$$\mathbf{C} = \mathbf{r} + 2\mathbf{r} + \mathbf{r} = 4\mathbf{r}$$

$$r = C/4 = \frac{7.2691 \times 10^{-8} \text{ cm}}{4} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.8173 \times 10^{-10} \text{ m}$$

#### **Summary Equations**

Heat Involved in Temperature Change within a Phase  $q = n \times C \times \Delta T$ 

Heat Involved in Change of PhaseEndothermic $q = n \times \Delta H_{vap}$  (liquid to gas) $q = n \times \Delta H_{fus}$  (solid to liquid)Exothermic $q = n \times (-\Delta H_{vap})$  (gas to liquid) $q = n \times (-\Delta H_{fus})$  (liquid to solid)

#### **Equation Summary**

Clausius - Clapeyron Equation  $\ln P = \left(\frac{-\Delta H_{vap}}{R}\right) \left(\frac{1}{T}\right) + C$   $y = m \quad x \quad + b$   $slope \qquad intercept$ 

$$\ln \frac{P_{\frac{2}{2}}}{P_{1}} = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right) = \frac{-\Delta H_{vap}}{R} \left(\frac{T_{\frac{1}{2}} - T_{\frac{2}{2}}}{T_{\frac{2}{2}} \times T_{1}}\right)$$

 $R = 8.31447 \text{ J/mol} \bullet \text{K}$  $R = 0.0821 \text{ (atm} \bullet \text{L})/(\text{mol} \bullet \text{K})$
## **Equation Summary**

