

Unit 3: STATES OF MATTER

Chapter 5: Gases

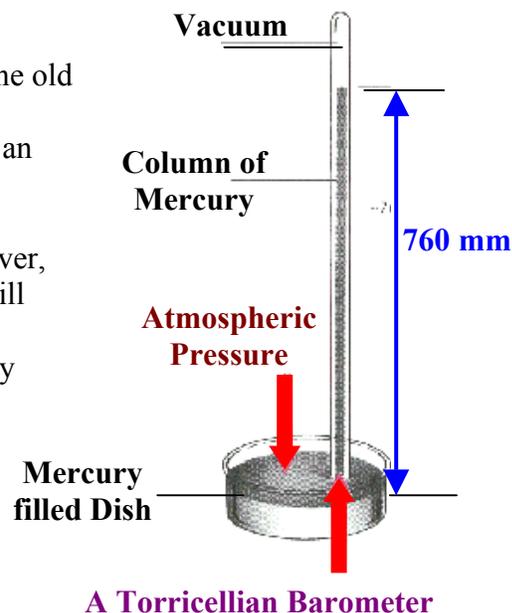
5.1: Pressure

Pressure: - the amount of force per unit of area [$1 \text{ N/m}^2 = 1 \text{ Pascal (Pa)}$], measured in **kiloPascal (kPa)**, **mm Hg**, **torr**, **atmospheric pressure (atm)**.

- in a pressurized container, a pressure can be felt as the particles pushed on the inside wall of the container.

Barometer: - an instrument (invented by Evangelista Torricelli, hence, the old unit of pressure *torr* was named after him) to measure atmospheric pressure using a dish filled with mercury and an inverted glass tube filled with mercury.

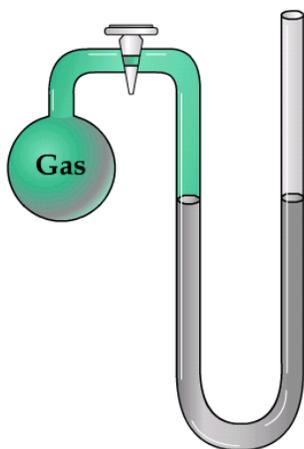
- when the glass tube is placed into the dish filled with mercury, the level of mercury in the tube will drop. However, the atmospheric pressure of the surface of mercury dish will keep the mercury column at a certain level.
- the higher the atmospheric pressure, the higher the mercury is in the column.
- at normal atmospheric pressure at sea level, the mercury column is at 760 mm.



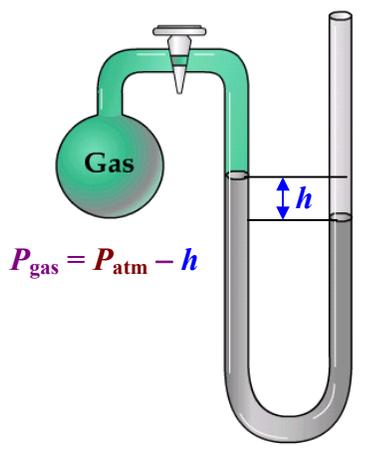
Manometer: - a device consists of a tube connected to a container of gas to measure the pressure in the gas container.

- there are two kinds of manometer: an **open-ended manometer** and a **close-ended manometer**.

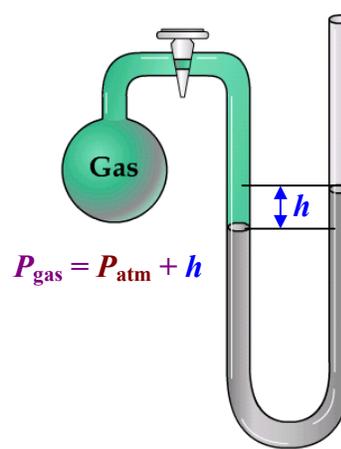
1. **Open-Ended Manometer:** - the tube is open ended to allow atmospheric pressure to come in.



**Gas Pressure =
Atmospheric Pressure**

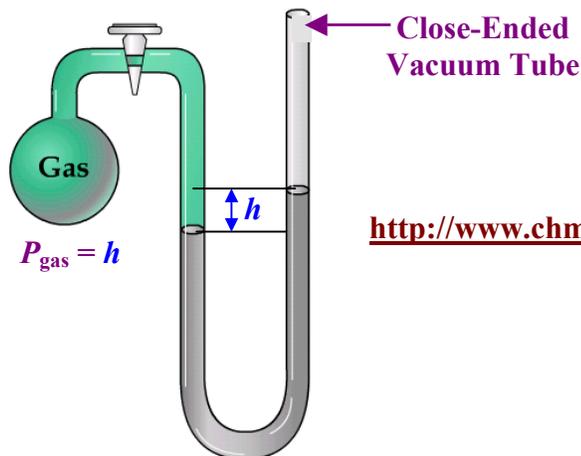


**Gas Pressure <
Atmospheric Pressure**



**Gas Pressure >
Atmospheric Pressure**

2. Close-Ended Manometer: - the tube is a vacuum that is closed ended. The difference in height of the U-tube is the pressure of the gas container.



(Check out animation at <http://www.chm.davidson.edu/ChemistryApplets/GasLaws/Pressure.html> under Part 1: Reading a Manometer)

Units of Pressure

1 standard atmosphere (atm) = 760 mm Hg = 760 torr = 101.325 kPa

Note: 1mm Hg = 1 torr

Example 1: Convert 525 mm Hg to torr, atm and kPa.

$$525 \text{ mm Hg} = \mathbf{525 \text{ torr}} \quad (1 \text{ mm Hg} = 1 \text{ torr})$$

$$525 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = \mathbf{0.691 \text{ atm}}$$

$$525 \text{ mm Hg} \times \frac{101.325 \text{ kPa}}{760 \text{ mm Hg}} = \mathbf{70.0 \text{ kPa}}$$

Example 2: Convert 350 kPa to atm, torr and mm Hg.

$$350 \text{ kPa} \times \frac{1 \text{ atm}}{101.325 \text{ kPa}} = \mathbf{3.45 \text{ atm}}$$

$$350 \text{ kPa} \times \frac{760 \text{ torr}}{101.325 \text{ kPa}} = 2625.2 \text{ torr} = \mathbf{2.62 \times 10^3 \text{ torr}}$$

$$2.62 \times 10^3 \text{ torr} = \mathbf{2.62 \times 10^3 \text{ mm Hg}} \\ (1 \text{ mm Hg} = 1 \text{ torr})$$

5.2: The Gas Laws of Boyle, Charles, Guy-Lussac, Avogadro & the Combined Gas Law**Variables to Describe a Gas:**

1. **Pressure (P)**: - the amount of force per unit of area, measures in **kiloPascal (kPa)** or **standard atmosphere (atm)**.
2. **Volume (V)**: - the amount of space the gas is occupied; measures in **Litre (L)**.
3. **Temperature (T)**: - the average of kinetic energy of the gas; measures in **Kelvin (K)**.
4. **Moles (n)**: - the amount of gas particle in a closed system; measures in **moles (mol)**.

Laws that Relate Gas Variables:

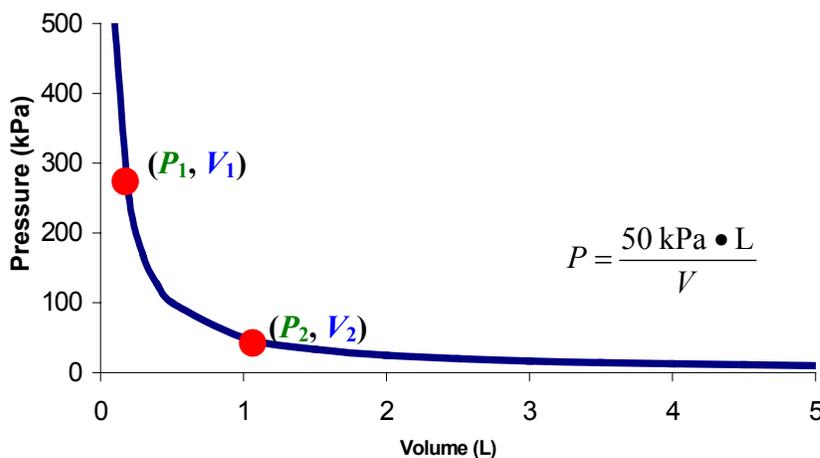
1. **Boyle's Law**: - at a constant temperature and moles, **pressure is inversely proportional to the volume**.

$$P \propto \frac{1}{V}$$

$$P = \frac{k}{V} \quad \text{or} \quad PV = k$$

$k = \text{constant of proportion}$

Volume \uparrow Pressure \downarrow

Boyle's Law (Constant Temperature)**Boyle's Law**

$$P_1V_1 = P_2V_2$$

$P_1 = \text{Pressure at Initial Condition}$ $V_1 = \text{Volume at Initial Condition}$

$P_2 = \text{Pressure at Final Condition}$ $V_2 = \text{Volume at Final Condition}$

Example 1: A gas cylinder changed its volume from 2.50 L to 6.25 L. If it were at 101.325 kPa initially, what would be its final pressure?

$$P_1 = 101.325 \text{ kPa}$$

$$P_2 = ?$$

$$V_1 = 2.50 \text{ L}$$

$$V_2 = 6.25 \text{ L}$$

$$P_1V_1 = P_2V_2$$

$$\frac{P_1V_1}{V_2} = P_2$$

$$P_2 = \frac{(101.325 \text{ kPa})(2.50 \text{ L})}{(6.25 \text{ L})}$$

$$P_2 = 40.5 \text{ kPa}$$

As Volume \uparrow , Pressure \downarrow

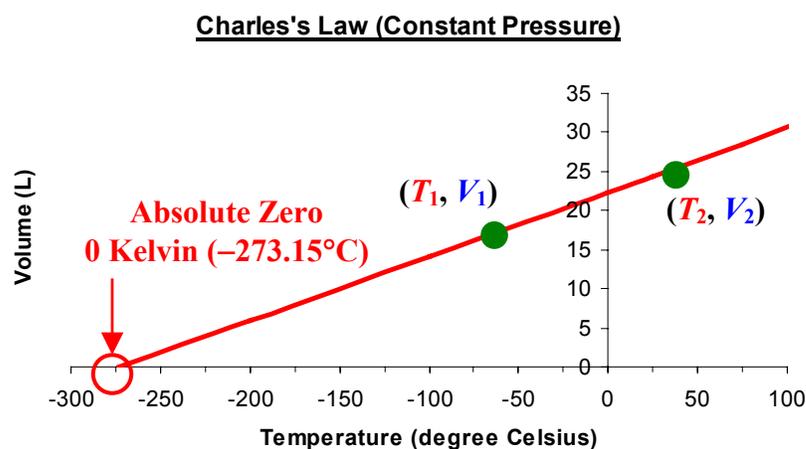
2. **Charles's Law:** - at constant pressure and moles, **volume is directly proportional to the temperature.**

$$V \propto T$$

$$V = kT \quad \text{or} \quad \frac{V}{T} = k$$

$k = \text{constant of proportion}$

Temperature ↑ Volume ↑



Charles's Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$T_1 = \text{Temperature at Initial Condition}$
 $T_2 = \text{Temperature at Final Condition}$

$V_1 = \text{Volume at Initial Condition}$
 $V_2 = \text{Volume at Final Condition}$

- Example 2:** A balloon has a volume of 3.25 L at 25.0°C. Determine the volume of the same balloon when the temperature is dropped to 5.00°C.

$$V_1 = 3.25 \text{ L}$$

$$T_1 = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$V_2 = ?$$

$$T_2 = 5.00^\circ\text{C} = 278.15 \text{ K}$$

(Change °C to K)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V_1 T_2}{T_1} = V_2$$

$$V_2 = \frac{(3.25 \text{ L})(278.15 \text{ K})}{(298.15 \text{ K})}$$

As Temp ↓, Volume ↓

$$V_2 = 3.03 \text{ L}$$

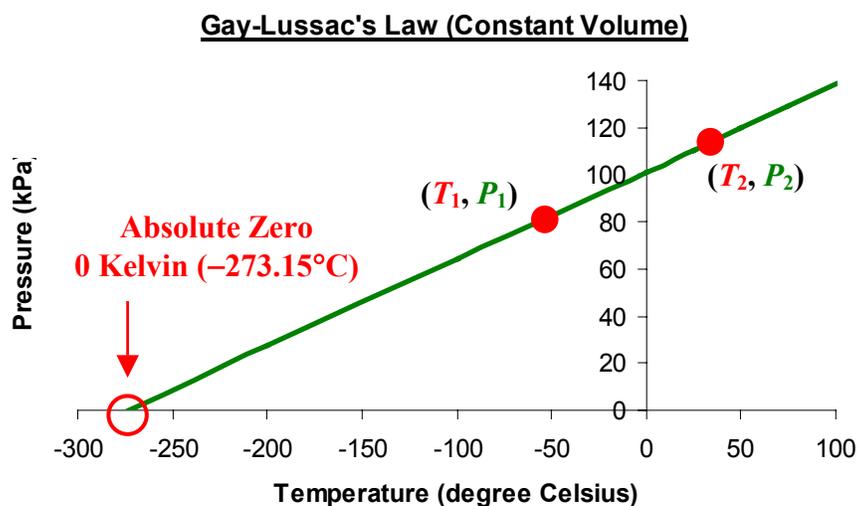
3. **Gay-Lussac's Law:** - at constant moles and volume, **pressure is directly proportional to the temperature.**

$$P \propto T$$

$$P = kT \quad \text{or} \quad \frac{P}{T} = k$$

$k = \text{constant of proportion}$

Temperature ↑ Pressure ↑



Gay-Lussac's Law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

T_1 = Temperature at Initial Condition
 T_2 = Temperature at Final Condition

P_1 = Pressure at Initial Condition
 P_2 = Pressure at Final Condition

Example 3: A canister is has a pressure of 8.00 atm at 15.0°C. Calculate its pressure if the temperature was to increase to 100.0°C. (**Don't do this at home!**)

$$P_1 = 8.00 \text{ atm}$$

$$T_1 = 15.0^\circ\text{C} = 288.15 \text{ K}$$

$$P_2 = ?$$

$$T_2 = 100.0^\circ\text{C} = 373.15 \text{ K}$$

(Change °C to K)
(P can be in atm)

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{P_1 T_2}{T_1} = P_2$$

As Temp ↑, Pressure ↑

$$P_2 = \frac{(8.00 \text{ atm})(373.15 \text{ K})}{(288.15 \text{ K})}$$

$$P_2 = 10.4 \text{ atm}$$

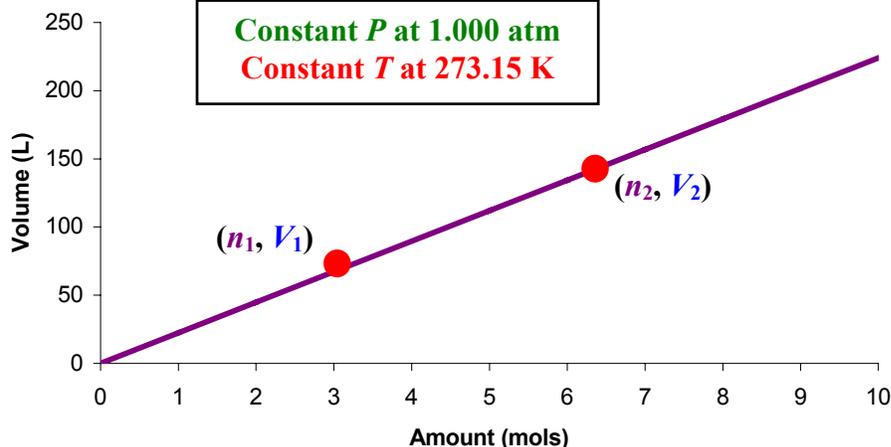
4. Avogadro's Law: - at constant pressure and temperature, **volume is directly proportional to amount of moles of gas present.**

$$V \propto n$$

$$V = kn \quad \text{or} \quad \frac{V}{n} = k$$

k = constant of proportion

Moles ↑ Volume ↑

Avogadro' Law (Constant Temperature and Pressure)Avogadro's Law

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

n_1 = Amount of Moles at Initial Condition
 n_2 = Amount of Moles at Final Condition

V_1 = Volume at Initial Condition
 V_2 = Volume at Final Condition

- Example 4:** An excess amount of solid phosphorus is reacted with 9.00 mol of chlorine gas at 223.2 L to produce phosphorus trichloride gas under constant temperature and pressure.
- Write a balanced equation for this reaction.
 - Assuming a complete reaction, what is the volume of phosphorus trichloride produced?

a.
$$\text{P}_4(\text{s}) + 6 \text{Cl}_2(\text{g}) \rightarrow 4 \text{PCl}_3(\text{g})$$

b.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{n_2 V_1}{n_1} = V_2$$

$n_1 = 9.00 \text{ mol } (\text{Cl}_2)$
 $V_1 = 223.2 \text{ L}$

$n_2 = 9.00 \text{ mol } \text{Cl}_2 \times \frac{4 \text{ mol } \text{PCl}_3}{6 \text{ mol } \text{Cl}_2}$
 $n_2 = 6.00 \text{ mol } (\text{PCl}_3)$
 $V_2 = ?$

$V_2 = \frac{(6.00 \text{ mol})(223.2 \text{ L})}{(9.00 \text{ mol})}$ **As Moles ↓, Volume ↓**

$V_2 = 149 \text{ L}$

5. **Combined Gas Law:** - a formula that summarizes Boyle's Charles's and Guy-Lussac's Gas Laws.
 - allows the user of the formula to determine the change in conditions of the same amount of gas.

Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$P_1 = \text{Pressure at Initial Condition}$ $P_2 = \text{Pressure at Final Condition}$
 $V_1 = \text{Volume at Initial Condition}$ $V_2 = \text{Volume at Final Condition}$
 $T_1 = \text{Temperature at Initial Condition}$ $T_2 = \text{Temperature at Final Condition}$

- Example 5:** A high altitude weather balloon has a volume of 57.2 L at 700 mm Hg and 25.0°C. Determine its volume at its maximum height where the pressure is 0.365 atm and the temperature is at -45.0°C.

$V_1 = 57.2 \text{ L}$
 $P_1 = 700 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}}$
 $P_1 = 0.9210526316 \text{ atm}$
 $T_1 = 25.0^\circ\text{C} = 298.15 \text{ K}$
 $V_2 = ?$
 $P_2 = 0.365 \text{ atm}$
 $T_2 = -45.0^\circ\text{C} = 228.15 \text{ K}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P_1 V_1 T_2}{T_1 P_2} = V_2$$

$$V_2 = \frac{(0.9210526316 \text{ atm})(57.2 \text{ L})(228.15 \text{ K})}{(298.15 \text{ K})(0.365 \text{ atm})}$$

$V_2 = 110 \text{ L}$

(Change °C to K)
 (P can be in atm)

Because $P \downarrow$ much more than $T \downarrow$, the final Volume \uparrow .

Assignment

5.1 pg. 232–233 #25 to 27, 29
 5.2 pg. 233 #31 to 34

5.3: The Ideal Gas Law

Ideal Gas Law: - a formula that relates pressure, volume, amount, and temperature of an **ideal gas** (gaseous volume does not account for total particles volumes) at one specific condition.

Ideal Gas Law

$$PV = nRT$$

P = Pressure (kPa)

V = Volume (L)

n = Amount of Gas (mol)

T = Temperature (K)

R = Gas Constant = 0.08206 (L • atm) / (K • mol) or 8.31 J / (K • mol) or 8.31 (L • kPa) / (K • mol)

Example 1: Determine the mass of propane if it is in a 200 L container at 15.0°C and at 32.0 atm.

$$V = 200 \text{ L}$$

$$T = 15.0^\circ\text{C} = 288.15 \text{ K}$$

$$P = 32.0 \text{ atm}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm) / (K} \cdot \text{mol)}$$

$$m = ?$$

$$n = ? \text{ (need to find } n \text{ first)}$$

$$PV = nRT$$

$$\frac{PV}{RT} = n$$

$$n = \frac{(32.0 \text{ atm})(200 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(288.15 \text{ K})}$$

$$n = 270.6635897 \text{ mol}$$

For propane, C_3H_8 , $M = 44.11 \text{ g/mol}$

$$m = nM$$

$$m = (270.6635897 \text{ mol})(44.11 \text{ g/mol})$$

$$m = 11938.97094 \text{ g}$$

$$m = 1.19 \times 10^4 \text{ g} = 11.9 \text{ kg}$$

Example 2: A 0.852 mol of xenon sample is heated from 23.0°C to 148.0°C. The pressure the gas has also changed from 752 mm Hg to 2854 mm Hg. What is the change in volume the sample of xenon gas is experienced?

$$n = 0.852 \text{ mol}$$

$$T_1 = 23.0^\circ\text{C} = 296.15 \text{ K}$$

$$T_2 = 148.0^\circ\text{C} = 421.15 \text{ K}$$

$$P_1 = 752 \text{ mm-Hg} \times \frac{1 \text{ atm}}{760 \text{ mm-Hg}}$$

$$P_1 = 0.9894736842 \text{ atm}$$

$$P_2 = 2854 \text{ mm-Hg} \times \frac{1 \text{ atm}}{760 \text{ mm-Hg}}$$

$$P_2 = 3.755263158 \text{ atm}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm) / (K} \cdot \text{mol)}$$

$$V_1 = ?$$

$$V_2 = ?$$

This might seem to be a combined gas law problem, but we don't have either *volume* to find both V_1 and V_2 .

$$P_1V_1 = nRT_1$$

$$V_1 = \frac{nRT_1}{P_1} = \frac{(0.852 \text{ mol})\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(296.15 \text{ K})}{(0.9894736842 \text{ atm})}$$

$$V_1 = 20.92563261 \text{ L}$$

$$V_2 = \frac{nRT_2}{P_2} = \frac{(0.852 \text{ mol})\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(421.15 \text{ K})}{(3.755263158 \text{ atm})}$$

$$V_2 = 7.840929264 \text{ L}$$

$$\Delta V = V_2 - V_1 = 7.840929264 \text{ L} - 20.92563261 \text{ L}$$

$$\Delta V = -13.1 \text{ L}$$

(Volume has Decreased by 13.1 L)

Using the Ideal Gas Law formula, we can find the **Density (D)** or the **Molar Mass (M)** of any gas.

$$PV = nRT$$

$$PV = \left(\frac{m}{M}\right)RT \quad \text{(Substitute } \frac{m}{M} \text{ for } n)$$

Solve for $\frac{m}{V}$ for **Density ($D = \frac{m}{V}$)**

$$\frac{PM}{RT} = \frac{m}{V}$$

Density (g/L) $D = \frac{PM}{RT}$

Solve for **Molar Mass (M)**

$$M = \frac{mRT}{PV}$$

$$M = \left(\frac{m}{V}\right) \frac{RT}{P} \quad M = \frac{DRT}{P}$$

Note: Do NOT memorize these formulas but learn the derivations!

Example 3: Calculate the molar mass of a gaseous compound containing carbon and hydrogen if its density is 0.645 g/L at 100.0 kPa and at 25.0°C.

$$D = 0.645 \text{ g/L}$$

$$P = 100.0 \text{ kPa}$$

$$T = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$R = 8.31 \text{ (L} \cdot \text{kPa) / (K} \cdot \text{mol)}$$

(We use this R because we are given P in kPa)

$$M = ?$$

$$M = \frac{DRT}{P} = \frac{(0.645 \text{ g/L}) \left(8.31 \frac{\text{L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}}\right) (298.15 \text{ K})}{(100.0 \text{ kPa})}$$

$$M = 15.98069093 \text{ g/mol}$$

$$M = 16.0 \text{ g/mol}$$

Example 4: Calculate the density in g/L of a sulfur dioxide gas at 724 torr and at -8.47°C.

$$P = 724 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}$$

$$P = 0.9526315789 \text{ atm}$$

$$T = -8.47^\circ\text{C} = 264.68 \text{ K}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm) / (K} \cdot \text{mol)}$$

For sulfur dioxide, SO_2 ,

$$M = 64.06 \text{ g/mol}$$

$$D = ?$$

$$D = \frac{PM}{RT} = \frac{(0.9526315789 \text{ atm})(64.06 \text{ g/mol})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right) (264.68 \text{ K})}$$

$$D = 2.809695589 \text{ g/L}$$

$$D = 2.81 \text{ g/L}$$

5.4: Gas Stoichiometry

Mole-Volume Relationships:

- Standard Temperature and Pressure (STP):** - the amount of any gas at 0°C and 101.325 kPa (Earth's atmospheric pressure at sea level).
- Standard Ambient Temperature and Pressure (SATP):** - the amount of any gas at 25°C and 100 kPa.

$$\text{STP} = 22.4 \text{ L/mol @ } 0.00^\circ\text{C and } 101.325 \text{ kPa (1 atm)}$$

$$\text{SATP} = 24.8 \text{ L/mol @ } 25.00^\circ\text{C and } 100.0 \text{ kPa}$$

Note: The amount of gas is determined by temperature, pressure and volume. The type of gas particles has no effect on these variables. (*Avogadro's Hypothesis*)

Example 1: Determine the amount of oxygen gas in a 5.00 L container under STP and SATP.

a. STP

$$\text{STP} = 22.4 \text{ L/mol}$$

$$n = 5.00 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}}$$

$$n = 0.223 \text{ mol}$$

b. SATP

$$\text{SATP} = 24.8 \text{ L/mol}$$

$$n = 5.00 \text{ L} \times \frac{1 \text{ mol}}{24.8 \text{ L}}$$

$$n = 0.202 \text{ mol}$$

Example 2: Determine the volume of 3.50 g of nitrogen gas under STP and SATP.

a. STP

$$n = \frac{m}{M} = \frac{3.50 \text{ g}}{28.014 \text{ g/mol}} = 0.1249375312 \text{ mol}$$

$$\text{STP} = 22.4 \text{ L/mol}$$

$$V = (0.1249375312 \text{ mol})(22.4 \text{ L/mol})$$

$$V = 2.80 \text{ L}$$

b. SATP

$$n = \frac{m}{M} = \frac{3.50 \text{ g}}{28.014 \text{ g/mol}} = 0.1249375312 \text{ mol}$$

$$\text{SATP} = 24.8 \text{ L/mol}$$

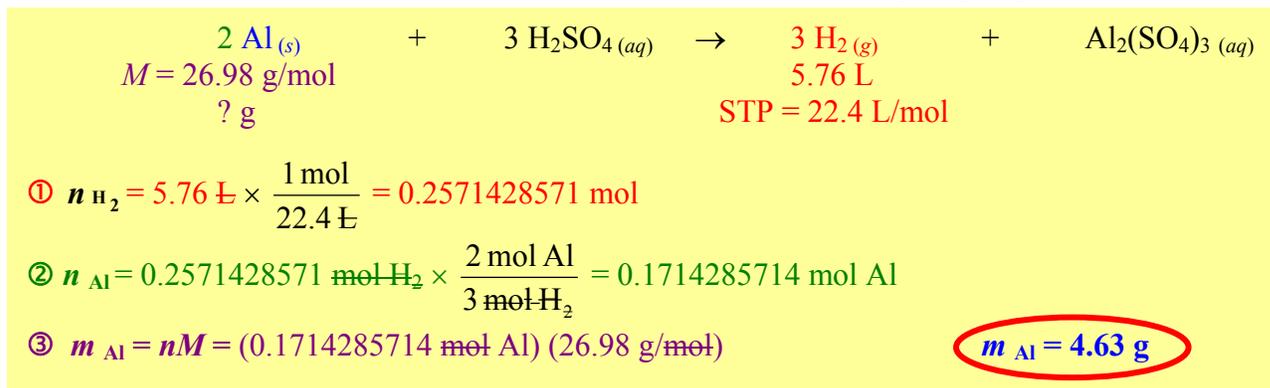
$$V = (0.1249375312 \text{ mol})(24.8 \text{ L/mol})$$

$$V = 3.10 \text{ L}$$

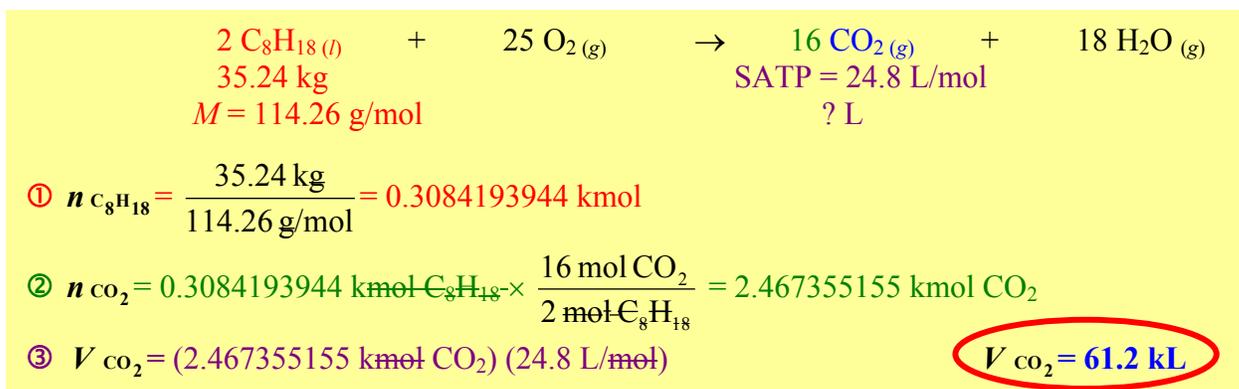
Gaseous Stoichiometry Procedure (Ideal Gas, STP, or SATP)

- Predict the products and balance the chemical equation.
- Put all the information given under the appropriate chemicals.
- Find the moles of the given chemical: $\left(n = \frac{m}{M}\right)$ or $(n = CV)$ or $\left(n = \frac{PV}{RT}\right)$ or
(at STP: $n = \text{Volume} \times \frac{1 \text{ mol}}{22.4 \text{ L}}$; at SATP: $n = \text{Volume} \times \frac{1 \text{ mol}}{24.8 \text{ L}}$).
- Check for limiting reagent if necessary** (if you are given enough information to find the moles of two chemicals). Use the Limiting Reagent for further calculation. Ignore the Excess Reagent.
- Find the mole of the required chemical using mole ratio:
$$\left(\text{mol of require} = \text{mol of given} \times \frac{\text{require coefficient}}{\text{given coefficient}}\right)$$
- Convert mole of the required chemical to its mass, concentration or volume equivalence: $(m = nM)$ or
 $\left(C = \frac{n}{V}\right)$ or $(PV = nRT)$ or (at STP: $V = n \times 22.4 \text{ L/mol}$; at SATP: $V = n \times 24.8 \text{ L/mol}$).

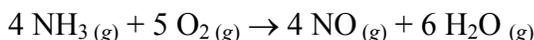
Example 3: A piece aluminium metal is placed in an excess amount of sulfuric acid until all the metal is reacted. Calculate the mass of the aluminium used if 5.76 L of hydrogen gas is evolved at STP.



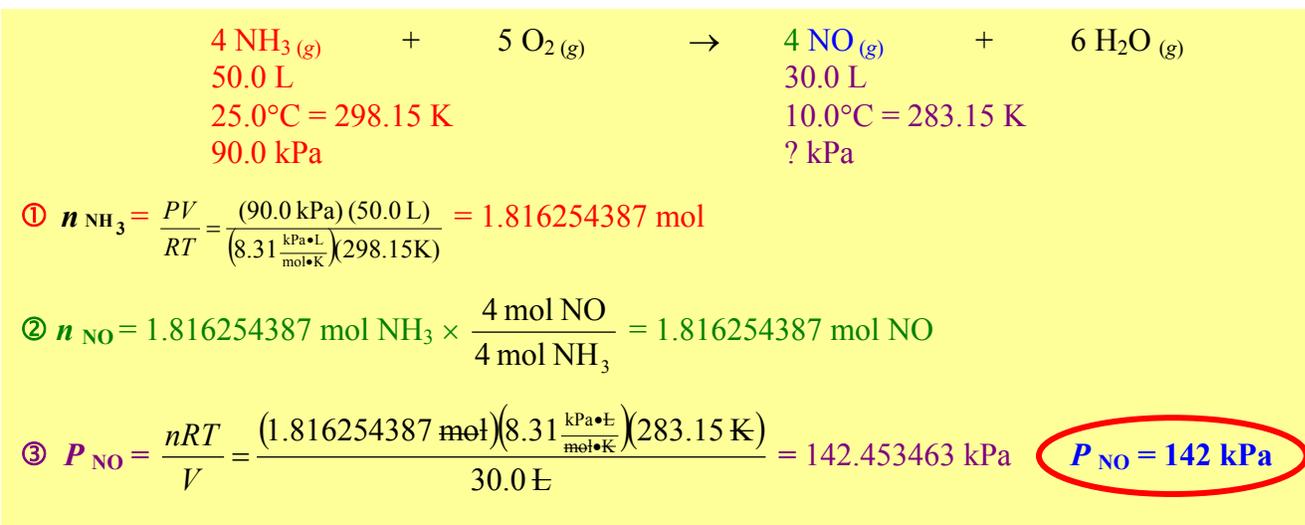
Example 4: 35.24 kg of liquid octane is burned under excess oxygen. Determine the volume of carbon dioxide gas produced at SATP.



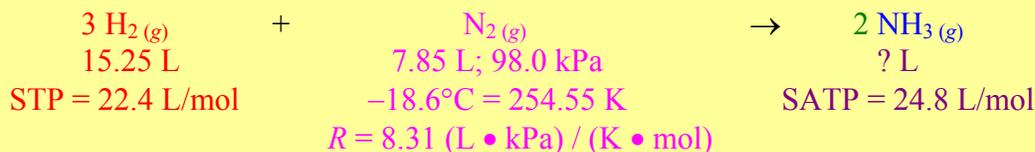
Example 5: Ammonia is reacted with oxygen to form nitrogen monoxide and water vapour.



If 50.0 L of ammonia at 90.0 kPa at 25.0°C were allowed to react with excess oxygen, what would be the pressure of nitrogen monoxide in a collector vessel measuring 30.0 L at a temperature of 10.0°C?



Example 6: If 15.25 L of hydrogen at STP is reacted with 7.85 L of nitrogen at 98.0 kPa and at -18.6°C , determine the volume of ammonia formed at SATP.



Since there is enough information to determine the moles of two reactants, we need to determine which one is the limiting reagent.

$$\textcircled{1} n_{\text{H}_2} = 15.25 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 0.6808035714 \text{ mol H}_2$$

$$\textcircled{2} n_{\text{N}_2} = \frac{PV}{RT} = \frac{(98.0 \text{ kPa})(7.85 \text{ L})}{\left(8.31 \frac{\text{L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}}\right)(254.55 \text{ K})} = 0.363681833 \text{ mol N}_2$$

Let's assume N_2 is the limiting reagent. Calculate the mol H_2 actually needed.

$$\textcircled{3} n_{\text{H}_2} = 0.363681833 \text{ mol N}_2 \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} = 1.091045499 \text{ mol H}_2 \text{ needed}$$

But we don't have 1.091045499 mol of H_2 , we only have 0.6808035714 mol of H_2 . Therefore, H_2 is the limiting reagent. (Note: the limiting reagent is NOT always the chemical with the smaller number of moles. You have to always compare like we did above.)

Now, we calculate the moles of NH_3 formed by using moles of limiting reagent, H_2 .

$$\textcircled{4} n_{\text{NH}_3} = 0.6808035714 \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = 0.4538690476 \text{ mol NH}_3$$

Finally, we determine the volume of NH_3 produced.

$$\textcircled{5} V_{\text{NH}_3} = (0.4538690476 \text{ mol NH}_3)(24.8 \text{ L/mol}) = 11.25595 \dots \text{ L}$$

$$V_{\text{NH}_3} = 11.3 \text{ L}$$

Assignment

5.3 pg. 233–234 #35 to 45, 47

5.4 pg. 234–235 #49 to 62

5.5: Dalton's Law of Partial Pressures**Partial Pressure:** - the pressure exerted by one component of a gas mixture.**Dalton's Law of Partial Pressures:** - the total pressure in a gas mixture is equal to the sum of the pressures exerted by individual gaseous components.**Dalton's Law of Partial Pressures**

$$P_{\text{Total}} = P_1 + P_2 + P_3 + \dots$$

(Using Ideal Gas Law $P = \frac{nRT}{V}$)

$$\frac{n_{\text{Total}}RT}{V} = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \dots$$

(R, T, and V are common to all components in gas mixture)

$$n_{\text{Total}} \left(\frac{RT}{V} \right) = \left(\frac{RT}{V} \right) (n_1 + n_2 + n_3 + \dots)$$

(Take out Common Factor $\frac{RT}{V}$ and cancel both sides)

$$n_{\text{Total}} = n_1 + n_2 + n_3 + \dots \text{ (Mole Components of Gas Mixtures)}$$

Example 1: Write the equations for partial pressures and mole components for air, which is composed of N₂, O₂, Ar, CO₂, and other trace gases (<http://www.mistupid.com/chemistry/aircomp.htm>).

$$P_{\text{total}} = P_{\text{N}_2} + P_{\text{O}_2} + P_{\text{Ar}} + P_{\text{CO}_2} + P_{\text{trace gases}}$$

$$n_{\text{total}} = n_{\text{N}_2} + n_{\text{O}_2} + n_{\text{Ar}} + n_{\text{CO}_2} + n_{\text{trace gases}}$$

Mole Fraction: - a **unit-less ratio** of the mole of any one component to the mole of the entire gas mixture.
- since pressure is directly proportional to mole ($PV = nRT$), mole fraction is also the ratio between the partial pressure of one gaseous component to the total pressure of the entire gas mixture.

$$\text{Mole Fraction} = \frac{\text{Mole of a Gas Component}}{\text{Total Moles in Gas Mixture}} = \frac{\text{Partial Pressure of a Gas Component}}{\text{Total Pressure in Gas Mixture}}$$

$$\chi_1 = \frac{n_1}{n_{\text{Total}}} = \frac{P_1}{P_{\text{Total}}}$$

 χ = Mole Fraction (χ is pronounced *chi* – like *chi-tea*, not *tai-chi*) has NO UNITS.**Example 2:** Air is composed of 0.20947 of oxygen. (We would spontaneously combust if air has over 23% oxygen.) Determine the amount, in moles, and the pressure of oxygen if a compressed air tank at 4.50 atm has a total volume of 6.50 L and it is at 18.0°C.

$\chi = 0.20947$

$P_{\text{Total}} = 4.50 \text{ atm}$

$V = 6.50 \text{ L}$

$T = 18.0^\circ\text{C} = 291.15 \text{ K}$

$n_{\text{oxygen}} = ?$

$P_{\text{oxygen}} = ?$

$\chi_{\text{oxygen}} = \frac{P_{\text{O}_2}}{P_{\text{Total}}}$

$P_{\text{oxygen}} = \chi_{\text{oxygen}} P_{\text{Total}} = (0.20947)(4.50 \text{ atm})$

$P_{\text{oxygen}} = 0.943 \text{ atm}$

$P_{\text{Total}}V = n_{\text{Total}}RT$

$$n_{\text{Total}} = \frac{P_{\text{Total}}V}{RT} = \frac{(4.50 \text{ atm})(6.50 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(291.15 \text{ K})} = 1.224271003 \text{ mol}$$

$\chi_{\text{oxygen}} = \frac{n_{\text{O}_2}}{n_{\text{Total}}}$

$n_{\text{oxygen}} = \chi_{\text{oxygen}} n_{\text{Total}} = (0.20947)(1.224271003 \text{ mol})$

$n_{\text{oxygen}} = 0.256 \text{ mol}$

Example 3: A 36.0 g of sample of oxygen gas and 8.25 g of hydrogen gas is mixed in a 3.00 L container at 20.0°C before reacting them to make water. What is the partial pressure of each gas and total pressure of the entire gas mixture?

$$n_{\text{oxygen}} = \frac{m_{\text{O}_2}}{M_{\text{O}_2}} = \frac{36.0 \text{ g}}{32.00 \text{ g/mol}}$$

$$n_{\text{oxygen}} = 1.125 \text{ mol}$$

$$n_{\text{hydrogen}} = \frac{m_{\text{H}_2}}{M_{\text{H}_2}} = \frac{8.25 \text{ g}}{2.02 \text{ g/mol}}$$

$$n_{\text{hydrogen}} = 4.084158416 \text{ mol}$$

$$V = 3.00 \text{ L}$$

$$T = 20.0^\circ\text{C} = 293.15 \text{ K}$$

$$P_{\text{oxygen}} = ?$$

$$P_{\text{hydrogen}} = ?$$

$$P_{\text{Total}} = ?$$

$$P_{\text{oxygen}}V = n_{\text{oxygen}}RT$$

$$P_{\text{oxygen}} = \frac{n_{\text{O}_2}RT}{V} = \frac{(1.125 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (293.15 \text{ K})}{(3.00 \text{ L})}$$

$$P_{\text{oxygen}} = 9.02 \text{ atm}$$

$$P_{\text{hydrogen}}V = n_{\text{hydrogen}}RT$$

$$P_{\text{hydrogen}} = \frac{n_{\text{H}_2}RT}{V} = \frac{(4.084158416 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (293.15 \text{ K})}{(3.00 \text{ L})}$$

$$P_{\text{hydrogen}} = 32.7 \text{ atm}$$

$$P_{\text{Total}} = P_{\text{oxygen}} + P_{\text{hydrogen}} = 9.02 \text{ atm} + 32.7 \text{ atm}$$

$$P_{\text{Total}} = 41.8 \text{ atm}$$

Example 4: A 2.50 L flask of hydrogen gas at 850 torr is connected to a 1.50 L flask of ethene by a valve. When the valve is opened, the final pressure of the mixture is 0.867 atm, what was the initial pressure of ethene in the 1.50 L flask?

$$V_{\text{hydrogen}} = 2.50 \text{ L}$$

$$P_{\text{hydrogen}} = 850 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}$$

$$P_{\text{hydrogen}} = 1.118421053 \text{ atm}$$

(This is the initial partial pressure, not the final partial pressure of H₂. We cannot subtract P_{Total} with 1.12 atm for P_{ethene})

$$V_{\text{ethene}} = 1.50 \text{ L}$$

$$P_{\text{ethene}} = ?$$

$$V_{\text{Total}} = 2.50 \text{ L} + 1.50 \text{ L} = 4.00 \text{ L}$$

$$P_{\text{Total}} = 0.867 \text{ atm}$$

(Note that P_{Total} is already SMALLER than P_{hydrogen}. Total pressure should always be greater than partial pressure. This is telling you the partial pressure given was at initial conditions).

Since we do not have T, we have to solve for nT.

$$P_{\text{total}}V_{\text{Total}} = n_{\text{total}}RT$$

$$n_{\text{total}}T = \frac{P_{\text{Total}}V_{\text{Total}}}{R} = \frac{(0.867 \text{ atm})(4.00 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right)} = 42.26175969 \text{ mol} \cdot \text{K}$$

The number of moles for both H₂ and C₂H₄ is the same before and after they mix together.

$$P_{\text{hydrogen}}V_{\text{hydrogen}} = n_{\text{hydrogen}}RT$$

$$n_{\text{hydrogen}}T = \frac{P_{\text{H}_2}V_{\text{H}_2}}{R} = \frac{(1.118421053 \text{ atm})(2.50 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right)} = 34.07327116 \text{ mol} \cdot \text{K}$$

$$n_{\text{total}}T = n_{\text{hydrogen}}T + n_{\text{ethene}}T \Rightarrow n_{\text{ethene}}T = n_{\text{total}}T - n_{\text{hydrogen}}T$$

$$n_{\text{ethene}}T = (42.261... \text{ mol} \cdot \text{K}) - (34.073... \text{ mol} \cdot \text{K}) = 8.1884... (\text{mol} \cdot \text{K})$$

Finally, find initial partial pressure of ethene before the mixing.

$$P_{\text{ethene}}V_{\text{ethene}} = n_{\text{ethene}}RT$$

$$P_{\text{ethene}} = \frac{(n_{\text{C}_2\text{H}_4}T)R}{V_{\text{C}_2\text{H}_4}} = \frac{(8.188488528 \text{ mol} \cdot \text{K}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right)}{(1.50 \text{ L})}$$

$$P_{\text{ethene}} = 0.448 \text{ atm}$$

5.6: The Kinetic Molecular Theory of Gas

In order to explain the behaviour of an ideal gas as we have related with pressure, volume, moles and temperature, a model is needed to give us a picture of how gas particles behave in the molecular level. This model is called the **Kinetic Molecular Theory (KMT) of Gas**.

The Kinetic Molecular Theory of Gas

1. **All gaseous particles are so small that their volumes are essentially zero** especially compared to the amount of space between them.
2. **All gaseous particles are constantly moving (hence the word “kinetic”)**. Pressure exists because of the collision of these gaseous particles against the wall of the container.
3. There are no attracting or repelling forces between the particles (again due to the large distances between them).
4. **Temperature, express in Kelvin, is the average kinetic energy of the gas particles.** (*This is also the definition of temperature.*)

Root Mean Square Velocity (\bar{u} or u_{rms}): - the average velocity of a single gaseous molecule or atom in a closed system.

<u>Average Kinetic Energy</u>	
$(E_k)_{avg}$ per Atom / Molecule = $\frac{1}{2} m \bar{u}^2$	$(E_k)_{avg}$ per Mole = $N_A(E_k)_{avg} = N_A \left(\frac{1}{2} m \bar{u}^2 \right)$
$(E_k)_{avg}$ = Average Kinetic Energy	\bar{u} = Root Mean Square Velocity
m = mass of one atom or molecule in kg	N_A = Avogadro's Number

Derivation of Pressure as it relates to Average Kinetic Energy

This derivation is a complicated procedure (see Appendix 2 of page A14 to A17 in the textbook – if you have background in senior physics!). In any case, the **total pressure** of a gas relates to **kinetic energy** by the formula below.

$$P = \frac{2}{3} \left[\frac{nN_A (E_k)_{avg}}{V} \right] \qquad N_A(E_k)_{avg} = \text{Average Kinetic Energy per Mole}$$

Relating Temperature and Average Kinetic Energy

Starting with

$$P = \frac{2}{3} \left[\frac{nN_A (E_k)_{avg}}{V} \right]$$

$$\frac{PV}{n} = \frac{2}{3} N_A (E_k)_{avg} \qquad \text{(Manipulating to almost isolate } (E_k)_{avg} \text{)}$$

$$RT = \frac{2}{3} N_A (E_k)_{avg} \qquad \text{(Ideal Gas Law: } PV = nRT \Rightarrow \frac{PV}{n} = RT \text{)}$$

$$\frac{3}{2}RT = N_A(E_k)_{avg} \quad (\text{In the AP Info Sheet: } \boxed{KE \text{ per mol} = \frac{3}{2}RT})$$

$$\frac{3}{2}RT = N_A \frac{1}{2}m\overline{u^2} \quad (\text{Substitute } \frac{1}{2}m\overline{u^2} \text{ for } (E_k)_{avg})$$

$$\frac{3RT}{N_A m} = \overline{u^2} \quad (\text{Solving for } \overline{u})$$

$$\overline{u} = \sqrt{\frac{3RT}{N_A m}} \quad [N_A m = M \text{ (Molar Mass in kg/mol) because } m \text{ is in kg for Physics}]$$

OR
$$\overline{u} = \sqrt{\frac{3kT}{m}} \quad \left(\frac{R}{N_A} \text{ is replaced by } k = \text{Boltzmann's Constant}\right)$$

Root Mean Square Velocity

$$u_{rms} = \overline{u} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

$R = 8.31 \text{ J / (mol} \cdot \text{K)}$

$M = \text{Molar Mass in kg/mol}$

$m = \text{mass of one atom / molecule in kg}$

$k = \text{Boltzmann's Constant} = 1.38 \times 10^{-23} \text{ J/K}$

Example 1: A sample of argon gas is at STP in a halogen tube.

- Determine the average kinetic energy per mole of the gas.
- Calculate the root mean square velocity of an argon atom.
- Will the average kinetic energy be decreased, increased or remain the same for the following conditions?
 - the temperature is increased to 400°C as electricity is applied into the tube.
 - the volume is allowed to double as the argon gas is evacuated into a larger tube.
 - the number of moles is halved as a vacuum is used to draw out some of the argon gas.
- If the argon gas is replaced by the same amount of neon gas under STP, describe the change in the average kinetic energy and the average velocity.

At STP:

$T = 273.15 \text{ K}$

$P = 1.000 \text{ atm}$

$M = 39.95 \text{ g/mol}$

$M = 0.03995 \text{ kg/mol}$

$R = 8.31 \text{ J / (mol} \cdot \text{K)}$

$KE \text{ per mol} = ?$

$u_{rms} = ?$

$$\text{a. } KE \text{ per mol} = \frac{3}{2}RT = \frac{3}{2}(8.31 \text{ J / (mol} \cdot \text{K)})(273.15 \text{ K}) = 3404.81475 \text{ J/mol}$$

$$KE \text{ per mol} = 3.40 \times 10^3 \text{ J/mol} = 3.40 \text{ kJ/mol}$$

b. Since we do not have the mass of Ar, we have to use the first variation of the u_{rms} formula.

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(273.15 \text{ K})}{(0.03995 \text{ kg/mol})}} = \sqrt{170453.8048 \text{ J/kg}}$$

$$u_{rms} = 412 \text{ m/s}$$

c. (i) As $T \uparrow$, $KE \uparrow$

(ii) As $V \downarrow$, KE remain unchanged (KE depends on T only)

(iii) As $n \downarrow$, KE remain unchanged (KE depends on T only)

d. As Ar is replaced by Ne, T remains unchanged, therefore KE remains unchanged. However, $M \downarrow$, $u_{rms} \uparrow$

Assignment

5.5 pg. 235 #63 to 71

5.6 pg. 235–236 #73 to 80

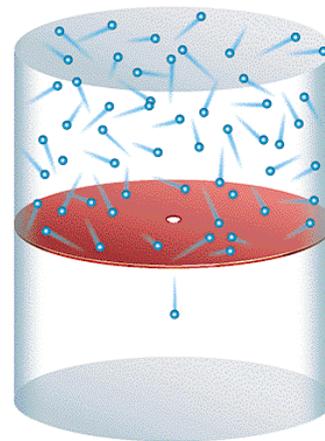
5.7: Effusion and Diffusion

Effusion: - when gas passes through from one container to the next through a small hole.

Rate of Effusion: - the speed of which a gas pass through a small hole between two containers.

- it is the same as the root mean square velocity, u_{rms} . This is because the small hole on the separating wall of the two containers allow one gas particle to pass through at a time.
- Therefore, the rate of effusion = u_{rms}

- **rate of effusion is generally measures in mL/min**



Graham's Law of Effusion: - the ratio between the effusion rate of two gases.

$$\frac{\text{Rate of Effusion (Gas 1)}}{\text{Rate of Effusion (Gas 2)}} = \frac{u_{rms} \text{ (Gas 1)}}{u_{rms} \text{ (Gas 2)}}$$

$$\frac{r_1}{r_2} = \frac{\left(\sqrt{\frac{3RT}{M_1}}\right)}{\left(\sqrt{\frac{3RT}{M_2}}\right)} = \left(\frac{\cancel{\sqrt{3RT}}}{\sqrt{M_1}}\right) \times \left(\frac{\sqrt{M_2}}{\cancel{\sqrt{3RT}}}\right)$$

Graham's Law of Effusion

$$\frac{\text{Rate of Effusion for Gas 1}}{\text{Rate of Effusion for Gas 2}} = \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

M = Molar Mass in g/mol or kg/mol

$M \downarrow$ (g/mol), Effusion Rate \uparrow (mL/min)

Example 1: Calculate the ratio of effusion rates between NH_3 (g) and HCl (g) under the same temperature.

$$M_{\text{HCl}} = 36.46 \text{ g/mol}$$

$$M_{\text{NH}_3} = 17.04 \text{ g/mol}$$

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = ?$$

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.46 \text{ g/mol}}{17.04 \text{ g/mol}}}$$

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = 1.463$$

NH_3 effuse about 1.5 times faster than HCl .

Example 2: Determine the effusion rate F_2 through a porous barrier if the effusion rate of N_2 through the same barrier is 274 mL/min.

$$r_{\text{N}_2} = 274 \text{ mL/min}$$

$$M_{\text{F}_2} = 38.00 \text{ g/mol}$$

$$M_{\text{N}_2} = 28.02 \text{ g/mol}$$

$$r_{\text{F}_2} = ?$$

$$\frac{r_{\text{F}_2}}{r_{\text{N}_2}} = \sqrt{\frac{M_{\text{N}_2}}{M_{\text{F}_2}}}$$

$$r_{\text{F}_2} = \frac{(r_{\text{N}_2})\sqrt{M_{\text{N}_2}}}{\sqrt{M_{\text{F}_2}}} = \frac{(274 \text{ mL/min})\sqrt{28.02 \text{ g/mol}}}{\sqrt{38.00 \text{ g/mol}}}$$

Since F_2 is bigger than N_2 , r_{F_2} is less than r_{N_2}

$$r_{\text{F}_2} = 235 \text{ mL/min}$$

Example 3: Using the Effusion Rate Animation by the Chemistry Department of Iowa State University (http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/gaslaw/effusion_macro.html), the volumes and times for a selected gas are determined. Complete the table below and find the molar mass of unknown gas X.

Gas	Molar Mass (g/mol)	Volume	Time	Effusion Rate (mL/min)
H ₂		100 mL	5 sec	
O ₂		100 mL	20 sec	
Xe		100 mL	40.6 sec	
Kr		100 mL	32.4 sec	
Unknown X	?	100 mL	23.5 sec	

Gas	Molar Mass (g/mol)	Volume	Time	Effusion Rate (mL/min)
H ₂	2.02	100 mL	5.00 sec	$\frac{100 \text{ mL}}{(5.00 / 60) \text{ min}} = 1200$
O ₂	32.00	100 mL	20.0 sec	$\frac{100 \text{ mL}}{(20.0 / 60) \text{ min}} = 300.0$
Xe	131.29	100 mL	40.6 sec	$\frac{100 \text{ mL}}{(40.6 / 60) \text{ min}} = 147.8$
Kr	83.80	100 mL	32.4 sec	$\frac{100 \text{ mL}}{(32.4 / 60) \text{ min}} = 185.2$
Unknown X	?	100 mL	23.5 sec	$\frac{100 \text{ mL}}{(23.5 / 60) \text{ min}} = 255.3$

We can use any gas to set up a ratio with r_X . We choose O₂ because its rate is an even number.

$$r_{\text{O}_2} = 300 \text{ mL/min}$$

$$M_{\text{O}_2} = 32.00 \text{ g/mol}$$

$$r_X = 255.3 \text{ mL/min}$$

$$M_X = ?$$

$$\frac{r_{\text{O}_2}}{r_X} = \frac{\sqrt{M_X}}{\sqrt{M_{\text{O}_2}}}$$

$$\frac{(r_{\text{O}_2})\sqrt{M_{\text{O}_2}}}{(r_X)} = \sqrt{M_X}$$

$$\left(\frac{(r_{\text{O}_2})\sqrt{M_{\text{O}_2}}}{(r_X)}\right)^2 = M_X \quad M_X = \frac{(r_{\text{O}_2})^2(M_{\text{O}_2})}{(r_X)^2} = \frac{(300 \text{ mL/min})^2(32.00 \text{ g/mol})}{(255.3 \text{ mL/min})^2}$$

Since r_X is less than r_{O_2} , X is bigger than O₂.

$$M_X = 44.2 \text{ g/mol}$$

Diffusion: - the natural tendency of a gas from an area of high concentration travels to an area where it has a lower concentration without any barriers (we sometimes called it “*moving down the concentration gradient*”) until an equilibrium state is reached.

- **in general, the Rate of Diffusion is SLOWER than the Rate of Effusion.** This is because even without the barrier, there are air particles the gas has to “fight” through to reach the area of low concentration. This is also true where both areas have roughly equal pressures.
- **the only time where the Rate of Diffusion is Greater than the Rate of Effusion is when the gas is traveled FROM an are of High Pressure to very Low Pressure (near vacuum)** – like a breach on the hull of a starship or a plane.

(See Diffusion Animation at <http://www.biologycorner.com/resources/diffusion-animated.gif>)

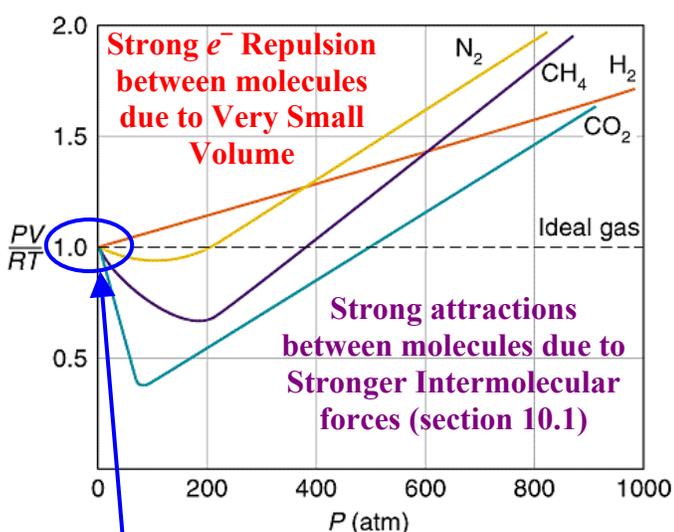
5.8: Real Gases

Real Gas: - a gas where its properties deviate from an ideal gas.

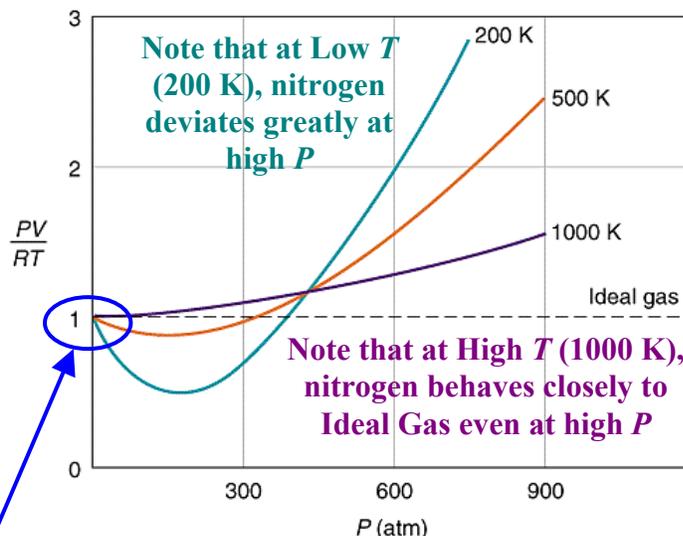
- **when we account for the fact that gaseous particles have volume, and they actually have attraction between particles (intermolecular bonds), the ideal gas law become less accurate.**
- this happens mainly **when pressure is extremely high, volume is small** and **temperature is low**. At such conditions, the small volume will make the particle size an important matter. This is the same for attraction forces between particles because temperature is low and they are moving a lot slower.

<u>Ideal Gas</u>	<u>Real Gas</u>
Low Pressure	High Pressure
High Temperature	Low Temperature

Various Gases under High Pressures at 200 K



Nitrogen Gas at various Temperatures



Commonly use Low Pressures (0 to 10 atm) and conditions that conform to an Ideal Gas ($PV = nRT$)

van der Waals Equation: - Johannes van der Waals first proposed **correctional factors** (volume and pressure due to intermolecular attractions) to correct for real gases under low volume and high pressure.

$$P_{\text{real}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

Real Gas Pressure → P_{real}
Container Volume → V
Volume Correction → nb
Pressure Correction → $a\left(\frac{n}{V}\right)^2$

$$P_{\text{real}} = P' - a\left(\frac{n}{V}\right)^2$$

$$V_{\text{actual}} = V_{\text{container}} - nb$$

n = number of moles

b = van der Waals Volume Constant

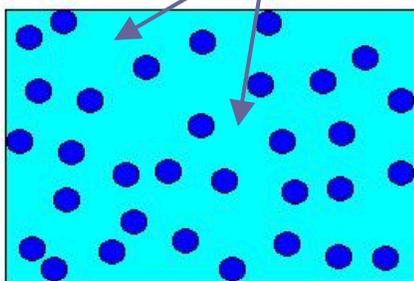
V_{actual} = Volume of Spaces between Molecules

n = number of moles

a = van der Waals Pressure Constant

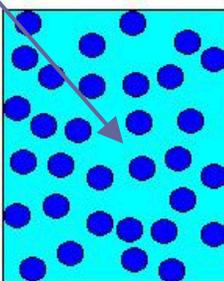
V = Volume of Container

P' = Pressure with volume correction but prior to Pressure Correction



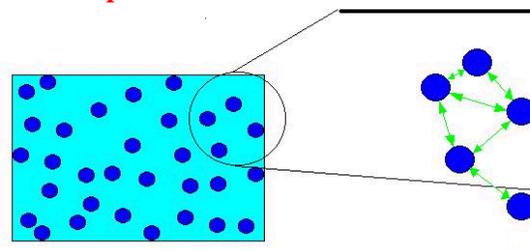
At low pressure, there are a lot of spaces between molecules. Therefore,

$$V_{\text{actual}} \approx V_{\text{container}} \text{ and } (nb \approx 0).$$



At high pressure, there is a lot less space between molecules and

$$V_{\text{actual}} < V_{\text{container}} \text{ and } (nb \text{ is significant}).$$



Intermolecular Forces or Electron Repulsions can significantly affect the u_{rms} and the collision rate against the wall of the container. This causes pressure to behave differently than ideal gas.

van der Waals Constants for Various Gases

Gas	M (g/mol)	a (atm • L ²) / mol ²	b (L/mol)
He	4.00	0.0341	0.0237
Ne	20.18	0.211	0.0171
Ar	39.95	1.35	0.0322
Kr	83.80	2.32	0.0398
Xe	131.29	4.19	0.0511
NH ₃	17.04	4.17	0.0371
H ₂ O	18.02	5.46	0.0305

Gas	M (g/mol)	a (atm • L ²) / mol ²	b (L/mol)
H ₂	2.02	0.244	0.0266
N ₂	28.02	1.39	0.0391
O ₂	32.00	1.36	0.0318
Cl ₂	70.90	6.49	0.0562
CH ₄	16.05	2.25	0.0428
CO ₂	44.01	3.59	0.0427
CCl ₄	153.81	20.4	0.1383

- Note:** - **In general, $a \gg b$** (\gg much bigger). This is because intermolecular forces has a greater effect on pressure than the amount of volume need to be corrected due to increase pressure.
- **As $M \uparrow$, a and $b \uparrow$.** This is due to more electrons available for intermolecular forces (section 10.1)
 - **Polar Molecules especially the ones with hydrogen bonds** (NH₃ and H₂O) **have bigger a and b values than non-polar molecules** with the similar molar mass due to stronger intermolecular forces.

van der Waals Equation for Real Gases

$$P_{\text{real}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (\text{rearranged to solve for } nRT - \text{ as it appears in the AP Information Sheet})$$

Example 1: 150 kg of oxygen gas is being transported in a 200 L truck under high pressure at -150°C (boiling point of oxygen is -183°C). Determine the pressure in the tank of the truck using ideal gas law and van der Waals equation of real gas. Contrast the differences in the results.

$$n = \frac{150 \times 10^3 \text{ g}}{32.00 \text{ g/mol}} = 4687.5 \text{ mol}$$

$$V = 200 \text{ L}$$

$$T = -150^\circ\text{C} = 123.15 \text{ K}$$

$$R = 0.0821 \text{ (atm} \cdot \text{L) / (mol} \cdot \text{K)}$$

$$a = 1.36 \text{ (atm} \cdot \text{L}^2) / \text{mol}^2$$

$$b = 0.0318 \text{ L/mol}$$

$$P_{\text{ideal}} = ?$$

$$P_{\text{real}} = ?$$

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{(4687.5 \text{ mol})(0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}})(123.15 \text{ K})}{200 \text{ L}}$$

$$P_{\text{ideal}} = 237 \text{ atm}$$

$$P_{\text{real}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

$$P_{\text{real}} = \frac{(4687.5 \text{ mol})(0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}})(123.15 \text{ K})}{\left[200 \text{ L} - (4687.5 \text{ mol})(0.0318 \frac{\text{L}}{\text{mol}})\right]} - \left(1.36 \frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)\left(\frac{4687.5 \text{ mol}}{200 \text{ L}}\right)^2$$

$$P_{\text{real}} = 183 \text{ atm}$$

(P_{ideal} is like Theoretical result and P_{real} is like Experimental result)

$$\% \text{ Pressure Difference} = \frac{|P_{\text{ideal}} - P_{\text{real}}|}{P_{\text{ideal}}} \times 100\%$$

$$\% \text{ Pressure Difference} = \frac{|237 \text{ atm} - 183 \text{ atm}|}{237 \text{ atm}} \times 100\%$$

$$\% \text{ Pressure Difference} = 22.8\%$$

$P_{\text{real}} < P_{\text{ideal}}$ by 22.8%, which is a significant margin. The drop in pressure is due to the **low temperature** and the **high pressure** (pressure correction, an^2/V^2 , alone is 747 atm). These two conditions combined with a relatively **small volume** for **the large number of moles** ($nb = 149 \text{ L}$ of molecules' volume out of 200 L of container space) caused the **intermolecular force to attract the molecules much more** than otherwise. This result is **a significant drop in the overall pressure**.

Assignment

5.7 pg. 236 #81 to 84

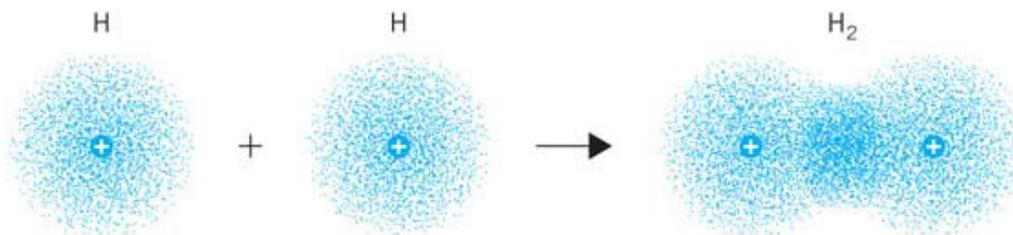
5.8 pg. 236 #85 and 86

Chapter 10: Liquids and Solids10.1: Intermolecular Forces

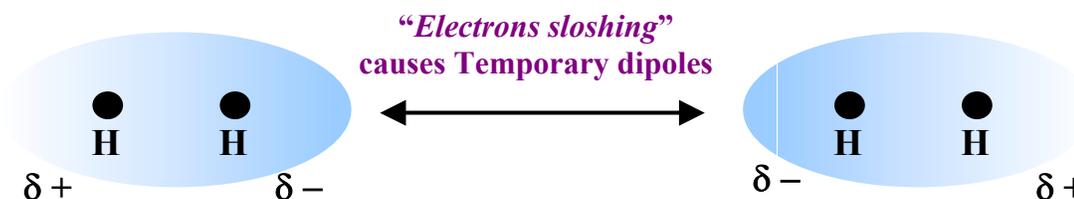
Intermolecular Forces: - attraction forces between molecules in a compound

- the strengths of the intermolecular forces **explain** the **physical properties of compounds** (solubility, boiling and freezing points).

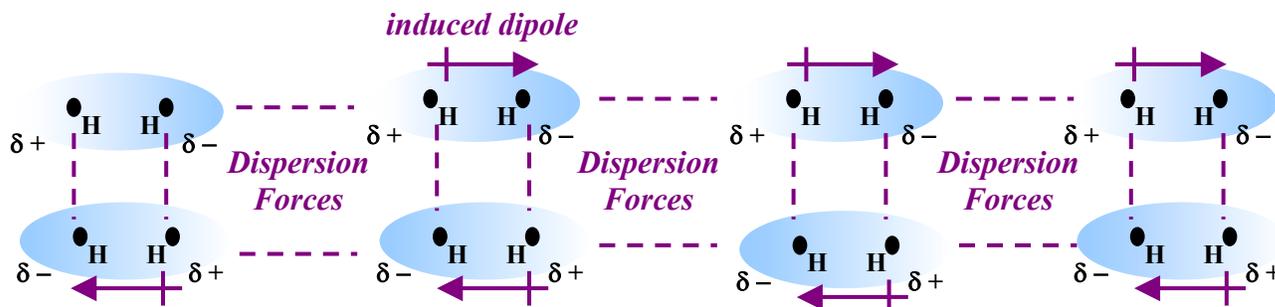
- a. **van der Waals Forces:** - named after Johannes van der Waals who studied real gases and interaction between molecules.
- there are two kinds of van der Waals forces.
 - they are **Dispersion Forces** and **Dipole-Dipole Interactions**.
- i. **Dispersion Forces:** - also known as **London Dispersion Forces** (named after Fritz London who first proposed how this force works).
- on average, the non-polar molecules do not have any permanent dipoles like polar molecules



- the “*dispersion*” is the **temporary dipole** that forms within the molecules even in non-polar molecules due to the constant motions of electrons. In one instance, they can move to one side of the molecule making it temporary polar. In another instance, electrons will move and the direction of this temporary dipole will switch.



- This constant “sloshing around” of electrons causes non-polar molecules to have these **temporary dipoles**. These temporary “*induced*” dipoles are what cause the attractions between non-polar molecules.



- even monoatomic element like Helium has London Forces. ([Check out animation at http://www.super-tech.ro/teoretic.html](http://www.super-tech.ro/teoretic.html))
- in general, *the higher the molar mass or the more electrons there are in a molecule, the stronger the London Dispersion Force* (attraction between molecules – intermolecular force). *This causes an increase in melting and boiling points of the chemical.*
- Note: All molecules have electrons. Hence, ALL molecules have London Dispersion Force.*

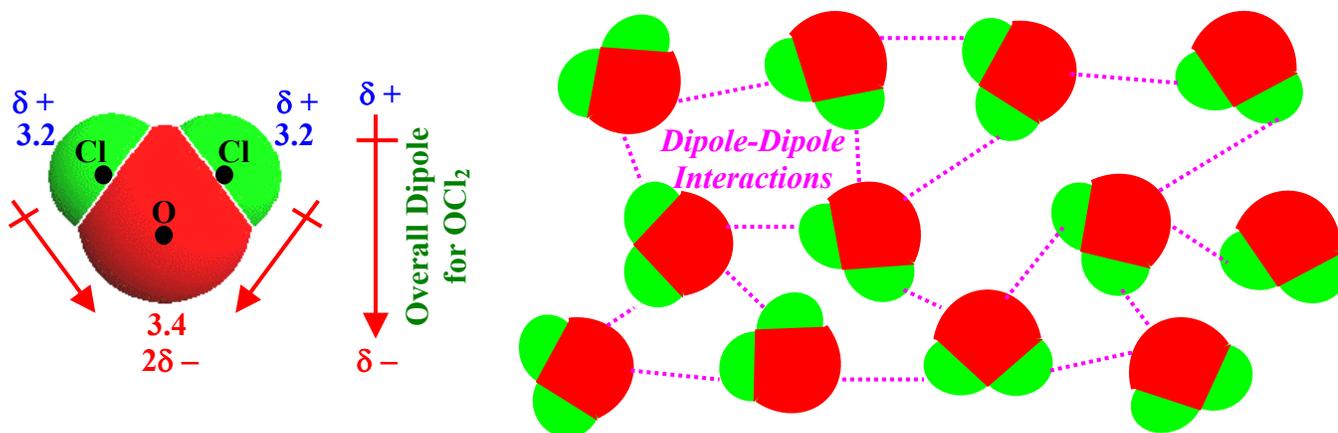
of e^- or molar mass in atom or molecule \uparrow , London Dispersion Force \uparrow , Melting and Boiling Point \uparrow

Example 1: Explain the boiling points and the melting points of the noble gases.

Noble Gases	# of e^-	Molar Mass (g/mol)	Melting Point	Boiling Point
He	2	4.00	-272°C (1 K)	-269°C (4 K)
Ne	10	20.18	-249°C (24 K)	-246°C (27 K)
Ar	18	39.95	-189°C (84 K)	-186°C (87 K)
Kr	36	83.80	-157°C (116 K)	-153°C (120 K)
Xe	54	131.29	-112°C (161 K)	-108°C (165 K)
Rn	86	222.00	-71°C (202 K)	-62°C (211 K)

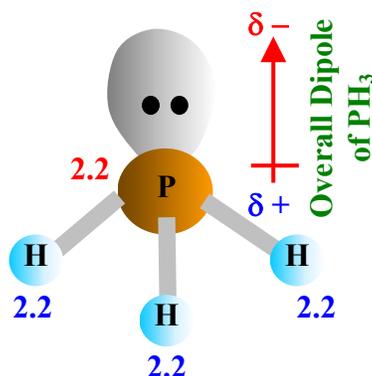
All atoms of noble gases are monoatomic non-polar. The only intermolecular force that governs the melting and boiling points is the London Dispersion Force. As the number of electrons in the noble gases increase, London dispersion force makes the attraction between the atoms greater. This in turn has an effect of increasing the boiling and melting point of the noble gas as one goes down the column.

- ii. Dipole-Dipole Interactions: - also known as simply Dipole Interactions.
 - intermolecular forces resulted from polar molecules.
 - dipole interaction is much stronger than Dispersion Force.

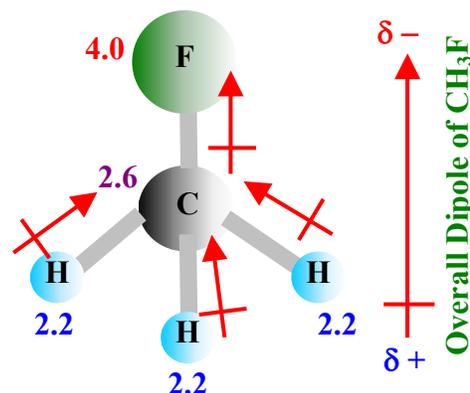


Example 2: Order the boiling points from the least to greatest for the following compounds with similar molar mass. PH_3 (34.00 g/mol), CH_3F (34.04 g/mol), and SiH_4 (32.13 g/mol)

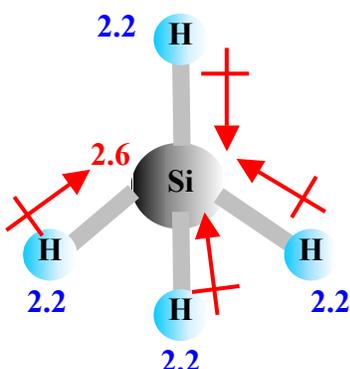
Since PH_3 , CH_3F and SiH_4 have similar molar mass, any differences in boiling points cannot be due to London Dispersion forces. Since dipole-dipole interactions exist in polar molecules, we have to examine the molecular geometry and structure of each compound.



PH_3 has a trigonal pyramid geometry (VSEPR) and is Polar. Even though the P–H bonds have no polarity (electronegativities of P and H are the same), the lone pair on one end of the P atom causes an uneven distribution of electrons.



CH_3F has a tetrahedral geometry and is very polar. The C–F bond along with the C–H bonds have strong polarity. The overall dipole moment for the molecule has electrons around the F atom.

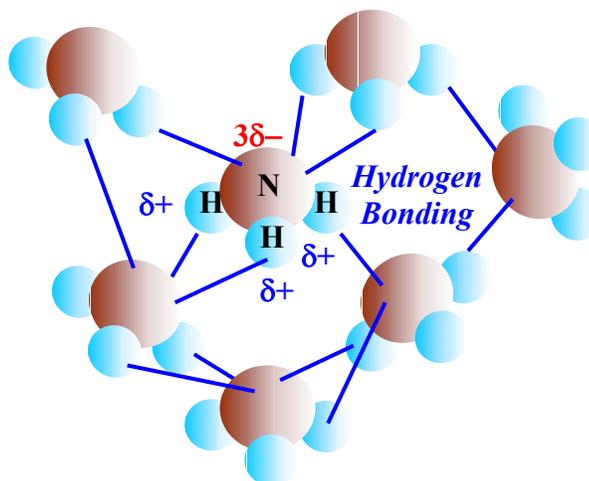
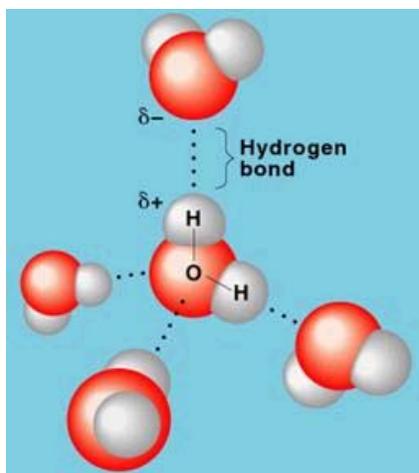


SiH_4 has a tetrahedral geometry with equal dipoles of Si–H bonds cancels out all bond polarities. Hence, SiH_4 is Non-Polar.

Since non-polar molecule have no dipole interactions, SiH_4 should have the lowest boiling point. PH_3 is less polar than CH_3F due to the difference in electronegativities between P–H bond and C–F with C–H bonds. Therefore, CH_3F must have the highest boiling point.

Boiling Point: $\text{SiH}_4 < \text{PH}_3 < \text{CH}_3\text{F}$

- b. **Hydrogen Bonds:** - are intermolecular bonds that involve hydrogen atom with very electronegative atom that also consists of lone pairs.
- these include O–H, N–H, and H–X (halogen atoms) bonds.
 - the resulting molecule is always polar. Therefore, all hydrogen bonding molecules also have dipole interactions.
 - hydrogen bond is the **STRONGEST** of the intermolecular bonds.

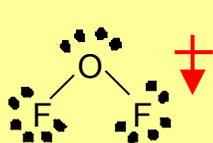


(Check out the Hydrogen Bond Animation at <http://www.northland.cc.mn.us/biology/Biology111/animations/hydrogenbonds.html>)

Example 3: Account for the differences in the boiling points of the compounds listed below.

Molecule	Molar Mass (g/mol)	London Dispersion Forces	Dipole Interactions	Hydrogen Bonds	Boiling Point
OF ₂	54.00	✓	✓	✗	-145°C (128 K)
Ne	20.18	✓	✗	✗	-246°C (27 K)
HF	20.01	✓	✓	✓	19°C (292 K)
H ₂ O	18.02	✓	✓	✓	100°C (373 K)
NH ₃	17.04	✓	✓	✓	-33°C (240 K)
CH ₄	16.05	✓	✗	✗	-161°C (112 K)

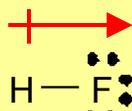
Again, we need to draw the structural formulas of these molecules and compare their polarities.



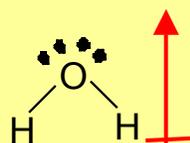
OF₂ is polar with dipole interactions



Ne is non-polar with dispersion forces only



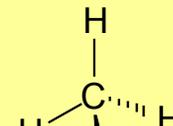
HF is polar with hydrogen bonds



H₂O is polar with hydrogen bonds



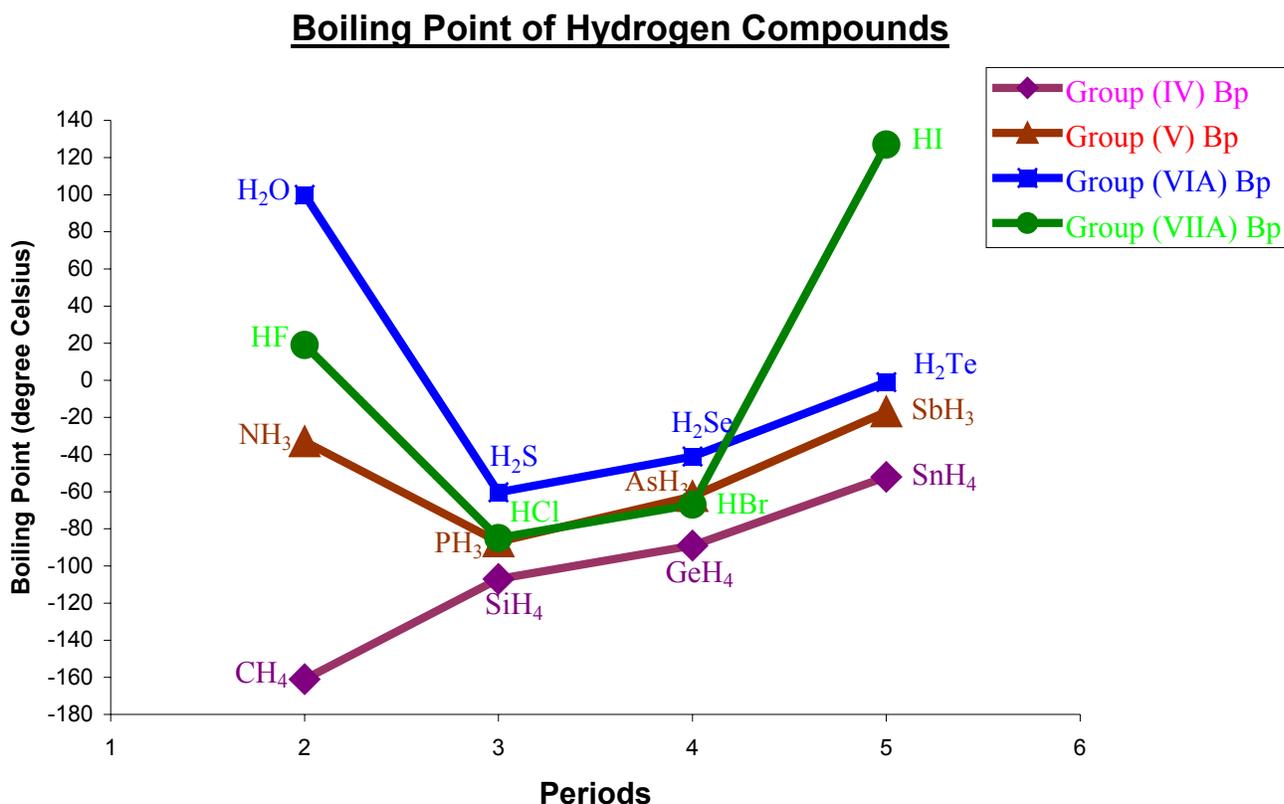
NH₃ is polar with hydrogen bonds



CH₄ is non-polar with dispersion forces only

Notice that the hydrogen bond molecules (HF, H₂O and NH₃) have boiling points much higher than molecule with just dipole interactions (OF₂) and the ones with only London Dispersion Forces (Ne and CH₄).

Example 4: Given the graph below on the boiling points of hydrogen compounds with different group series, explain the following using the concepts of chemical bonding.



- The hydrogen compounds in the Group (VIA) series have higher boiling points than hydrogen compounds in the other series.
- The first hydrogen compounds in Groups (VA), (VIA) and (VIIA), namely NH₃, H₂O and HF, have higher boiling points than most other hydrogen compounds in their respective series. On the other hand CH₄ has a lowest boiling point in its own Group (IVA) series.

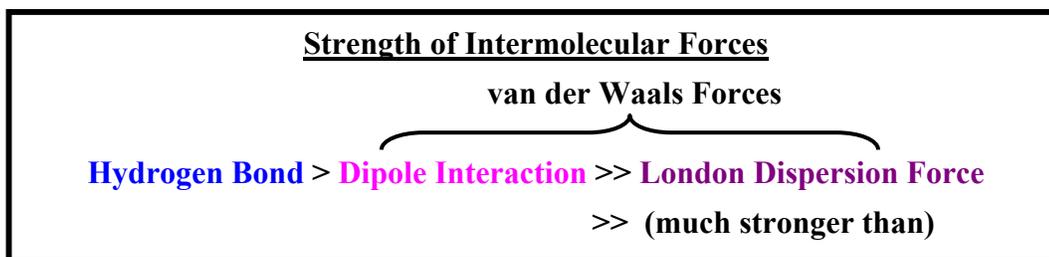
a. All hydrogen compounds in the Group (VIA) series are very polar and have hydrogen bonds. The V-shape molecules characterized in Group (VIA) create a greater dipole moment than other series (Group (VA) with its trigonal pyramid shape and Group (VIIA) with its linear form). On the other hand, all hydrogen compounds in the Group (IVA) series are non-polar and only have London dispersion forces. Since hydrogen bonds are stronger intermolecular forces than London dispersion forces, the hydrogen compounds in the Group (IVA) series have the lowest boiling points than the counterparts in the other series.

b. NH₃, HF and H₂O have stronger hydrogen bonds than most other hydrogen compounds in their series. The difference between the electronegativities with H is the greatest in row 2 (Electronegativities increase from left to right and from bottom to top of the Table). This huge difference in electronegativities in NH₃, HF and H₂O is what causes their boiling points to buckle the trend. After NH₃, HF and H₂O the rest of the hydrogen compounds in the respective series follow the effect of London dispersion forces, the higher the molar mass, the stronger the dispersion forces, and the increase in boiling points is the result.

CH₄ in the Group (IVA) series do not buckle the trend because the entire series are non-polar. The only intermolecular force at work is the London dispersion force. Hence, CH₄ has a lower boiling point than SiH₄.

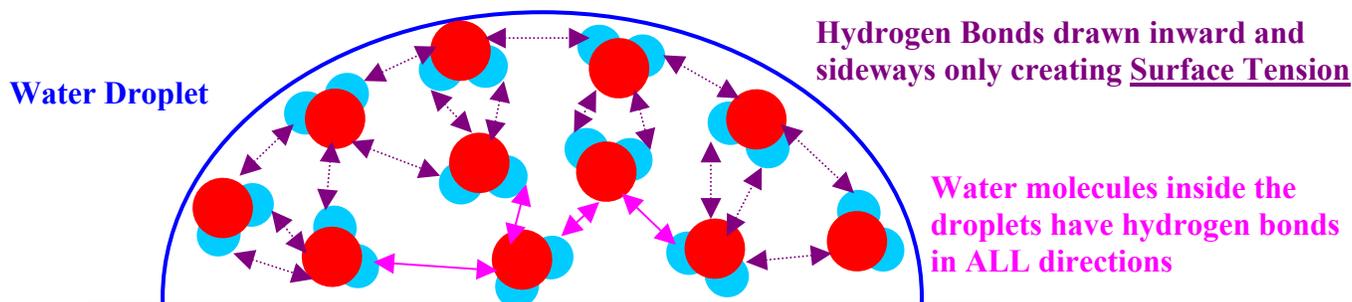
Summary of Intermolecular Forces

1. Intermolecular Bonds involve in a compound explain its physical properties such as solubility (“like dissolves like”), boiling and melting points (energy involved in physical phase change).
2. van der Waals Forces consist of London Dispersion forces (apply to all molecules) and Dipole Interactions (apply to polar molecules).
3. Hydrogen Bonding is the *strongest* of all intermolecular bonds.

10.2: The Liquid State

Surface Tension: - the inward force of a liquid to minimize its surface area.

- water’s hydrogen bond cannot attract with molecules in the air. Therefore, the higher net force is pushed inward, leaving a spherical surface with a higher surface tension.

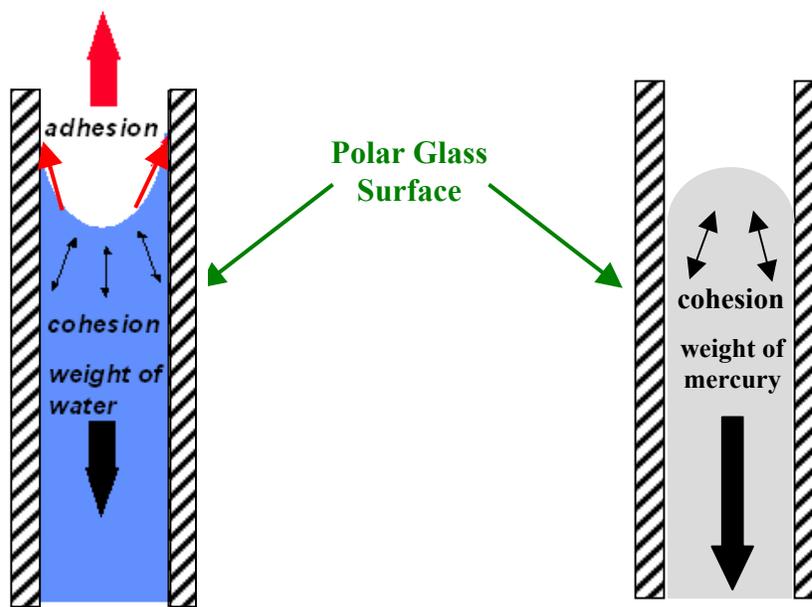


Surfactant: - a surface-active agent that decreases the surface tension (**example:** detergent).

Capillary Action: - when liquid suddenly rises in a narrow tube.

- there are two forces that causes capillary action to occur. They are **cohesive forces** and **adhesive forces**.

- Cohesive Forces:** - forces between molecules (intermolecular forces like London Dispersion Force, Dipole interactions, and Hydrogen Bonding).
- Adhesive Forces:** - forces between the liquid and the inner surface of the container.
 - in the case of capillary action, it would be the inside of the narrow tube.
 - **polar liquid molecules with inner surface of the container that are also polar** will create a large adhesive force (**example:** water and glass).
 - **non-polar liquid molecules with polar inner surface of the container** will create a small adhesive force (**example:** mercury and glass).



Both adhesion and cohesion forces are both strong.
 However, **adhesion** > **cohesion**.
 Therefore, water meniscus is **concave**.

Cohesion forces are weak (Hg is non-polar).
 There is no adhesion.
 However, **cohesion** > **adhesion**.
 Therefore, mercury meniscus is **convex**.

Viscosity: - the measure of a liquid resistance to flow.

- **polar liquids tend to have high viscosity** because they have both adhesive force (with the container's inner surface) and cohesive forces (with other molecules within the liquid). These attractions slows down the flow rate. Thus, viscosity increases.

Assignment

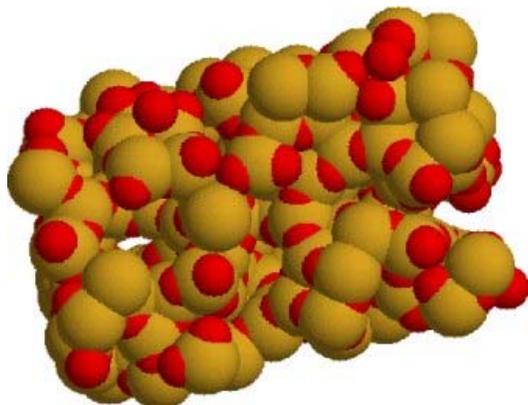
10.1 pg. 500–501 #35 to 40

10.2 pg. 501 #41 to 44

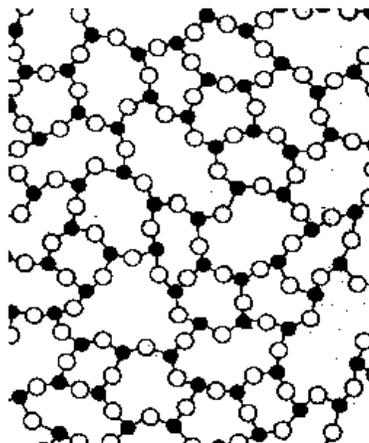
10.3: An Introduction to Structure and Types of Solids**Structural Classification of Solids**

1. **Amorphous Solids**: - solids where the arrangements of atoms are very disorganized with no repeating patterns.

Examples: glass (heated silica), quartz glass (quartz crystal has a crystalline structure) and opal.



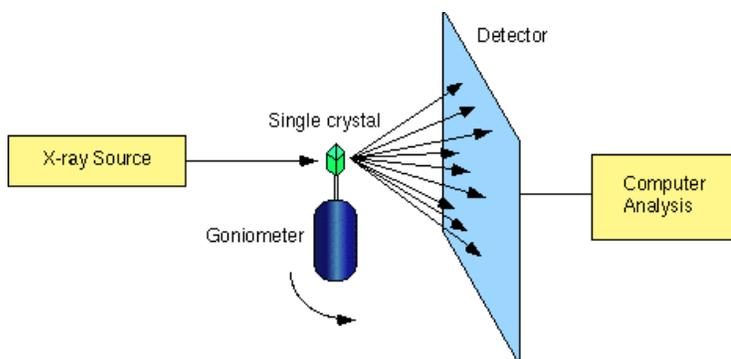
Structure of Silica



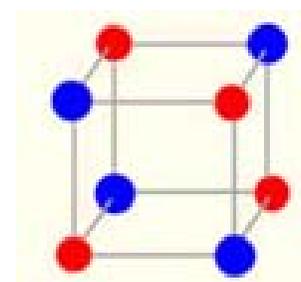
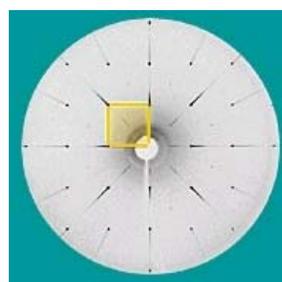
There is no regular molecular arrangement in a quartz glass

2. **Crystalline Solids**: - solids where the arrangements of atoms are highly organized.
 - the 3-dimensional positions of the atoms in a crystalline solid is called a **lattice**.
 - the smallest repeating structure in a lattice is called a **unit cell**.

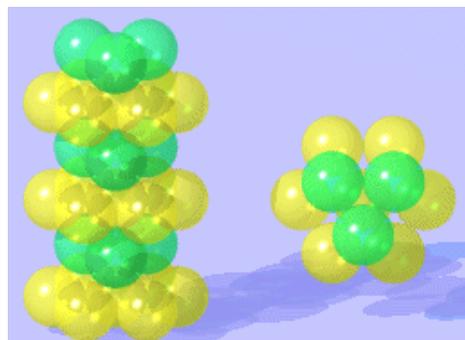
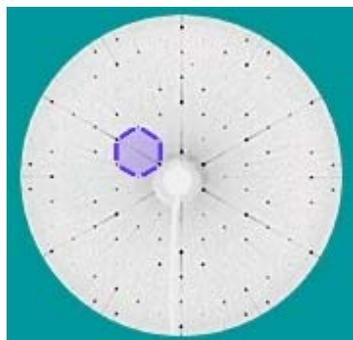
X-Ray Diffraction: - a diffraction method using x-ray to analysis the crystalline structure of a solid.
 - basically the x-ray is scattered because the crystalline solid provides an opening in the unit cell to interfere the x-ray.



Basic Concept of X-Ray Diffraction



X-Ray Diffraction and the representation of a simple cubic unit cell (one out of many cubic crystalline structures)



X-Ray Diffraction and the representation of a hexagonal closest packed unit cell (one out of many closest packing arrangement)

Intramolecular Forces: - attraction forces between atoms **WITHIN** a molecule.
 - **the strengths of the intramolecular forces explain the amount of energy involved in a chemical change.**

Types of Crystalline Solids

- Ionic Solids**: - solids that involved a combination of metal and non-metal elements.
 - intramolecular bonds are ionic bonds.
- Covalent Solids**: - solids that involved a combination of **different** non-metals.
- Atomic Solids**: - elemental solids that involve:
 - physical mixtures of metals (metal alloys) and metal elements** (gold, lead ... etc.).
 - metalloids** (elements close to the staircase of the Table – carbon, silicon ... etc.).
 - Group (VIII A) Elements** ($\text{He}_{(s)}$, $\text{Ne}_{(s)}$, $\text{Ar}_{(s)}$, $\text{Kr}_{(s)}$ and $\text{Xe}_{(s)}$) at extremely low temperature where the noble gases freeze.

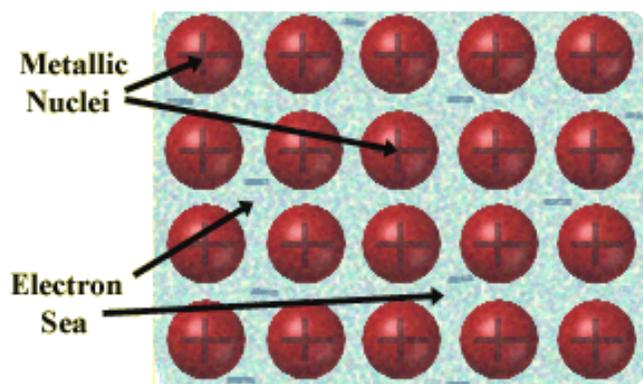
10.4 & 10.5: Structure and Bonding in Metal & Network Atomic Solids

Different Types of Atomic Solids

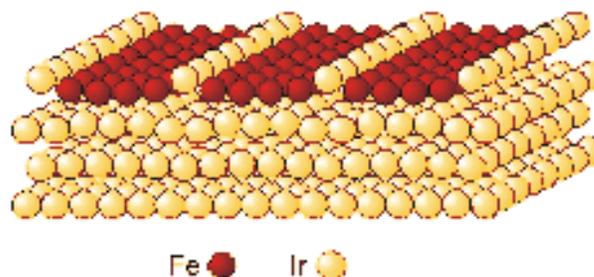
- Metals and Alloys**: - characterized by **delocalized non-directional covalent bonds** (can be pictured as a bunch of positive charged nuclei floating in a “*sea of valence electrons*”).

See animation (<http://mychemistrypage.future.easyspace.com/General/bonding/metallic.htm>)

- These valence electrons have not been ionized, but they are usually so far removed from the nucleus that they can be viewed as ionized (hence the word **delocalized**). There is no dipole interactions involved in metallic bonds (therefore the term **non-directional**), but they do **exhibit small covalent properties** due to their close proximity to each other.
- since there is a sea of valence electrons, metals and alloys are very **good conductors of electricity**.
- all metals and alloys are **closest packing (atoms are packed in layers to minimize spaces in between)**. This explains the **high densities, good heat conductivities**.
- have **different ranges of hardness and melting points**.

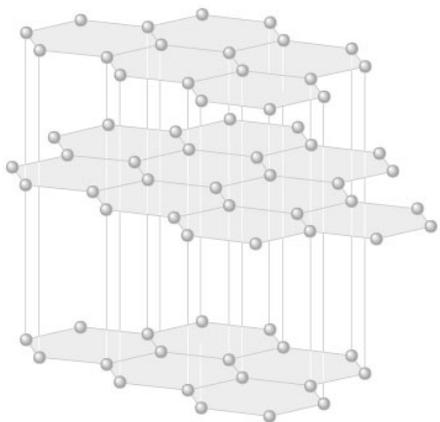


Metallic Bonds in metals and Alloys with metallic nuclei in a sea of valence electrons

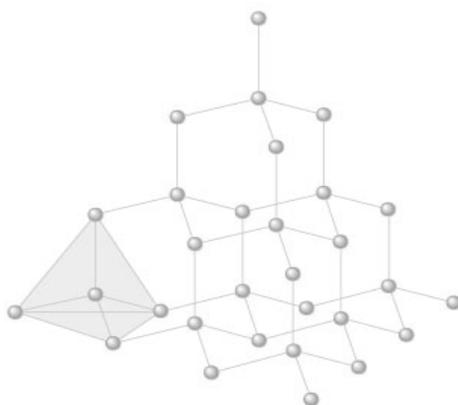


Iron-Iridium Alloy where atoms are organized in layers

2. **Metalloids**: - consists of elements near the “*staircase*” of the Table (examples are carbon in a form of diamond and silicon dioxide in a form of quartz crystal).
- commonly called **network solids** because they **form giant molecules characterized by directional covalent bonding**.
 - contains **no discrete molecular units where an array or network of atoms are held together by conventional covalent bonds** (which are directional with dipoles) of **neighboring atoms**.
 - due to a more organized crystalline structure, they are typically **hard and have high melting points**.
 - because there is no “sea of valence electrons” as in metallic solids, network solids tend to be **poor electric conductors (good insulator)**. Exception is with silicon elements. Si has smaller networks than diamonds, allowing some electrons to pass through. Therefore, **silicon is sometimes called a semiconductor**.



Carbon as **Graphite** has weak layered network with delocalized bonding network (only some carbon atoms are connected)



Carbon as **Diamond** has strong tetrahedral network where all four bonding sites of each carbon atoms are connected

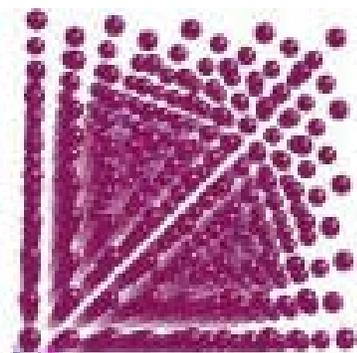


Carbon Network as **C₆₀**, Buckminsterfullerene, was discovered in 1985.

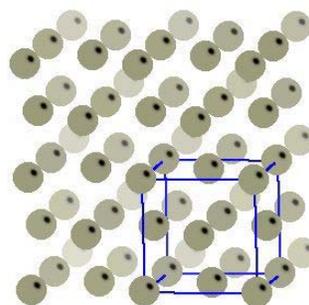


Quartz crystal has a hexagonal network structure. For a 3-D look, [check out the website at Exploring Earth](http://earthsci.terc.edu/content/investigations/es0506/es0506page06.cfm) (<http://earthsci.terc.edu/content/investigations/es0506/es0506page06.cfm>)

3. **Solid Group (VIIIA) Elements**: - when noble gases freeze, they form a **cubic closest packing structures, but are non-directional and non-covalent**.
- the only intermolecular forces between them are **London Dispersion forces**.



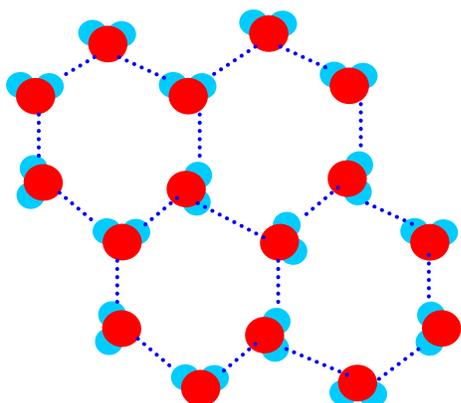
Solid Ne Crystal Structure



Solid Ar Crystal Structure

10.6: Molecular SolidsProperties of Molecular (Covalent) Compounds

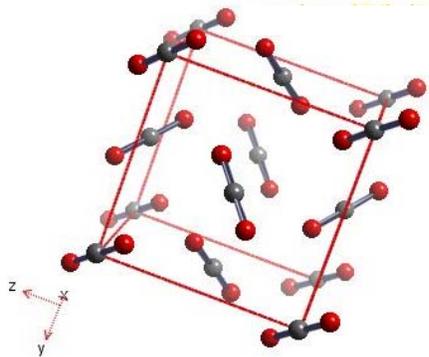
1. **Molecular Compounds tend to have much Lower Boiling and Melting Points than ionic compounds.** This is because solid covalent compounds use **weak intermolecular forces to form their lattice structures**, which does not take much energy to break them. Their boiling points are lower than ionic compounds because there are **no ion interactions in liquid state, only intermolecular forces**.
2. **Molecular Compounds are Soft.** Again, covalent compounds **have a weak lattice structure made of intermolecular bonds** that makes them soft.
3. **Molecular Compounds tend to be More Flammable than ionic compound.** This is due to some non-metals like carbon and sulfur, which **combine readily with oxygen in combustion reactions**.
4. **Most Molecular Compounds are Insoluble in Water.** Because **water is very polar** and has lots of hydrogen bonds, it can only dissolve covalent compounds that are polar as well **“Like Dissolves Like”**. Since **most covalent compounds are fairly non-polar**, they do not dissolve in polar water well.
5. **Molecular Compounds do NOT Conduct Electricity in their Solid States** due to a lack of delocalized electrons.
6. **Soluble Molecular Compounds do NOT Conduct Electricity in Water.** This is simply due to the fact that covalent compounds **do not dissociate into ions or electrolytes** like soluble ionic compounds do.



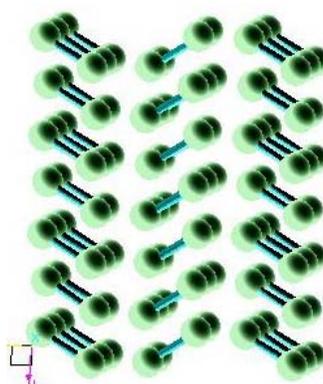
Due to the hydrogen bonds in water, it forms a *honeycomb shape* and expands in volume when it crystallizes into ice



Even though no two snowflakes are alike, all of them have a basic hexagonal shape as dictated by the bent shape of water molecule and its hydrogen bonds



Dry Ice, $\text{CO}_2(s)$, is a covalent compound that has a crystalline structure



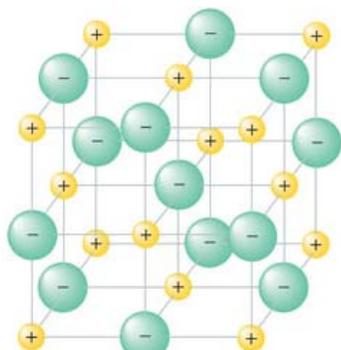
Even a halogen like $\text{I}_2(s)$ has a crystalline structure



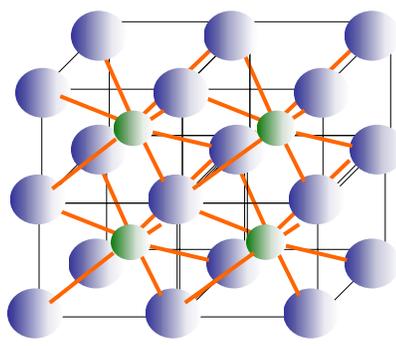
Phosphorus, $\text{P}_4(s)$ can form crystalline structure

10.7: Ionic Solids**Properties of Ionic Compounds**

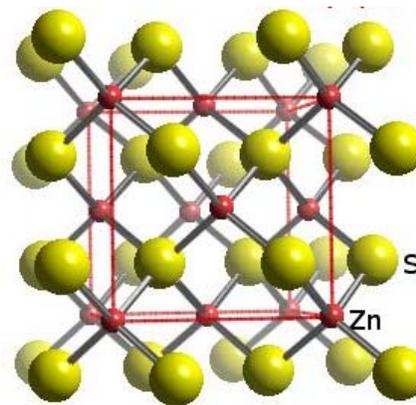
1. **Ionic Compounds have a definite Crystalline Structure and are Poor Conductors of Electricity and Heat in their Solid Form.** Conduction of electricity and heat requires ions to move freely within the solid. The lattice structures of the solid ionic compounds do not allow ions to move freely.



⊕ Na⁺ ⊖ Cl⁻
**Simple Cubic
 Unit Crystalline
 Structure of NaCl**



⊕ Cs⁺ ⊖ Cl⁻
**Body Centred Cubic
 Unit Crystalline
 Structure of CsCl**



**Face Centred Cubic
 Unit Crystalline
 Structure of ZnS**

2. **Ionic solids are generally High Melting Points (typically 300°C to 1000°C).** Since a strong force can only shatter the crystal but not bend it as in metals, **the energy needed to completely break up the lattice structure (lattice energy) is very large** and it is the same energy needed to melt the ionic compounds.
3. **Ionic solids are Hard and Brittle.** The lattice structure of all ionic compounds holds the ions in definite positions. When the compound encountered a strong force, the close proximity of the ions stay close together. This causes the crystal to **shatter**, not bent like metal solid would.
4. **Ionic solids can be Melted to form Liquids that are Electrical Conductors.** Ionic solids melt when the ions gain enough energy to break the lattice structure. They are move freely and can carry electrical charge through the liquid. This explains why a molten ionic substance conducts electricity, but a solid ionic material doesn't. The ions move through the liquid can carry charge from one place to another.
5. **Soluble ionic solids dissolve to form solutions that are Electrical Conductors.** (Not all ionic substances are soluble in water.) Soluble ionic compounds form **electrolytes (ions in aqueous from)** that allow the conduction of electricity.

General Strength of Intramolecular Bonds in Solids

Metallic > *Ionic > Network > Molecular > Group (VIIIA)



Intramolecular Bonds >> Intermolecular Bonds

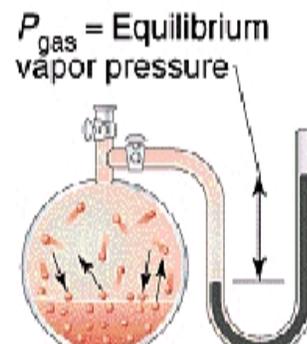
***Ionic Bonds can be Stronger than some Metallic Bonds (depending on the metal / alloy)**

Assignment

10.7 pg. 502–503 #67, 68

10.8: Vapour Pressure

Vapour Pressure: - the pressure existed above a liquid when its rate of evaporation is the same as the rate of its condensation.
 - sometimes refers to as **equilibrium vapour pressure** because **equilibrium** means the same rate of a two-way process.



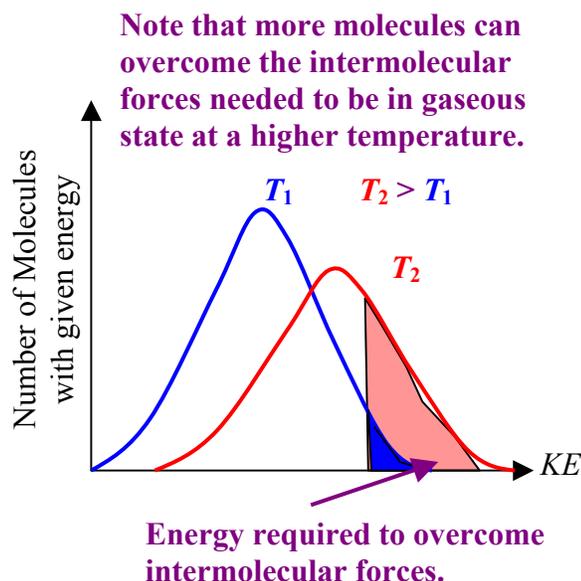
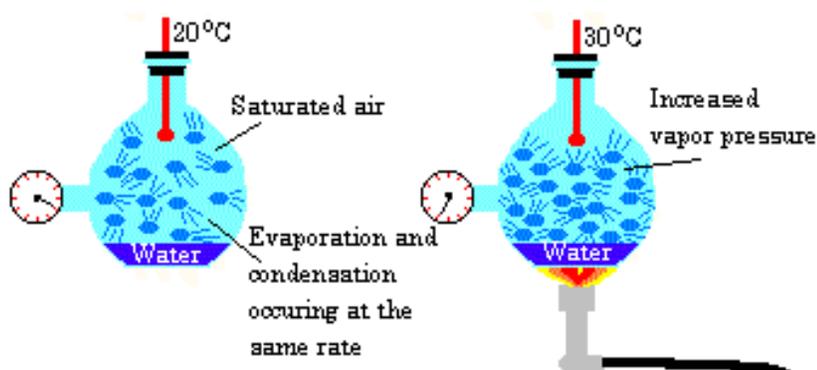
Vapour Pressure

$$P_{\text{atmosphere}} = P_{\text{vapour}} + P_{\text{Hg column}}$$

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

- in general, for a particular compound, **as temperature increases, the vapour pressure increases.**
- This is because the **higher the temperature, kinetic energy increases** and **more liquid molecules will overcome the intermolecular forces** to become a gas. Therby, **increasing vapour presuure.**

Temperature \uparrow , Vapour Pressure \uparrow



Volatile: - when liquids has a high vapour pressure.
 - when comparing compounds at the same temperature, the compound that has a lower boiling point is considered more volatile because it will have a higher vapour pressure.
 - when **intermolecular forces are weak**, the **compound is more volatile**. This is simply because it takes **less energy for the liquid to evaporate**.

Heat of Vaporization (ΔH_{vap}): - amount of heat needed to boil 1 mole of a compound from liquid to gas at its boiling point.
 - the **stronger the intermolecular force, the higher the heat of vaporization**.

Intermolecular Force \uparrow , ΔH_{vap} \uparrow

Calculating Vapour Pressure

P_{vap} = Vapour Pressure (torr) ΔH_{vap} = Heat of Vaporization (J/mol) T = Temperature in K
 R = Gas Constant (8.3145 J/ (K • mol))
 A = Constant Factor relating to Vapour Pressure of a Particular Liquid

$$P_{\text{vap}} = A e^{\frac{-\Delta H_{\text{vap}}}{RT}}$$

$$\ln(P_{\text{vap}}) = \ln\left(Ae^{\frac{-\Delta H_{\text{vap}}}{RT}}\right)$$

$$\ln(P_{\text{vap}}) = \ln(A) + \ln\left(e^{\frac{-\Delta H_{\text{vap}}}{RT}}\right)$$

$$\ln(P_{\text{vap}}) = \ln(A) + \frac{-\Delta H_{\text{vap}}}{RT}$$

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

(P_{vap} is an exponential function of the reciprocal of T)

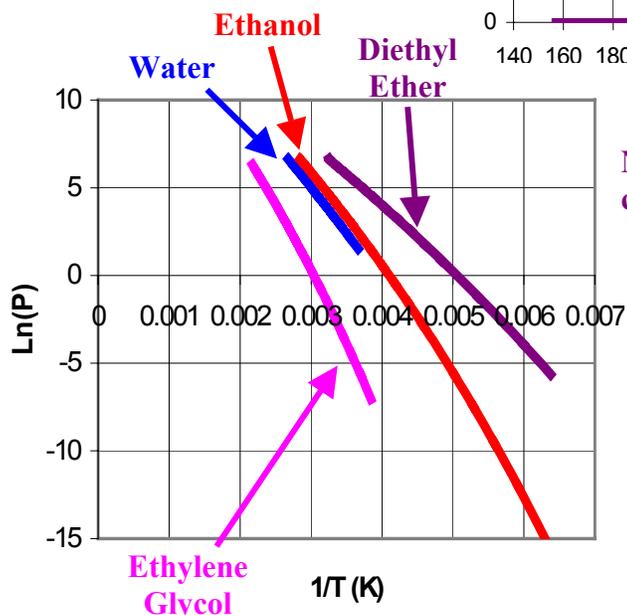
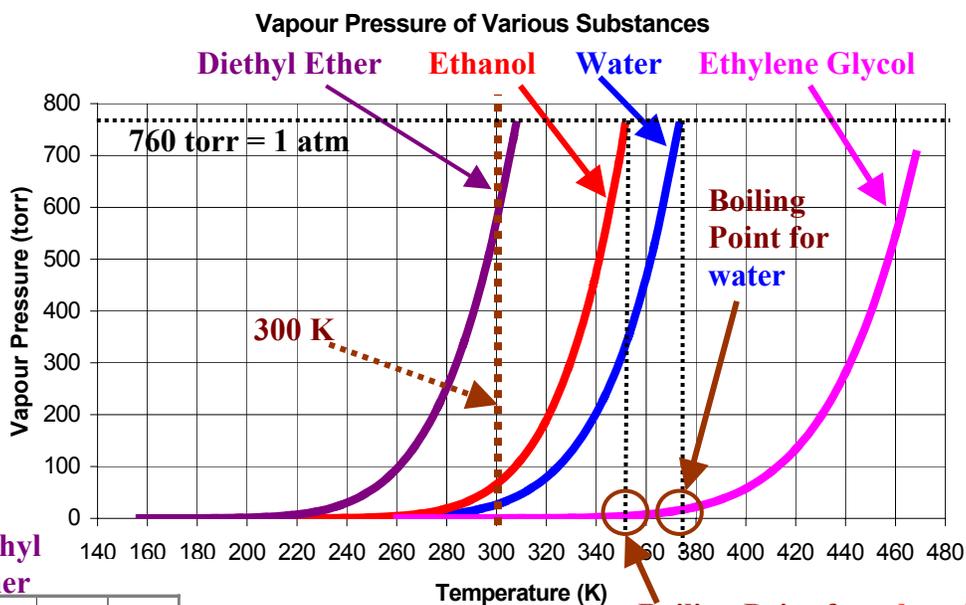
(Natural Log [ln] both sides of the equation can bring the exponent of the natural number down)

[Using Logarithm Law: $\ln(MN) = \ln(M) + \ln(N)$]

[$\ln(e^x) = x$] and let $\ln(A) = C$

[Now, $\ln(P_{\text{vap}})$ has a linear relationship with $(1/T)$]

Note that at a certain temperature, let's say 300 K, the P_{vap} in increasing order is Ethylene Glycol < Water < Ethanol < Diethyl Ether. This is because diethyl ether, unlike other compounds has no hydrogen bonding (least intermolecular forces), and therefore largest P_{vap} .



Note: For substances, when $P_{\text{vap}} = 1 \text{ atm} = 760 \text{ torr}$, the corresponding temperature represents the boiling point.

When $y = \ln(P_{\text{vap}})$ is plotted against $x = (1/T)$, the graphs turned linear

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

with *slope* = $\frac{-\Delta H_{\text{vap}}}{R}$ and *y-intercept* = $C = \ln(A)$

(Check out Animation at

http://cwx.prenhall.com/petrucci/medialib/media_portfolio/text_images/030_VaporPvsTemp.MOV)

Example 1: The following data is collected for octane. Using your TI-83 Plus Calculator,

- graph P_{vap} versus T .
- linearized the previous graph by graphing $\ln(P_{\text{vap}})$ versus $(1/T)$.
- obtain the equation of the linearized graph.
- calculate the ΔH_{vap} of octane.
- determine the normal boiling point at 760 torr.

Temperature (K)	Vapour Pressure (torr)
277	3.88
297	13.32
317	37.83
337	92.68
357	201.59
377	398.13

a. Graph P_{vap} versus T .

Entering Data using TI-83 Plus Calculator:

STAT **ENTER** **Enter Values**

1:Edit...
 2:SortA(
 3:SortD(
 4:ClrList
 5:SetUpEditor

L1	L2	L3	Z
277	3.88	-----	
297	13.32		
317	37.83		
337	92.68		
357	201.59		
377	398.13		

L2(6) =	398.13		

6th Score entered

Check if you entered the Correct Number of Data Values

To plot Scatter Plot on TI-83 Plus Calculator:

- Because we are plotting from a set of data, not from an equation, we have to turn on STAT PLOT.

2nd **STAT PLOT**
Y =

STAT PLOTS

1:Plot1...Off
 L1 L2

2:Plot2...Off
 L1 L2

3:Plot3...Off
 L1 L2

4:PlotsOff

ENTER

Plot1 Plot2 Plot3
 Off Off Off
 Type:

 Xlist:L1
 Ylist:L2
 Mark: + .

Select Scatter Plot

- Set Window by identifying the Minimum and Maximum Values of Both Variables

WINDOW

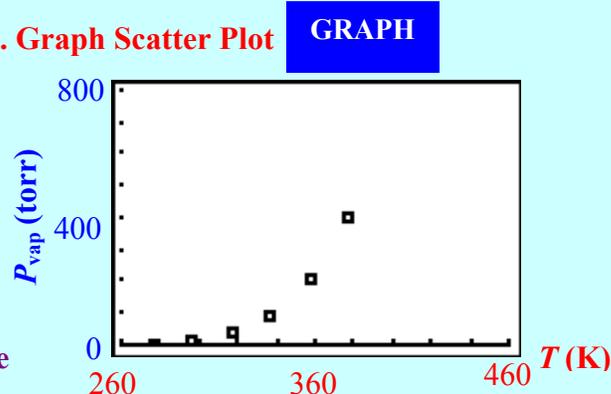
x: [260, 460, 20]
 y: [0, 800, 100]

WINDOW

Xmin=260
 Xmax=460
 Xscl=20
 Ymin=0
 Ymax=800
 Yscl=100
 Xres=1

The reason we set $Y_{\text{max}} = 800$ is because we will have to solve for the boiling point at 760 torr in part d.

- Graph Scatter Plot



b. Linearized the previous graph by graphing $\ln(P_{\text{vap}})$ versus $(1/T)$.

1. Use $L_3 = "1/L_1"$ to obtain $(1/T)$

L1	L2	#	# 3
277	3.88	.00361	
297	13.32	.00337	
317	37.83	.00315	
337	92.68	.00297	
357	201.59	.0028	
377	398.13	.00265	

Cursor must be on the column heading before entering formula

" must be used to enter formula

2nd

L1

1

ALPHA

MEM "

+

2. Use $L_4 = "ln(L_2)"$ to obtain $\ln(P_{\text{vap}})$

L2	L3	#	# 4
3.88	.00361	1.3558	
13.32	.00337	2.5893	
37.83	.00315	3.6331	
92.68	.00297	4.5292	
201.59	.0028	5.3062	
398.13	.00265	5.9868	

Cursor must be on the column heading before entering formula

" must be used to enter formula

2nd

L2

2

ALPHA

MEM "

+

3. Set up Plot 2

2nd

STAT PLOT

Y =

Select Plot 2

```

STAT PLOTS
1:Plot1...On
  ↳ L1 L2
2:Plot2...Off
  ↳ L1 L2
3:Plot3...Off
  ↳ L1 L2
4:PlotsOff
    
```

ENTER

Select On

```

Plot1: 2002 Plot3
Off Off
Type: [ ] [ ] [ ]
Xlist: L3
Ylist: L4
Mark: [ ] +
    
```

Select L3

2nd

L3

3

Select L4

4. Turn off Plot 1

2nd

STAT PLOT

Y =

Select Plot 1

```

STAT PLOTS
1:Plot1...On
  ↳ L1 L2
2:Plot2...On
  ↳ L3 L4
3:Plot3...Off
  ↳ L1 L2
4:PlotsOff
    
```

ENTER

Select Off

```

Plot1: 2002 Plot2 Plot3
On Off Off
Type: [ ] [ ] [ ]
Xlist: L1
Ylist: L2
Mark: [ ] +
    
```

2nd

L4

4

5. Set Window by Using ZoomStat (Automatic Adjusted Window Settings)

ZOOM

Select Option 9

```

ZOOM MEMORY
3:Zoom Out
4:ZDecimal
5:ZSquare
6:ZStandard
7:ZTrig
8:ZInteger
9:ZoomStat
    
```

ENTER

Graph will appear



1/T (K)

c. obtain the equation of the linearized graph

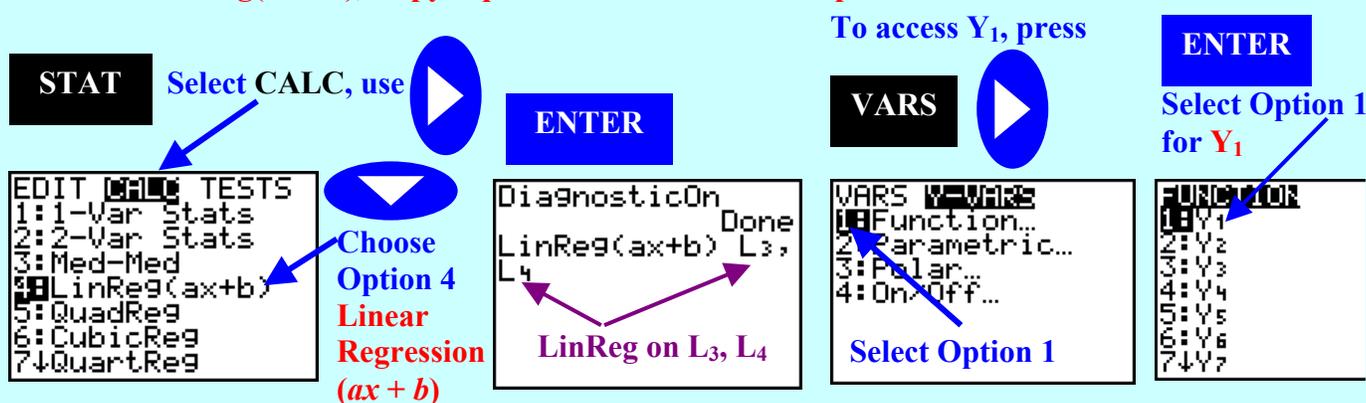
1. Turn Diagnostic On

Note: After Diagnostic On is selected, it will remain ON even when the calculator is turned Off. However, resetting the calculator will turn the Diagnostic Off (factory setting).

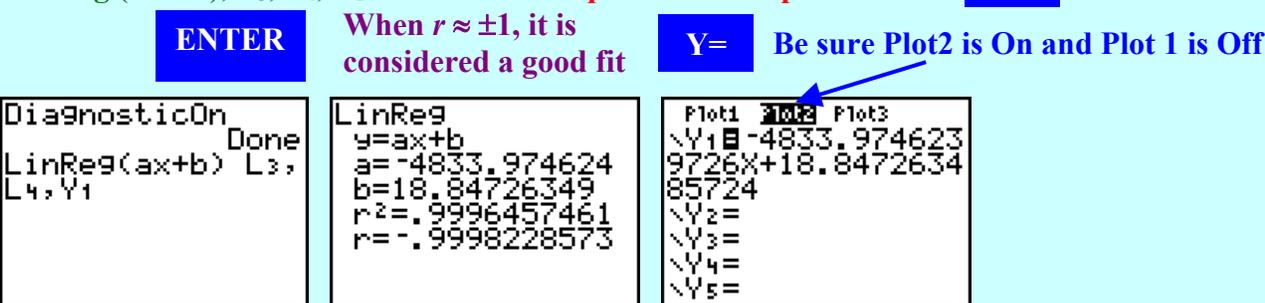


Turning Diagnostic On gives correlation (a measure of how well the equation fits the data points)

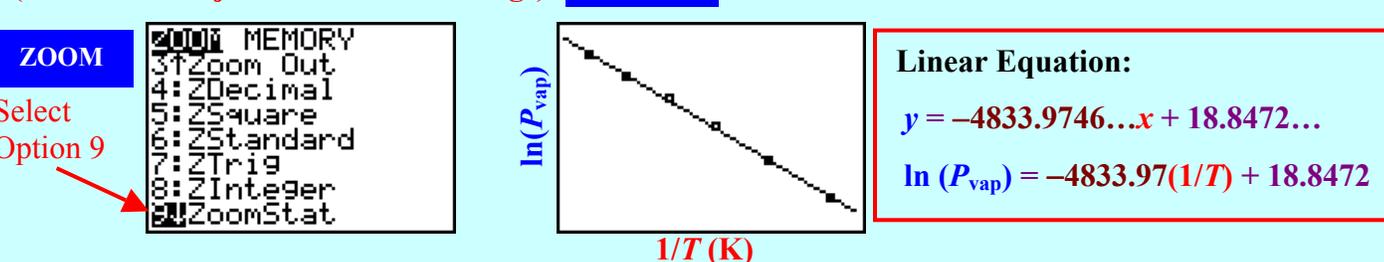
2. Obtain LinReg(ax + b), Copy Equation to Screen and Graph Best Fit Line on Scatter Plot



LinReg (a + bx), L3, L4, Y1 calculates the equation and copied into the Y= Screen.



3. Set Window by Using ZoomStat (Automatic Adjusted Window Settings)



d. Calculate the ΔH_{vap} of octane

$$\ln(P_{\text{vap}}) = -4833.97(1/T) + 18.8472$$

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

$$\Delta H_{\text{vap}} = 4.02 \times 10^4 \text{ J/mol} = 40.1 \text{ kJ/mol}$$

$$\text{slope} = \frac{-\Delta H_{\text{vap}}}{R} = -4833.97 \text{ K}$$

$$-\Delta H_{\text{vap}} = -4833.97 \text{ K} (8.3145 \text{ J/(K} \cdot \text{mol)})$$

e. Determine the normal boiling point at 760 torr.

$$P_{\text{vap}} = 760 \text{ torr}$$

$$\Delta H_{\text{vap}} = 4.02 \times 10^4 \text{ J/mol}$$

$$R = 8.3145 \text{ J/(K} \cdot \text{mol)}$$

$$\frac{-\Delta H_{\text{vap}}}{R} = -4833.97 \text{ K}$$

$$C = 18.8472$$

$$T = ?$$

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

$$\ln(760) = -4833.97(1/T) + 18.8472$$

$$\ln(760) - 18.8472 = -4833.97 (1/T)$$

$$\frac{\ln(760) - 18.8472}{-4833.97} = \frac{1}{T}$$

$$T = \frac{-4833.97}{\ln(760) - 18.8472}$$

$$T = 396 \text{ K} = 123^\circ\text{C}$$

Comparing P_{vap} of the Same Liquid at Two Different T :

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

(Equating each equation with C)

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

(Bring both P_{vap} and T on either side)

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

[Using Logarithmic Law $\ln(M) - \ln(N) = \ln\left(\frac{M}{N}\right)$]

Clausius-Clapeyron Equation of Vapour Pressures

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

$$P_{\text{vap},T_1} = P_{\text{vap}} \text{ (torr) at } T_1$$

ΔH_{vap} = Heat of Vaporization (J/mol)

$$P_{\text{vap},T_2} = P_{\text{vap}} \text{ (torr) at } T_2$$

T_1 and T_2 = Different Temperatures (K)

Example 2: At the top of Mount Everest with an altitude of 29,028 feet, the atmospheric pressure drops to 253 torr. Given that the heat of vaporization of water is 40.65 kJ/mol at its normal boiling point, which is 100°C at 1 atm, determine the boiling point of water at that elevation.

$$P_{\text{vap},T_1} = 1 \text{ atm} = 760 \text{ torr}$$

$$T_1 = 100^\circ\text{C} = 373.15 \text{ K}$$

$$P_{\text{vap},T_2} = 253 \text{ torr}$$

$$\Delta H_{\text{vap}} = 40.65 \text{ kJ/mol} \\ = 40650 \text{ J/mol}$$

$$R = 8.3145 \text{ J/(K} \cdot \text{mol)}$$

$$T_2 = ?$$

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

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

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

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

$$T_2 = \frac{1}{\left(\frac{8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}}{40650 \text{ J/mol}}\right) \ln\left(\frac{760 \text{ torr}}{253 \text{ torr}}\right) + \frac{1}{373.15 \text{ K}}} = \frac{1}{0.0029048655 \text{ K}^{-1}}$$

$$T_2 = 344 \text{ K} = 71.1^\circ\text{C}$$

Example 3: Liquid oxygen at -200°C has a vapour pressure of 10.7 kPa. It boils at -183°C . What pressure must be exerted to gaseous oxygen to condense it to a liquid at -120°C if its heat of vaporization is 6.82 kJ/mol?

$$P_{\text{vap},T_1} = 10.7 \text{ kPa} \times \frac{760 \text{ torr}}{101.325 \text{ kPa}} \\ = 80.3 \text{ torr}$$

$$T_1 = -200^\circ\text{C} = 73.15 \text{ K}$$

$$T_2 = -120.0^\circ\text{C} = 153.15 \text{ K}$$

$$\Delta H_{\text{vap}} = 6.82 \text{ kJ/mol} \\ = 6820 \text{ J/mol}$$

$$R = 8.3145 \text{ J/(K} \cdot \text{mol)}$$

$$P_{\text{vap},T_2} = ?$$

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

$$\ln\left(\frac{80.3 \text{ torr}}{P_{\text{vap},T_2}}\right) = \frac{(6820 \text{ J/mol})}{(8.3145 \text{ J/(K} \cdot \text{mol)})} \left(\frac{1}{153.15 \text{ K}} - \frac{1}{73.15 \text{ K}}\right)$$

$$\ln\left(\frac{80.3 \text{ torr}}{P_{\text{vap},T_2}}\right) = -5.857427103$$

$$e^{\ln\left(\frac{80.3 \text{ torr}}{P_{\text{vap},T_2}}\right)} = e^{-5.857427103} \quad (e^{\ln(x)} = x)$$

$$\frac{80.3 \text{ torr}}{P_{\text{vap},T_2}} = 0.0028585891$$

$$P_{\text{vap},T_2} = \frac{80.3 \text{ torr}}{0.0028585891}$$

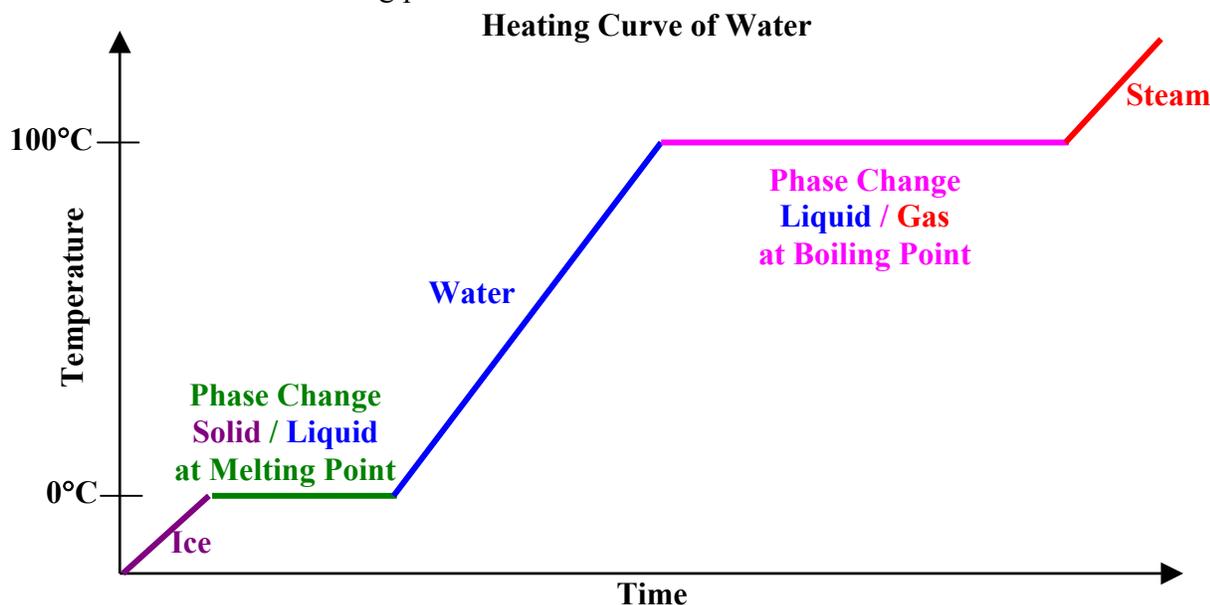
$$P_{\text{vap},T_2} = 2.81 \times 10^4 \text{ torr} = 37.0 \text{ atm}$$

An enormous pressure is needed to keep oxygen in liquid phase at a temperature above its regular boiling point.

Heating Curve: - a graph of temperature versus time as a substance is heated from a solid phase to a gaseous phase.

- when a substance is undergoing a **phase change**, its **temperature remains at a constant (the plateau on the heating curve)** until all molecules acquired enough energy to overcome the intermolecular forces necessary. This is commonly referred to as the **potential change** of a substance.
- when a substance is undergoing **temperature change** within a particular phase, it is referred to as **kinetic change**.

Heat of Fusion (ΔH_{fus}): - the amount of heat needed to melt one mole of substance from solid to liquid at its melting point.



Normal Melting Point: - the temperature where **vapour pressures of liquid is equaled to that of a solid** under normal atmospheric condition of 1 atm.

- when temperature is at the normal melting point, both liquid and solid coexist.
- when $T < \text{Melting Point}$, $P_{\text{vap}} \text{ Solid} < P_{\text{vap}} \text{ Liquid}$. Hence, any liquid's vapour pressure will be used by the solid to equilibrate its own vapour pressure. Thus, liquid will slowly become a solid below its melting point.
- when $T > \text{Melting Point}$, $P_{\text{vap}} \text{ Liquid} < P_{\text{vap}} \text{ Solid}$. As such, any solid's vapour pressure will be used by the liquid to equilibrate its own vapour pressure. Therefore, solid will slowly become a liquid above its melting point.

Normal Boiling Point: - the temperature where **vapour pressures of liquid is equaled to that of a gas** under normal atmospheric condition of 1 atm.

- when temperature is at the normal boiling point, both liquid and gas can coexist.
- when $T < \text{Boiling Point}$, $P_{\text{vap}} \text{ Liquid} < P_{\text{vap}} \text{ Gas}$. Hence, any vapour pressure of a gas will be used by the liquid to equilibrate its own vapour pressure. Thus, the gas will slowly become a solid below its boiling point.
- when $T > \text{Boiling Point}$, $P_{\text{vap}} \text{ Gas} < P_{\text{vap}} \text{ Liquid}$. As such, any liquid's vapour pressure will be used by the gas to equilibrate its own vapour pressure. Therefore, liquid will slowly become a gas above its boiling point.

Sublimation: - when a solid becomes a gas, and vice-versa, directly without undergoing a liquid phase in between.

Sublimation Point: - the temperature where **vapour pressures of solid is equaled to that of a gas**.

Normal Sublimation Point: - the temperature where **vapour pressures of solid is equaled to that of a gas** under standard atmospheric pressure of 1 atm.

Supercooled Liquid: - when a liquid is cooled too rapidly, its temperature is below the melting point.
- happens because molecules need time rearrange themselves for reystallization to become a solid.

Superheated Liquid: - when a liquid is heated too rapidly, its temperature is above the boiling point.
- happens because molecules need time to completely break apart their intermolecular bonds to become a gas.
- the bubbles of a **superheated liquid tend to be large that burst violently** (known as **bumping**) as it's vapour pressure of the liquid is greater than that of the atmospheric pressure.

Assignment

10.8 pg. 504 #75 to 81

10.9: Phase Diagrams

Phase Diagram: - a digaram with axes of Presuure versus Temperature to illustrate all three phases of a substance.
- it is more useful than a heating curve because boiling and melting points are pressure dependent, and the user now can see where the melting and boiling point are at any pressure. The curve of the vapour pressure versus temperature of a liquid is only a line on the phase diagram.
- it allows the user to identify the phase of a substance at a certain pressure and temperature.

Solid-Liquid Line: - a line that outlines the temperatures and the corresponding pressures where solid and liquid phases coexist.
- used to find the **melting point** of a substance at any given pressure.

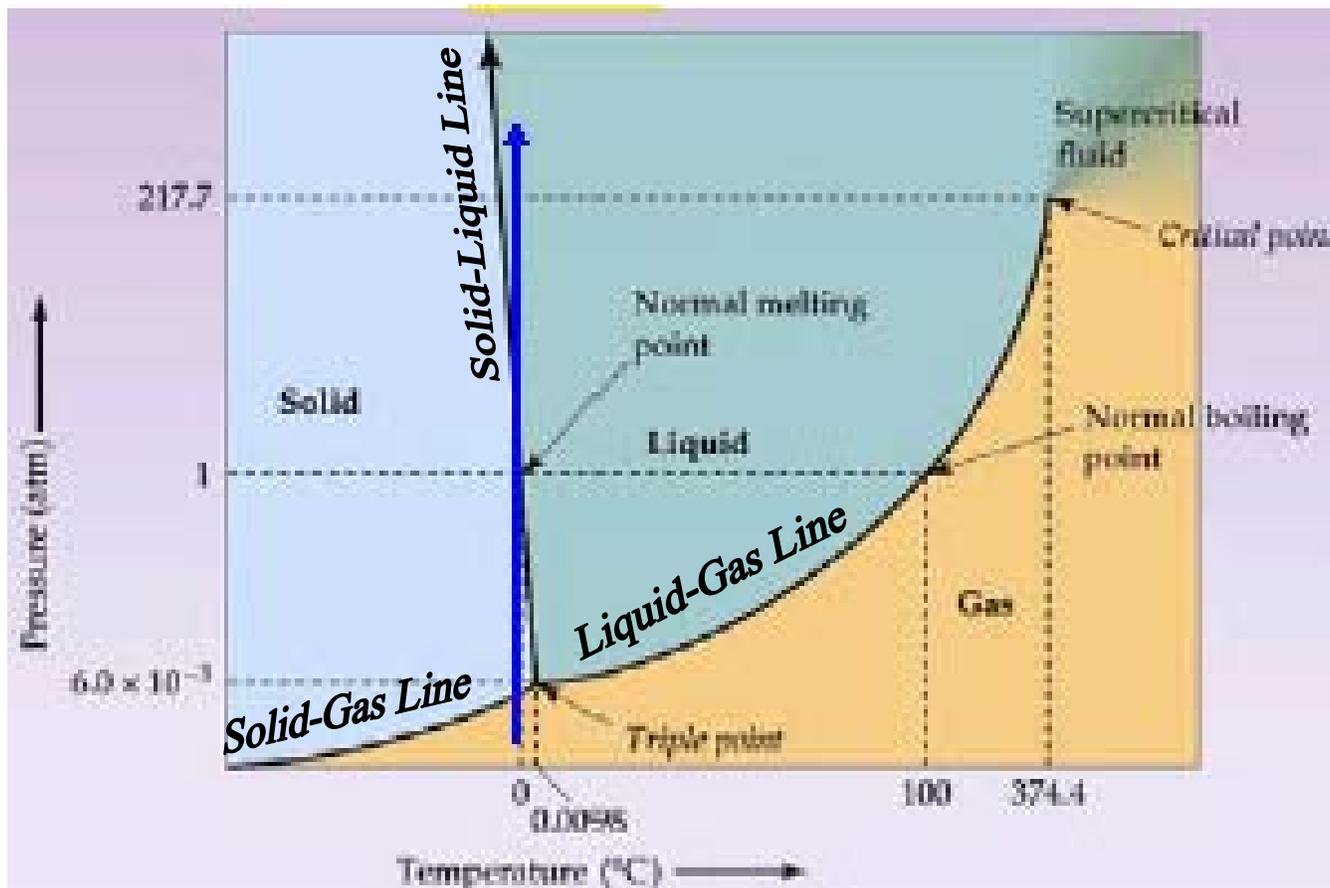
Liquid-Gas Line: - a line that outlines the temperatures and the corresponding pressures where liquid and gas phases coexist.
- used to find the **boiling point** of a substance at any given pressure.

Solid-Gas Line: - a line that outlines the temperatures and the corresponding pressures where solid and gas phases coexist.
- used to find the **sublimation point** of a substance at any given pressure.

Triple Point: - a point indicating the pressure and temperature where all solid-liquid, liquid solid, and solid-gas line meet.
- this is the **pressure and temepertaure conditions where all three phases can coexist**.

- Critical Point:** - a point at the end of the liquid-gas line which indicates an intermediate “fluid” region where liquid can be converted to gas instantaneously without waiting for phase change .
- the temperature at critical point is called critical temperature and the pressure at critical point is called critical pressure.
 - at this region (beyond the critical pressure and temperature), the liquid will become a gas without going through a change of state.

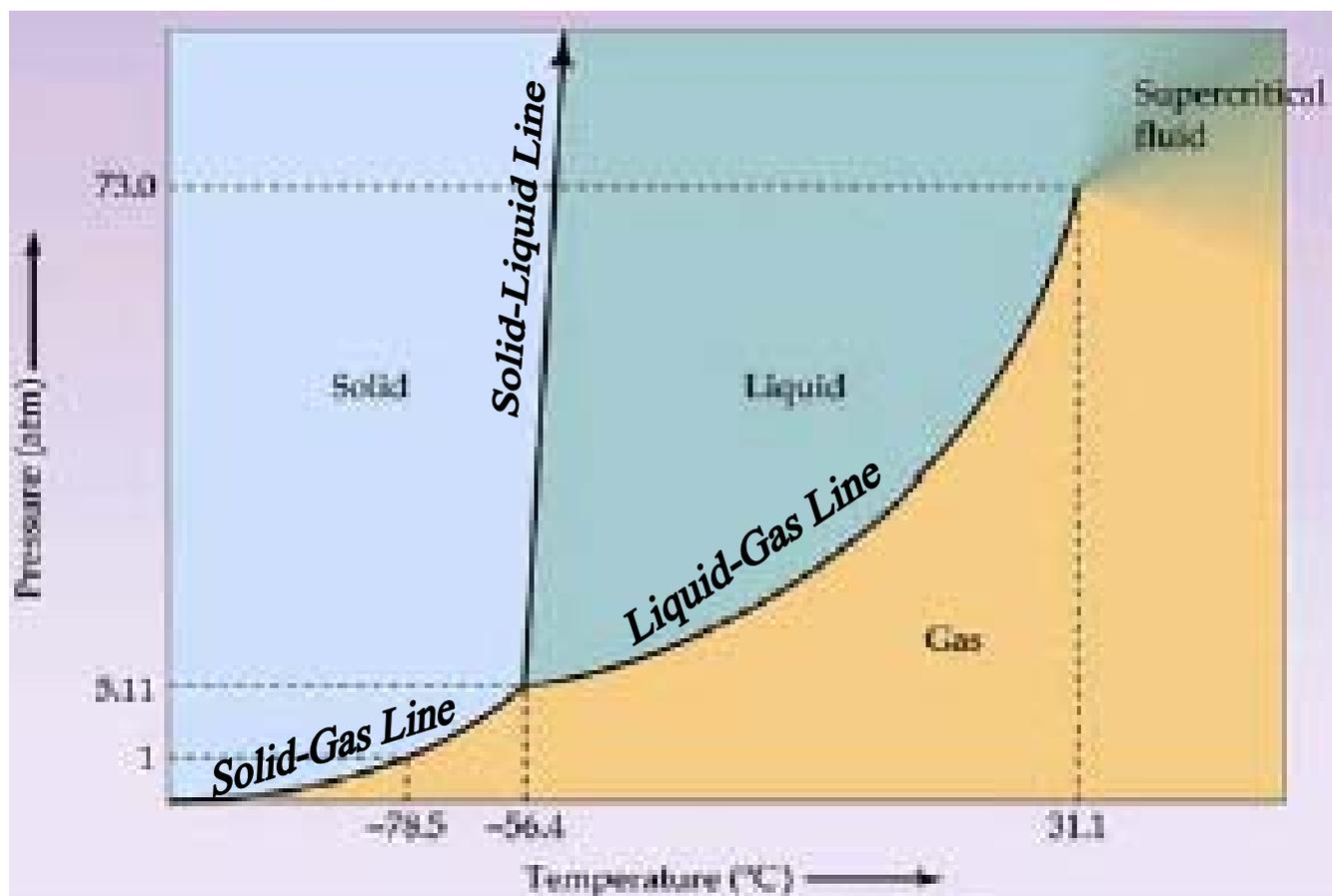
Phase Diagram of Water



From the phase diagram of water:

- at 1 atm, water has a normal melting point of 0°C and a normal boiling point at 100°C.
- there is no normal sublimation point because the solid-gas line ends well under 1 atm.
- the negative slope of the solid-liquid line indicates that as pressure increases, the melting point of water decreases.
- the positive slope of the liquid-gas line illustrates that as pressure increases, the boiling point of water also increases.
- the positive slope of the solid-gas line shows that as pressure increases, the sublimation point of water increases as well.
- the triple point, where all three phases can coexist, is at 0.0098°C and 6.0×10^{-3} atm (4.56 torr).
- the critical point of water is at 374.4°C and 217.7 atm. Beyond this critical temperature and pressure, water will become gaseous instantaneously.

Phase Diagram of Carbon Dioxide

**From the Phase Diagram of Carbon Dioxide:**

- at 1 atm, carbon dioxide has a normal sublimation point of -78.5°C .
- there is no normal melting and boiling points because carbon dioxide's solid-gas line is well above normal atmospheric condition of 1 atm.
- the positive slope of the solid-liquid line indicates that as pressure increases, the melting point of carbon dioxide increases.
- the positive slope of the liquid-gas line illustrates that as pressure increases, the boiling point of carbon dioxide also increases.
- the positive slope of the solid-gas line shows that as pressure increases, the sublimation point of carbon dioxide increases as well.
- the triple point, where all three phases can coexist, is at -56.4°C and 5.11 atm (518 kPa or 3884 torr).
- the critical point of carbon dioxide is at 31.1°C and 73 atm. Beyond this critical temperature and pressure, liquid carbon dioxide will become gaseous instantaneously.

Assignment
10.9 pg. 505 #87 to 89

Chapter 11: Properties of Solutions**11.1: Solution Composition**

Solution: - a homogeneous mixture of two or more substances (solute(s) and solvent).

Solvent: - the largest component of a solution.

Solutes: - the smaller components of a solution.

Molarity (Concentration): - moles of solute per Litre of solution ($M = \text{mol/L}$).

Molarity (Concentration)

$$C = \frac{n}{V}$$

$C = \text{Concentration (M = mol/L)}$ $n = \text{moles of Solute}$ $V = \text{Total Volume of Solution}$

Molality: - moles of solute per kilogram of solvent ($m = \text{mol/kg}$).

Molality

$$\text{Molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

$\text{Molality} = m \text{ (mol/kg)}$ $n = \text{moles of Solute}$ $m_{\text{solvent}} = \text{Mass of Solvent in kg}$

Mass Percent: - the ratio of mass of a solute (g) and mass of a solution (g) expressed in percent.

Mass Percent

$$\text{Mass Percent} = \frac{m_{\text{solute}}}{m_{\text{solution}}} \times 100\%$$

$m_{\text{solute}} = \text{Mass of Solute (g)}$ $m_{\text{solution}} = \text{Total Mass of Solution (g)}$

Mole Fraction (χ): - the ratio of the moles of a solute and the moles of the entire solution (solute and solvent).

Mole Fraction

$$\chi_A = \frac{n_A}{n_{\text{Total}}}$$

$n_A = \text{moles of component A}$ $n_{\text{Total}} = \text{Total Moles of Solution} = n_A + n_B + n_C + \dots$

Parts per Million (ppm): - the amount of solute (usually ion) in milligram per Litre of solution.
- use for measuring trace amount of solutes.

Parts per Billion (ppb): - the amount of solute (usually ion) in microgram per Litre of solution.
- use for measuring trace amount of solutes.

<u>Parts per Million</u>	<u>Parts per Billion</u>
$\text{ppm} = \frac{m_{\text{solute}} \text{ (mg)}}{V_{\text{solution}} \text{ (L)}}$	$\text{ppb} = \frac{m_{\text{solute}} \text{ (}\mu\text{g)}}{V_{\text{solution}} \text{ (L)}}$

Example 1: 40.0 g of 1-propanol with a density of 0.803 g/mL is dissolved in 150 mL of water. Describe the composition of the solution by

- molarity
- molality
- mass percent
- mole fraction

a. Molarity

$$n = \frac{40.0 \text{ g}}{60.0962 \text{ g/mol}} = 0.6655994888 \text{ mol C}_3\text{H}_7\text{OH}$$

$$V_{\text{propanol}} = \frac{40.0 \text{ g}}{0.803 \text{ g/mL}} = 49.8132005 \text{ mL}$$

$$V_{\text{Total}} = 150 \text{ mL} + 49.8132005 \text{ mL}$$

$$V_{\text{Total}} = 199.8132005 \text{ mL} = 0.1998132005 \text{ L}$$

$$C_{\text{propanol}} = [\text{C}_3\text{H}_7\text{OH}] = \frac{0.6655994888 \text{ mol}}{0.1998132005 \text{ L}}$$

$$[\text{C}_3\text{H}_7\text{OH}] = 3.33 \text{ mol/L}$$

b. Molality

$$n = \frac{40.0 \text{ g}}{60.0962 \text{ g/mol}} = 0.6655994888 \text{ mol C}_3\text{H}_7\text{OH}$$

$$m_{\text{solvent}} = 150 \text{ g} = 0.150 \text{ kg}$$

(Assume 1 g \approx 1 mL H₂O)

$$\text{Molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

$$\text{Molality} = \frac{0.6655994888 \text{ mol}}{0.150 \text{ kg}}$$

$$\text{Molality} = 4.44 \text{ m}$$

c. Mass Percent

$$m_{\text{propanol}} = 40.0 \text{ g}$$

$$m_{\text{solution}} = m_{\text{propanol}} + m_{\text{water}} = 40.0 \text{ g} + 150 \text{ g}$$

$$m_{\text{solution}} = 190 \text{ g}$$

$$\text{Mass Percent} = \frac{m_{\text{solute}}}{m_{\text{solution}}} \times 100\%$$

$$\text{Mass Percent} = \frac{40.0 \text{ g}}{190 \text{ g}} \times 100\%$$

$$\text{Mass Percent} = 21.1\%$$

d. Mole Fraction

$$n = \frac{40.0 \text{ g}}{60.0962 \text{ g/mol}} = 0.6655994888 \text{ mol C}_3\text{H}_7\text{OH}$$

$$n_{\text{water}} = \frac{150 \text{ g}}{18.0158 \text{ g/mol}} = 8.326024934 \text{ mol H}_2\text{O}$$

$$n_{\text{Total}} = n_{\text{propanol}} + n_{\text{water}}$$

$$n_{\text{Total}} = 0.6655994888 \text{ mol} + 8.326024934 \text{ mol}$$

$$n_{\text{Total}} = 8.991624422 \text{ mol}$$

$$\chi_{\text{propanol}} = \frac{n_{\text{propanol}}}{n_{\text{Total}}} = \frac{0.6655994888 \text{ mol}}{8.991624422 \text{ mol}}$$

$$\chi_{\text{propanol}} = 0.0740$$

Example 2: Alcoholic beverages have labels indicating alcoholic content (C₂H₅OH) using (%v/v), mL of solutes per mL of solution. Suppose a Canadian whiskey has a 35% alcohol content, and the density of pure ethanol is 0.789 g/cm³, determine the composition of the whiskey by

- molarity
- molality
- mass percent
- mole fraction

a. Molarity

$$35\% \text{ (v/v)} = \frac{35 \text{ mL C}_2\text{H}_5\text{OH}}{100 \text{ mL Total}}$$

$$m_{\text{ethanol}} = 0.789 \text{ g/cm}^3 \times 35 \text{ mL} = 27.615 \text{ g}$$

$$n = \frac{27.615 \text{ g}}{46.0694 \text{ g/mol}} = 0.599421742 \text{ mol C}_2\text{H}_5\text{OH}$$

$$V_{\text{Total}} = 100 \text{ mL} = 0.100 \text{ L}$$

$$C_{\text{ethanol}} = [\text{C}_2\text{H}_5\text{OH}] = \frac{0.599421742 \text{ mol}}{0.100 \text{ L}}$$

$$[\text{C}_2\text{H}_5\text{OH}] = 5.99 \text{ mol/L}$$

b. Molality

$$n = 0.599421742 \text{ mol C}_2\text{H}_5\text{OH}$$

$$V_{\text{solvent}} = V_{\text{Total}} - V_{\text{ethanol}} = 100 \text{ mL} - 35 \text{ mL} = 65 \text{ mL}$$

$$m_{\text{solvent}} = 65 \text{ g} = 0.065 \text{ kg} \quad (\text{Assume } 1 \text{ g} \approx 1 \text{ mL H}_2\text{O})$$

$$\text{Molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

$$\text{Molality} = \frac{0.599421742 \text{ mol}}{0.065 \text{ kg}}$$

$$\text{Molality} = 9.22 \text{ m}$$

c. Mass Percent

$$m_{\text{ethanol}} = 27.615 \text{ g}$$

$$m_{\text{solution}} = m_{\text{ethanol}} + m_{\text{water}} = 27.615 \text{ g} + 65 \text{ g}$$

$$m_{\text{solution}} = 92.615 \text{ g}$$

$$\text{Mass Percent} = \frac{m_{\text{solute}}}{m_{\text{solution}}} \times 100\%$$

$$\text{Mass Percent} = \frac{27.615 \text{ g}}{92.615 \text{ g}} \times 100\%$$

$$\text{Mass Percent} = 29.8\%$$

d. Mole Fraction

$$n_{\text{ethanol}} = 0.599421742 \text{ mol C}_2\text{H}_5\text{OH}$$

$$n_{\text{water}} = \frac{65 \text{ g}}{18.0158 \text{ g/mol}} = 3.607944138 \text{ mol H}_2\text{O}$$

$$n_{\text{Total}} = n_{\text{propanol}} + n_{\text{water}}$$

$$n_{\text{Total}} = 0.599421742 \text{ mol} + 3.607944138 \text{ mol}$$

$$n_{\text{Total}} = 4.20736588 \text{ mol}$$

$$\chi_{\text{propanol}} = \frac{n_{\text{propanol}}}{n_{\text{Total}}} = \frac{0.599421742 \text{ mol}}{4.20736588 \text{ mol}}$$

$$\chi_{\text{propanol}} = 0.142$$

Example 3: 4.25×10^{-2} g of sodium sulfate is dissolved in 500 mL of water. Calculate the concentration of sodium ion in ppm.

This is a Stoichiometry problem. We have to figure out the mass of Na⁺ in mg.



$$n_{\text{Na}_2\text{SO}_4} = \frac{4.25 \times 10^{-2} \text{ g}}{142.04 \text{ g/mol}} = 2.992114897 \times 10^{-4} \text{ mol Na}_2\text{SO}_4$$

$$n_{\text{Na}^+} = 2.9921 \times 10^{-4} \text{ mol Na}_2\text{SO}_4 \times \frac{2 \text{ mol Na}^+}{1 \text{ mol Na}_2\text{SO}_4} = 5.98423 \times 10^{-4} \text{ mol Na}^+$$

$$m_{\text{Na}^+} = 5.984229794 \times 10^{-4} \text{ mol Na}^+ \times 22.99 \text{ g/mol}$$

$$m_{\text{Na}^+} = 0.0137577443 \text{ g Na}^+ = 13.7577443 \text{ mg Na}^+$$

$$\text{ppm} = \frac{m_{\text{solute}} \text{ (mg)}}{V_{\text{solution}} \text{ (L)}}$$

$$\text{ppm} = \frac{13.7577443 \text{ mg}}{0.500 \text{ L}}$$

$$27.5 \text{ ppm}$$

Normality (N): - the number of equivalence (active chemical agent) per Litre of solution.
 - for Acid or Base Solutions, the equivalence = number of moles of H^+ or OH^- per molecular formula.

Normality

$$N = \text{Equivalence} \times \text{Molarity (C)}$$

Example 4: The density of a 0.327 M of barium hydroxide solution is 2.18 g/mL. Determine the composition of the solution in terms of its

- mass percent
- molality
- normality

a. Mass Percent

$$[\text{Ba}(\text{OH})_2] = 0.327 \text{ mol/L}$$

$$\text{In 1 L of solution, } m = 0.327 \text{ mol} \times 171.3458 \text{ g/mol}$$

$$m = 56.0300766 \text{ g Ba}(\text{OH})_2$$

$$\text{In 1 L of solution, } m_{\text{total}} = 2.18 \text{ g/mL} \times 1000 \text{ mL}$$

$$m_{\text{total}} = 2180 \text{ g}$$

$$\text{Mass Percent} = \frac{m_{\text{solute}}}{m_{\text{solution}}} \times 100\%$$

$$\text{Mass Percent} = \frac{56.0300766 \text{ g}}{2180 \text{ g}} \times 100\%$$

$$\text{Mass Percent} = 2.57\%$$

b. Molality

$$n = 0.327 \text{ mol Ba}(\text{OH})_2$$

$$m_{\text{solvent}} = m_{\text{Total}} - m_{\text{solute}}$$

$$m_{\text{solvent}} = 2180 \text{ g} - 56.0300766 \text{ g}$$

$$m_{\text{solvent}} = 2123.969923 \text{ g} = 2.123969923 \text{ kg}$$

$$\text{Molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

$$\text{Molality} = \frac{0.327 \text{ mol}}{2.123969923 \text{ kg}}$$

$$\text{Molality} = 0.154 \text{ m}$$

c. Normality



Since there are **2 moles of OH^-** for every **1 mole of $\text{Ba}(\text{OH})_2$** dissolves, the equivalence = 2.

$$\text{Normality} = 2 \times 0.327 \text{ M}$$

$$\text{Normality} = 0.654 \text{ N}$$

11.2: The Energies of Solution Formation**The Dissolving Process:**

- Solute Molecules need to overcome their Intermolecular Forces or the breaking up of the Lattice ($\Delta E_{\text{lattice}}$ = Change in Lattice Energy – Endothermic – Input Energy)**
- Solvent Molecules need energy input to overcome their Intermolecular Forces (ΔH_2).**
- The Molecules of Solute and Solvent Interact to release energy (ΔH_3 is exothermic – Energy is Released).**

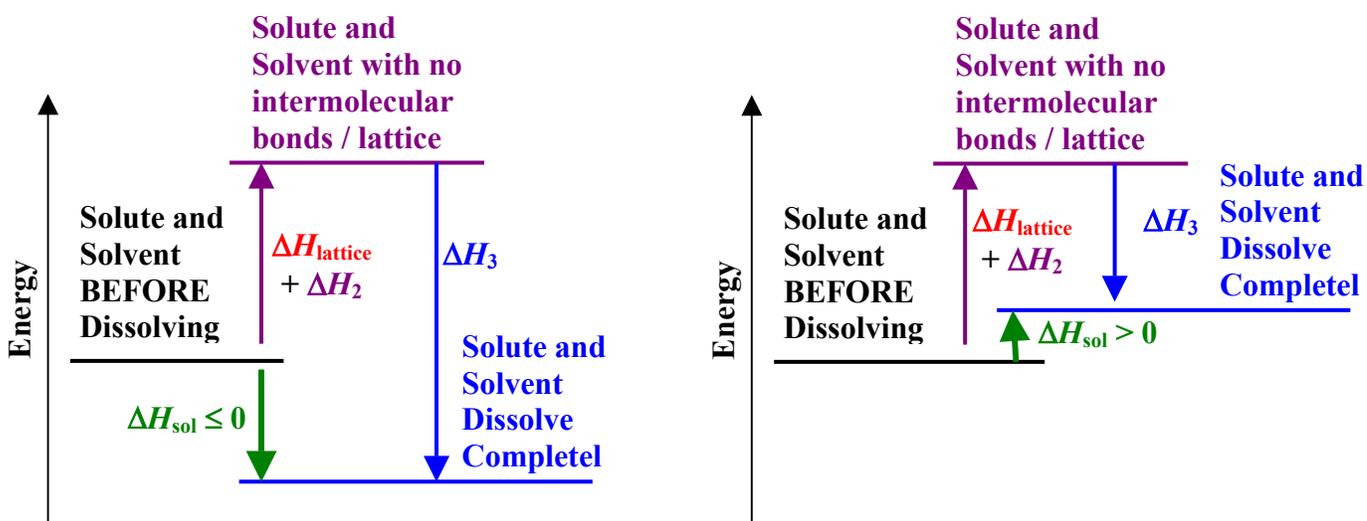
Enthalpy of Hydration (ΔH_{hyd}): - the combined energy of solvent's intermolecular forces (ΔH_2) and the release of energy between solute and solvent molecules (ΔH_3).

$$\Delta H_{\text{hyd}} = \Delta H_2 + \Delta H_3$$

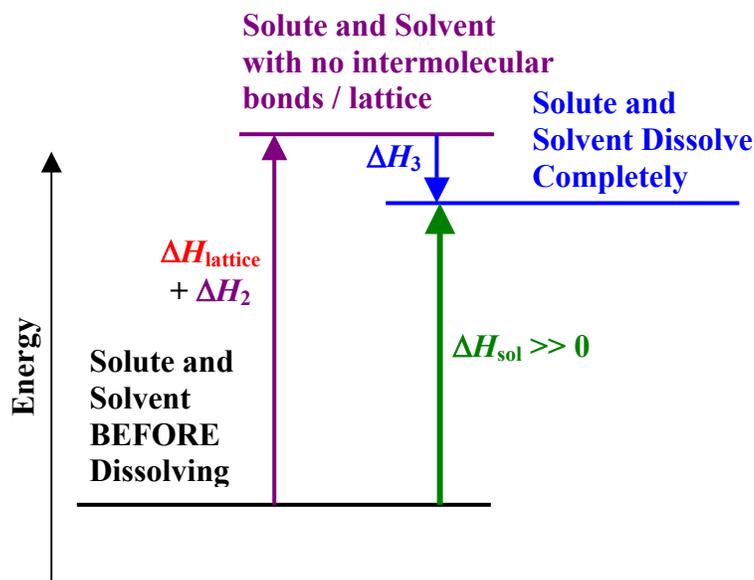
Enthalpy of Solution (ΔH_{sol}): - the total energy of dissolving a solute in a solvent.

$$\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hyd}}$$

“Like-Dissolves-Like”: - a dissolving rule that states polar solutes will dissolve in polar solvents and non-polar solutes will dissolve in non-polar solvents.
 - the reason why polar solutes cannot dissolve in non-polar solvents and vice versa is due to the relatively small ΔH_3 between solute and solvent molecules. Since non-polar and polar molecules do not interact, the remaining energies involved in the dissolving process ($\Delta H_{\text{lattice}}$ and ΔH_2) are too large (endothermic) for solution to form spontaneously.



When “Like Dissolves Like”, ΔH_{sol} is exothermic or slightly endothermic



When Polar and Non-polar molecules try to dissolve each other, ΔH_{sol} is highly endothermic because ΔH_3 is small.

Example 1: The lattice energy of silver chloride is 905 kJ/mol. If the hydration of silver chloride in water has an enthalpy of -757 kJ/mol, determine the heat of solution of silver chloride. Comment of the solubility of silver chloride based on your result.

$$\begin{aligned}\Delta H_{\text{lattice}} &= 905 \text{ kJ/mol} \\ \Delta H_{\text{hyd}} &= -757 \text{ kJ/mol} \\ \Delta H_{\text{sol}} &= ?\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{sol}} &= \Delta H_{\text{lattice}} + \Delta H_{\text{hyd}} \\ \Delta H_{\text{sol}} &= 905 \text{ kJ/mol} + (-757 \text{ kJ/mol})\end{aligned}$$

$$\Delta H_{\text{sol}} = 148 \text{ kJ/mol}$$

AgCl is only slightly soluble in water. This is because its ΔH_{sol} is quite endothermic, which indicates that ΔH_3 is every small compared to its lattice energy and ΔH_2 .

Example 2: The enthalpy of solution for magnesium chloride is -74 kJ/mol. Calculate its heat of hydration if magnesium chloride has a lattice energy of 2526 kJ/mol.

$$\begin{aligned}\Delta H_{\text{lattice}} &= 2526 \text{ kJ/mol} \\ \Delta H_{\text{sol}} &= -74 \text{ kJ/mol} \\ \Delta H_{\text{hyd}} &= ?\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{sol}} &= \Delta H_{\text{lattice}} + \Delta H_{\text{hyd}} \\ \Delta H_{\text{hyd}} &= \Delta H_{\text{sol}} - \Delta H_{\text{lattice}} \\ \Delta H_{\text{hyd}} &= (-74 \text{ kJ/mol}) - 2526 \text{ kJ/mol}\end{aligned}$$

$$\Delta H_{\text{hyd}} = -2600 \text{ kJ/mol}$$

Assignment

11.1 pg. 548 #25 to 32

11.2 pg. 548 #33 to 35, 37 to 39

11.3: Factors Affecting Solubility

Solubility: - the amount of solute that can dissolve in a given amount of solvent at a specific temperature and pressure.

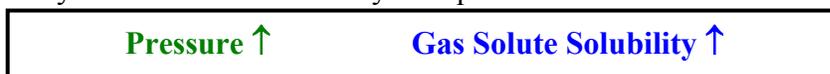
Factors Affecting Solubility

1. **Structure Effect:**- in general, **polar solutes dissolve in polar solvents whereas non-polar solutes dissolve in non-polar solvents** - “**Like Dissolves Like**”.
- **bigger molecules are harder to dissolve** (agitation might alleviate this problem).

Hydrophobic: - non-polar molecules “water fearing”. **Hydrophilic:** -polar molecules “water loving”.



2. **Pressure:** - as **pressure increases, solubility of gas solutes generally increases**. (More force is exerted down to force gas particles to dissolve in a denser liquid solvent).
- pressure has very little effect on solubility of liquid and solid solutes.



Henry’s Law: - states that the concentration of gas in a solution is directly proportional to the pressure above the solution.

Henry’s Law Constant (k): - relates concentration of gas in a solution with the pressure above the solution.
- dependant on temperature and the identity of the gas solute.

<p>Henry’s Law</p> <p>$C = kP$</p> <p>C = Concentration of Gas in Solution (mol/L) P = Pressure above the solution (atm) k = Henry’s Law Constant [mol / (L • atm)]</p>
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Example 1: Some health food vendors claim that drinking oxygenated beverage will increase physical performance. Suppose an oxygenated drink is under 7.50 atm and the Henry’s law constant for oxygen is 0.001322 mol / (L • atm) at 25°C.

- Calculate the concentration of oxygen in this beverage.
- If the partial pressure of oxygen in the atmosphere 0.20947 atm, what will be the concentration of oxygen in the beverage if it was left open for a long time.

<p>a.</p> <p>$k = 0.001322 \text{ mol / (L • atm)}$</p> <p>$P = 7.50 \text{ atm}$</p> <p>$C = ?$</p> <p>$C = kP = (0.001322 \text{ mol / (L • atm)}) (7.50 \text{ atm})$</p> <p style="text-align: center;">$C = 0.00992 \text{ mol/L}$</p>	<p>b.</p> <p>$k = 0.001322 \text{ mol / (L • atm)}$</p> <p>$P = 0.20947 \text{ atm}$</p> <p>$C = ?$</p> <p>$C = kP = (0.001322 \text{ mol / (L • atm)}) (0.20947 \text{ atm})$</p> <p style="text-align: center;">$C = 0.000277 \text{ mol/L}$</p>
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3. **Temperature:** - as **temperature increases**, solubility of **some solid solutes generally increases** (exceptions are sodium sulfate and cerium sulfate).
 - when solutes have $\Delta H_{\text{sol}} > 0$, the increase in temperature supplies the energy needed to facilitate the dissolving process. Thereby, solubility increases. (Examples are KNO_3 and NaNO_3)
 - when solutes have $\Delta H_{\text{sol}} < 0$, the increase in temperature hinders the energy needed to be released during the dissolving process. Thereby, solubility decreases. (Examples are Na_2SO_4 and $\text{Ce}_2(\text{SO}_4)_3$)
 - as **temperature increases**, **the solubility of gas solutes decreases**. (The increase temperature causes gas solutes to move faster, breaking the intermolecular bonds they established with the molecules of the liquid solvent.)

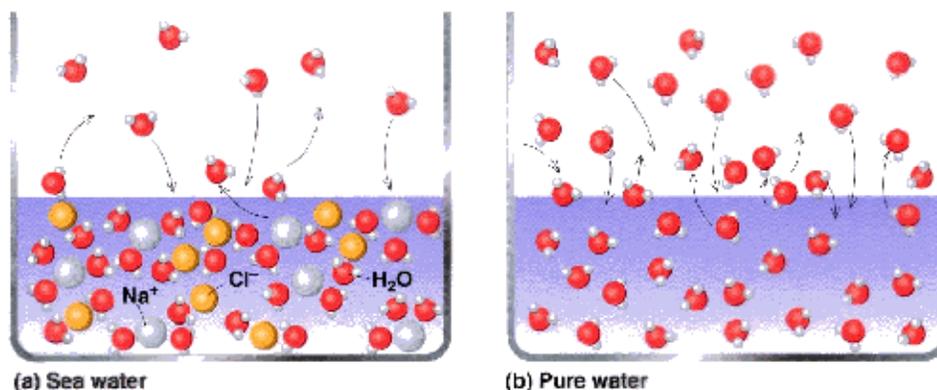
Temperature \uparrow Solid Solute Solubility \uparrow Gas Solute Solubility \downarrow

11.4: The Vapour Pressure of Solutions

Vapour Pressure of Solution: - in general, vapour pressure of solution tends to decrease as more solutes is dissolved into the solvent.

$\chi_{\text{solute}} \uparrow$ $\chi_{\text{solvent}} \downarrow$ $P_{\text{soln}} \downarrow$

- this is because the presence of solutes molecules create more intermolecular bonds that hinder the vaporization of the solvent.



Raoult's Law: - the vapour pressure of a solution is directly proportional to the mole fraction of the solvent
 - **pure solvent** ($\chi_{\text{solvent}} = 1$ and $\chi_{\text{solute}} = 0$) has the maximum vapour pressure.

Raoult's Law for Solid Solute in Liquid Solvent

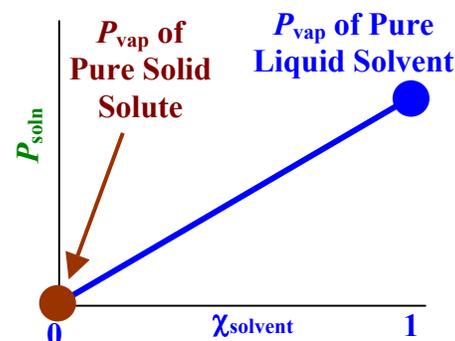
$$P_{\text{soln}} = \chi_{\text{solvent}} P^0_{\text{solvent}}$$

χ_{solvent} = Mole Fraction of Solvent

P^0_{solvent} = Vapour Pressure of Pure Solvent

P_{soln} = Vapour Pressure of Solution

Note: Moles of Ionic Solutes = Total Number of Ions Dissociated



- Example 1:** At 10°C, the vapour pressure of pure water is 9.23 torr. The density of water at 10°C is 0.9997 g/cm³. Determine the vapour pressure of the resulting solution if
- 5.00 g glucose is dissolved in 150 mL of water at 10°C.
 - 5.00 g of magnesium chloride is dissolved in 150 mL of water at 10°C.

a.

$$P_{\text{water}}^0 = 9.23 \text{ torr}$$

$$n_{\text{glucose}} = \frac{5.00 \text{ g}}{180.1608 \text{ g/mol}} = 0.0277529851 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$n_{\text{water}} = \frac{(150 \text{ mL})(0.9997 \text{ g/mL})}{18.0158 \text{ g/mol}} = 8.323527126 \text{ mol H}_2\text{O}$$

$$n_{\text{total}} = 0.0277529851 \text{ mol} + 8.323527126 \text{ mol}$$

$$n_{\text{total}} = 8.351280111 \text{ mol}$$

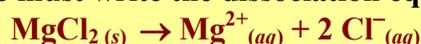
$$\chi_{\text{water}} = \frac{n_{\text{water}}}{n_{\text{Total}}} = \frac{8.323527126 \text{ mol}}{8.351280111 \text{ mol}}$$

$$\chi_{\text{water}} = 0.9966767987$$

$$P_{\text{soln}} = \chi_{\text{water}} P_{\text{water}}^0$$

$$P_{\text{soln}} = (0.9966767987)(9.23 \text{ torr})$$

$$P_{\text{soln}} = 9.20 \text{ torr}$$

b. Since MgCl₂ is an ionic solute, we must write the dissociation equation

$$P_{\text{water}}^0 = 9.23 \text{ torr}$$

$$n_{\text{ions}} = 3 \times \frac{5.00 \text{ g}}{95.206 \text{ g/mol}} = 0.1575530954 \text{ mol Mg}^{2+} \text{ and Cl}^{-} \text{ ions}$$

(need to multiply by 3 due to a total of 3 moles of ions produced)

$$n_{\text{water}} = \frac{(150 \text{ mL})(0.9997 \text{ g/mL})}{18.0158 \text{ g/mol}} = 8.323527126 \text{ mol H}_2\text{O}$$

$$n_{\text{total}} = 0.1575530954 \text{ mol} + 8.323527126 \text{ mol}$$

$$n_{\text{total}} = 8.481080221 \text{ mol}$$

$$\chi_{\text{water}} = \frac{n_{\text{water}}}{n_{\text{Total}}} = \frac{8.323527126 \text{ mol}}{8.481080221 \text{ mol}}$$

$$\chi_{\text{water}} = 0.981422992$$

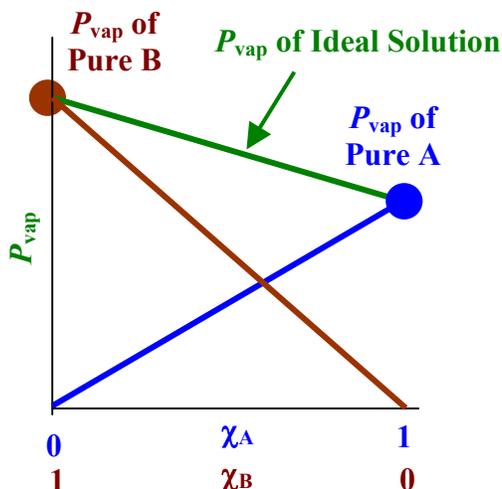
$$P_{\text{soln}} = \chi_{\text{water}} P_{\text{water}}^0$$

$$P_{\text{soln}} = (0.981422992)(9.23 \text{ torr})$$

$$P_{\text{soln}} = 9.06 \text{ torr}$$

Note that the P_{vap} of a Solution consists of a Solid Solute is LOWERED than that of a Pure Solvent.

- Ideal Solution:** - when liquid-solute and liquid-solvent solution follows Raoult's Law.
 - occurs when there are similar intermolecular forces between solute-solute, solvent-solvent, and solute-solvent molecules



Ideal Solution of Liquid-Solute and Liquid-Solvent

$$P_{\text{Total}} = \chi_{\text{A}} P_{\text{A}}^0 + \chi_{\text{B}} P_{\text{B}}^0 \quad (\chi_{\text{A}} + \chi_{\text{B}} = 1)$$

χ_{A} = Mole Fraction of Component A

P_{A}^0 = Vapour Pressure of Pure A

χ_{B} = Mole Fraction of Component B

P_{B}^0 = Vapour Pressure of Pure B

P_{Total} = Total Vapour Pressure of Solution

Example 2: Carbon tetrachloride (CCl_4) is commonly used to dissolve many non-polar liquid solutes. At 20°C , pure CCl_4 has a vapour pressure of 91.0 kPa. An 2.50 g of unknown liquid solute is dissolved in 90.0 g of CCl_4 . The resulting vapour pressure was determined to be 84.1 kPa. Assuming the solution is ideal, calculate the molar mass of this unknown liquid solute.

$$P_{\text{CCl}_4}^0 = 91.0 \text{ kPa} \quad P_{\text{soln}} = 84.1 \text{ kPa} \quad m_{\text{unknown}} = 2.50 \text{ g}$$

$$n_{\text{CCl}_4} = \frac{90.0 \text{ g}}{153.823 \text{ g/mol}} = 0.5850880558 \text{ mol CCl}_4 \quad \chi_{\text{CCl}_4} = ? \quad \chi_{\text{unknown}} = ? \quad n_{\text{unknown}} = ? \quad M_{\text{unknown}} = ?$$

$$P_{\text{soln}} = \chi_{\text{CCl}_4} P_{\text{CCl}_4}^0 \quad \chi_{\text{CCl}_4} = \frac{P_{\text{soln}}}{P_{\text{CCl}_4}^0} = \frac{84.1 \text{ kPa}}{91.0 \text{ kPa}} = 0.9241758242$$

$$\chi_{\text{unknown}} = 1 - \chi_{\text{CCl}_4} = 1 - 0.9241758242 = 0.0758241758$$

$$\chi_{\text{unknown}} = \frac{n_{\text{unknown}}}{n_{\text{Total}}} = \frac{n_{\text{unknown}}}{n_{\text{unknown}} + n_{\text{CCl}_4}}$$

$$0.0758241758 = \frac{n_{\text{unknown}}}{n_{\text{unknown}} + 0.5850880558 \text{ mol}}$$

$$0.0758241758 (n_{\text{unknown}} + 0.5850880558) = n_{\text{unknown}}$$

$$0.0758241758 n_{\text{unknown}} + 0.0443638196 = n_{\text{unknown}}$$

$$0.0758241758 n_{\text{unknown}} - n_{\text{unknown}} = -0.0443638196$$

$$-0.9241758242 n_{\text{unknown}} = -0.0443638196$$

$$n_{\text{unknown}} = \frac{-0.0443638196}{-0.9241758242} \quad n_{\text{unknown}} = 0.0480036574 \text{ mol}$$

$$M_{\text{unknown}} = \frac{m_{\text{unknown}}}{n_{\text{unknown}}} = \frac{2.50 \text{ g}}{0.0480036574 \text{ mol}} \quad M_{\text{unknown}} = 52.1 \text{ g/mol}$$

Example 3: At 60°C , the vapour pressures of benzene and toluene are 384 torr and 133 torr respectively. Determine the composition of a benzene-toluene solution if its vapour pressure is 200 torr assuming it behaves ideally.

$$P_{\text{benzene}}^0 = 384 \text{ torr} \quad \text{Since } \chi_{\text{benzene}} + \chi_{\text{toluene}} = 1, \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

$$P_{\text{toluene}}^0 = 133 \text{ torr}$$

$$P_{\text{Total}} = 200 \text{ torr}$$

$$\chi_{\text{benzene}} = ?$$

$$\chi_{\text{toluene}} = ?$$

$$P_{\text{Total}} = \chi_{\text{benzene}} P_{\text{benzene}}^0 + \chi_{\text{toluene}} P_{\text{toluene}}^0$$

$$P_{\text{Total}} = \chi_{\text{benzene}} P_{\text{benzene}}^0 + (1 - \chi_{\text{benzene}}) P_{\text{toluene}}^0$$

$$200 = \chi_{\text{benzene}} (384) + (1 - \chi_{\text{benzene}}) (133)$$

$$200 = 384\chi_{\text{benzene}} + 133 - 133\chi_{\text{benzene}}$$

$$200 - 133 = 384\chi_{\text{benzene}} - 133\chi_{\text{benzene}}$$

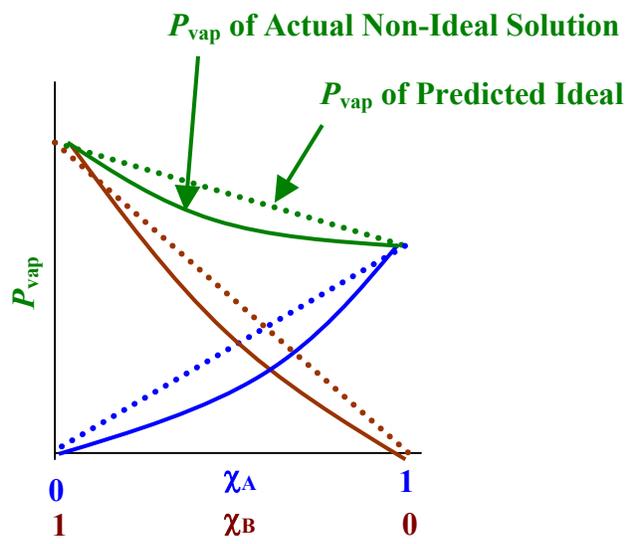
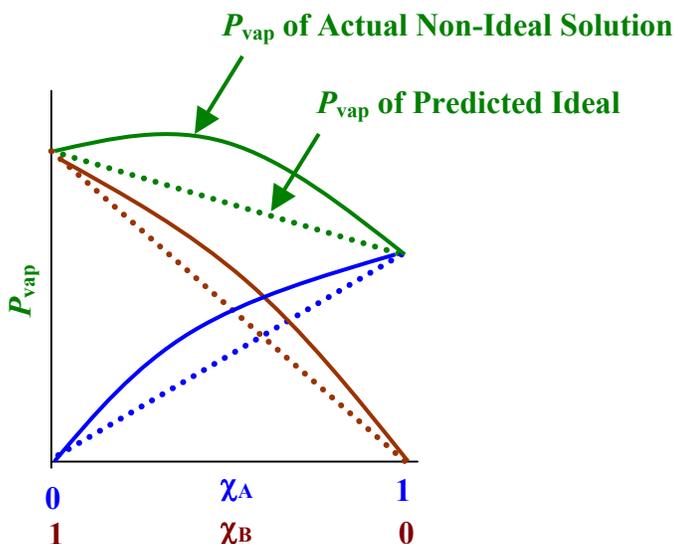
$$67 = 251\chi_{\text{benzene}}$$

$$\chi_{\text{benzene}} = \frac{67}{251} = 0.2669322709$$

$$\chi_{\text{toluene}} = 1 - \chi_{\text{benzene}} = 1 - 0.2669322709 = 0.7330677291$$

$$\chi_{\text{benzene}} = 0.267 \quad \chi_{\text{toluene}} = 0.733$$

Non-Ideal Solution: - when liquid-solute and liquid-solvent solution deviates from Raoult's Law.



Positive Deviation Non-Ideal Solution

- when $\Delta H_{\text{sol}} > 0$ (endothermic), solute-solvent molecules interactions are weak. Thereby, vapours from both components escape easily causing $P_{\text{actual}} > P_{\text{predicted}}$

Negative Deviation Non-Ideal Solution

- when $\Delta H_{\text{sol}} < 0$ (exothermic), solute-solvent molecules interactions are strong. Thereby, vapours from both components cannot escape easily causing $P_{\text{actual}} < P_{\text{predicted}}$

Example 4: At 25°C, the vapour pressures of pure ethanol and hexane are 7.87 kPa and 130 kPa . A solution of 24.0 g of ethanol and 15.0 g of hexane was found to have a vapour pressure of 54.4 kPa. Is the solution behaving ideally. Justify your answer mathematically.

$$P_{\text{ethanol}}^0 = 7.87 \text{ kPa}$$

$$P_{\text{hexane}}^0 = 130 \text{ kPa}$$

$$n_{\text{ethanol}} = \frac{24.0 \text{ g}}{46.4894 \text{ g/mol}} = 0.5162467143 \text{ mol C}_2\text{H}_5\text{OH}$$

$$m_{\text{ethanol}} = 24.0 \text{ g}$$

$$m_{\text{hexane}} = 15.0 \text{ g}$$

$$n_{\text{hexane}} = \frac{15.0 \text{ g}}{86.1766 \text{ g/mol}} = 0.1740611721 \text{ mol C}_6\text{H}_{14}$$

$$P_{\text{actual}} = 54.4 \text{ kPa}$$

$$P_{\text{Total (predicted)}} = ?$$

$$n_{\text{Total}} = 0.5162467143 \text{ mol} + 0.1740611721 \text{ mol}$$

$$n_{\text{Total}} = 0.6903078864 \text{ mol}$$

$$\chi_{\text{ethanol}} = \frac{0.5162467143 \text{ mol}}{0.6903078864 \text{ mol}}$$

$$\chi_{\text{hexane}} = \frac{0.1740611721 \text{ mol}}{0.6903078864 \text{ mol}}$$

$$\chi_{\text{ethanol}} = 0.7478499442$$

$$\chi_{\text{hexane}} = 0.2521500558$$

$$P_{\text{Total}} = \chi_{\text{ethanol}} P_{\text{ethanol}}^0 + \chi_{\text{hexane}} P_{\text{hexane}}^0$$

$$P_{\text{Total}} = (0.7478499442)(7.87 \text{ kPa}) + (0.2521500558)(130 \text{ kPa}) \quad P_{\text{predicted}} = 38.6 \text{ kPa}$$

Because $P_{\text{actual}} > P_{\text{predicted}}$, 54.4 kPa > 38.6 kPa, this is a non-ideal solution. In fact, it deviates positively from the ideal solution due to the non-polar nature of hexane dissolving a polar solvent of ethanol.

Assignment

11.3 pg. 549 #41, 43 and 44

11.4 pg. 549–550 #45 to 49, 51, 53, 55 and 56

11.5: Boiling-Point Elevation and Freezing-Point Depression

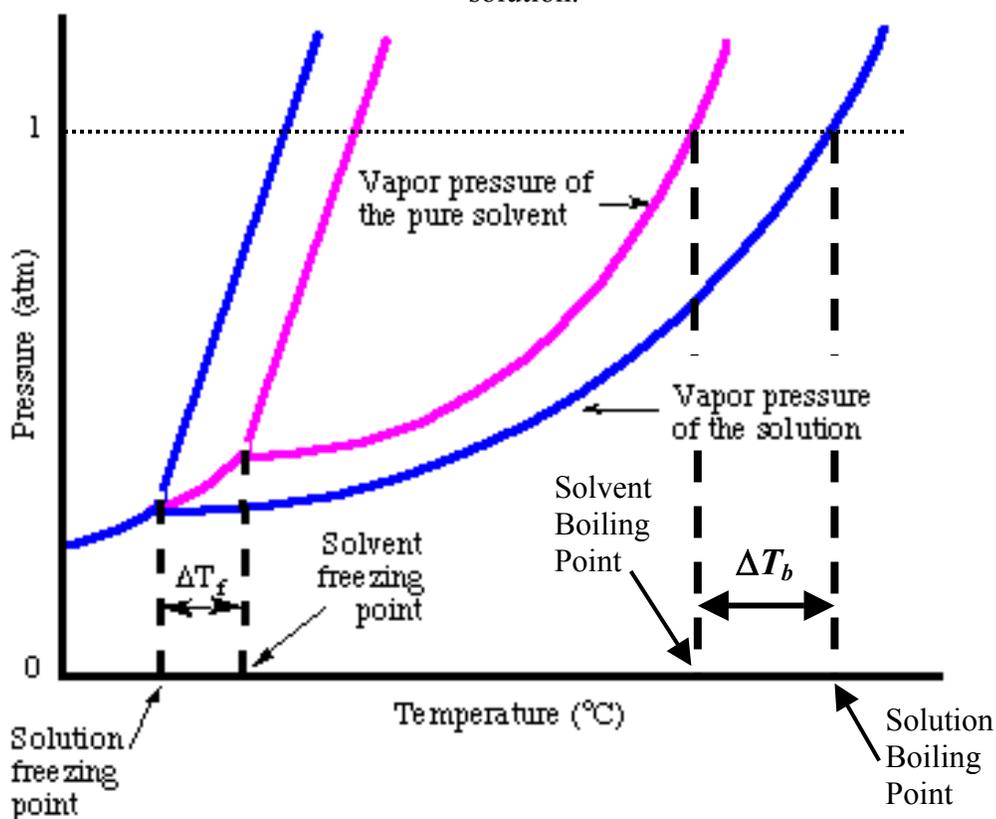
Colligative Properties: - changes in physically properties of a pure substance as it is mixed with a solute.
 - these include freezing-point depression, boiling-point elevation and osmotic pressure.

Boiling-Point Elevation: - the presence of solute in a solution raises the boiling point of a pure solvent due to the extra intermolecular forces between them (more energy is needed to boil the solution as vapour pressure is lowered).
 - the amount of temperature elevation to boil is directly proportional to the molality of the solute in the solution.
 - can be used to **determine molar mass of a solute**.

Molal Boiling-Point Elevation Constant (K_b): - a constant relating the change in boiling point temperature and the molality of the solute in the solution.

Freezing-Point Depression: - the presence of solute decreases the vapour pressure of the solvent. Since ice has a higher vapour pressure than that of water in the solution, the freezing point has effectively been lowered. (In order for ice to form, vapour pressure of the ice has to be lowered than that of water).
 - the amount of temperature depression to freeze is directly proportional to the molality of the solute in the solution.
 - used most commonly to **determine molar mass of a solute**.

Molal Freezing-Point Elevation Constant (K_f): - a constant relating the change in freezing point temperature and the molality of the solute in the solution.



Boiling Point Elevation and Freezing Point Depression of Non-Electrolytic Solutions

$$\Delta T_b = K_b \times \text{Molality}_{\text{solute}}$$

$$\Delta T_f = K_f \times \text{Molality}_{\text{solute}}$$

ΔT_b = Change in Boiling Point Elevation ($^{\circ}\text{C}$)

ΔT_f = Change in Freezing Point Depression ($^{\circ}\text{C}$)

K_b = Molal Boiling-Point Constant ($^{\circ}\text{C} \cdot \text{kg/mol}$)

K_f = Molal Freezing-Point Constant ($^{\circ}\text{C} \cdot \text{kg/mol}$)

$\text{Molality}_{\text{solute}}$ = Molality of Solute (mol/kg of solvent)

- Example 1:** Antifreeze, ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$), is commonly used to prevent water from freezing in the engine in cold temperature as well as overheating. The maximum temperature a radiator can reach is 120°C . Given the densities for ethylene glycol and water are 1.11 g/mL and 1.00 g/mL respectively, and K_b and K_f for water are $0.51^{\circ}\text{C} \cdot \text{kg/mol}$ and $1.86^{\circ}\text{C} \cdot \text{kg/mol}$,
- determine the volume of antifreeze needed to add to 10.0 L of water to sustain the maximum radiator temperature.
 - what is the freezing point of the solution?

a.

$$\Delta T_b = 120^{\circ}\text{C} - 100^{\circ}\text{C} = 20^{\circ}\text{C}$$

$$K_b = 0.51^{\circ}\text{C} \cdot \text{kg/mol}$$

$$m_{\text{water}} = 10.0 \times 10^3 \text{ mL} \times 1.00 \text{ g/mL}$$

$$m_{\text{water}} = 10.0 \times 10^3 \text{ g} = 10.0 \text{ kg}$$

$$D_{\text{antifreeze}} = 1.11 \text{ g/mL}$$

$$M_{\text{antifreeze}} = 62.0694 \text{ g/mol}$$

$$n_{\text{antifreeze}} = ? \quad m_{\text{antifreeze}} = ?$$

$$V_{\text{antifreeze}} = ?$$

$$\Delta T_b = K_b \times \text{Molality}_{\text{antifreeze}} = K_b \times \frac{n_{\text{antifreeze}}}{\text{kg of water}}$$

$$n_{\text{antifreeze}} = \frac{\Delta T_b (\text{kg of water})}{K_b} = \frac{(20^{\circ}\text{C})(10.0 \text{ kg})}{(0.51^{\circ}\text{C} \cdot \text{kg/mol})} = 392.1568627 \text{ mol}$$

$$m_{\text{antifreeze}} = (392.1568627 \text{ mol})(62.0694 \text{ g/mol}) = 24340.94117 \text{ g}$$

$$V_{\text{antifreeze}} = \frac{m_{\text{antifreeze}}}{D_{\text{antifreeze}}} = \frac{24340.94117 \text{ g}}{1.11 \text{ g/mL}} = 21928.77583 \text{ mL}$$

$$V_{\text{antifreeze}} = 21.9 \text{ L}$$

b.

$$K_f = 1.86^{\circ}\text{C} \cdot \text{kg/mol}$$

$$m_{\text{water}} = 10.0 \text{ kg}$$

$$n_{\text{antifreeze}} = 392.1568627 \text{ mol}$$

$$\Delta T_f = ?$$

$$\Delta T_f = K_f \times \text{Molality}_{\text{antifreeze}} = K_f \times \frac{n_{\text{antifreeze}}}{\text{kg of water}}$$

$$\Delta T_f = (1.86^{\circ}\text{C} \cdot \text{kg/mol}) \left(\frac{392.1568627 \text{ mol}}{10.0 \text{ kg}} \right) = 72.94117646^{\circ}\text{C}$$

$$\text{New Freezing Point} = 0^{\circ}\text{C} - 72.94117646^{\circ}\text{C}$$

$$T_f(\text{soln}) = -72.9^{\circ}\text{C}$$

- Example 2:** A 20.0 g of newly synthesized enzyme can lower the freezing point of 100.0 g CCl_4 by 4.70°C . Given that K_f for CCl_4 is $30.0^{\circ}\text{C} \cdot \text{kg/mol}$, calculate the molar mass of this new enzyme.

$$\Delta T_f = 4.70^{\circ}\text{C}$$

$$K_f = 30.0^{\circ}\text{C} \cdot \text{kg/mol}$$

$$m_{\text{CCl}_4} = 100.0 \text{ g} = 0.1000 \text{ kg}$$

$$m_{\text{enzyme}} = 20.0 \text{ g}$$

$$n_{\text{enzyme}} = ?$$

$$M_{\text{enzyme}} = ?$$

$$\Delta T_f = K_f \times \text{Molality}_{\text{enzyme}} = K_f \times \frac{n_{\text{enzyme}}}{\text{kg of CCl}_4}$$

$$n_{\text{enzyme}} = \frac{\Delta T_f (\text{kg of CCl}_4)}{K_f} = \frac{(4.70^{\circ}\text{C})(0.1000 \text{ kg})}{(30.0^{\circ}\text{C} \cdot \text{kg/mol})} = 0.0156666667 \text{ mol}$$

$$M_{\text{enzyme}} = \frac{m_{\text{enzyme}}}{n_{\text{enzyme}}} = \frac{20.0 \text{ g}}{0.0156666667 \text{ mol}} = 1276.595745 \text{ g/mol}$$

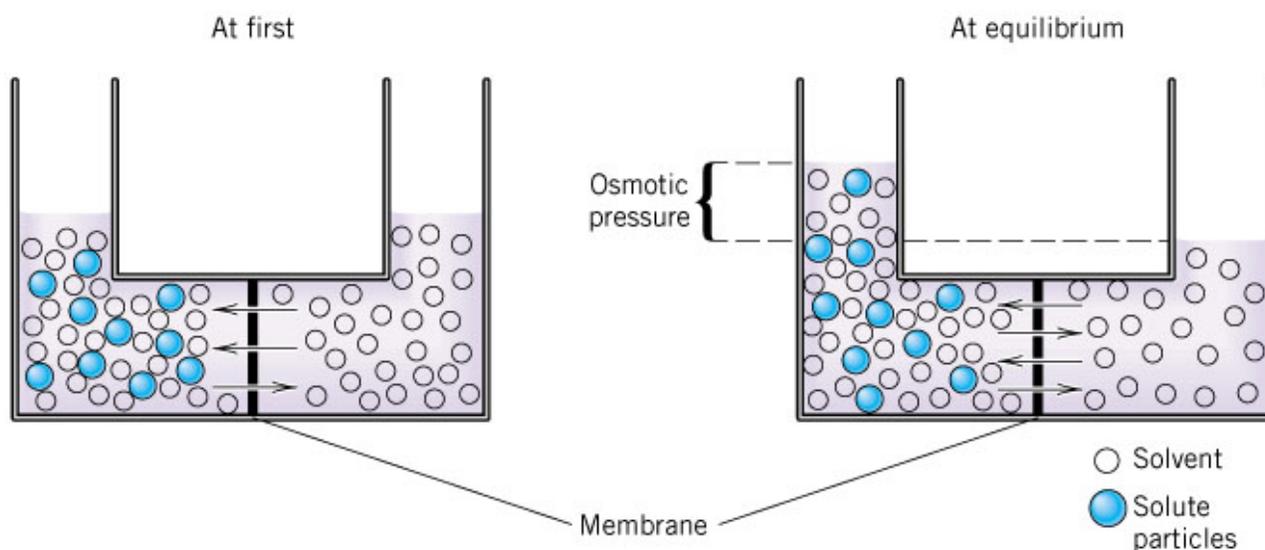
$$M_{\text{enzyme}} = 1.30 \times 10^3 \text{ g/mol}$$

11.6: Osmotic Pressure

Semipermeable Membrane: - a fine filter that allows solvent molecules to pass through but solute molecules are left behind the filter.

Osmosis: - the flow of solvent of a solution through a semipermeable membrane.
 - the pure solvent (high solvent concentration) will flow into the solution (low solvent concentration) until a state of equilibrium is reached.

Osmotic Pressure (Π): - the resulting pressure as pure solvent flows into a solution through the semipermeable membrane.
 - varies with temperature and molarity.
 - **the most easiest method to find molar mass of solute.**



Osmotic Pressure of Non-Electrolytic Solutions

$$\Pi = CRT = \frac{nRT}{V}$$

Π = Osmotic Pressure (atm)

C = Molarity (mol/L)

R = Gas Constant = 0.08206 (L • atm)/(mol • K)

T = Temperature (K)

Example 1: Calculate the molar mass of a newly synthesized progesterone (pregnancy hormone secreted by the ovaries) if its osmotic pressure at 37.0°C is 41.2 torr when 22.0 mg is dissolved in 50.0 mL of water.

$$T = 37.0^\circ\text{C} = 310.15 \text{ K}$$

$$\Pi = 41.2 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.0542105263 \text{ atm}$$

$$m_{\text{progesterone}} = 22.0 \text{ mg} = 22.0 \times 10^{-3} \text{ g}$$

$$V = 50.0 \text{ mL} = 0.0500 \text{ L}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm)/(mol} \cdot \text{K)}$$

$$M_{\text{progesterone}} = ?$$

$$\Pi = \frac{nRT}{V} = \left(\frac{m}{M}\right) \frac{RT}{V} \quad M_{\text{progesterone}} = \frac{mRT}{\Pi V}$$

$$M_{\text{progesterone}} = \frac{(22.0 \times 10^{-3} \text{ g}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (310.15 \text{ K})}{(0.0542105263 \text{ atm})(0.0500 \text{ L})}$$

$$M_{\text{progesterone}} = 207 \text{ g/mol}$$

Isotonic Solutions: - when solutions have exactly the same osmotic pressures.

Example 2: Calculate the concentration of an aqueous glucose solution needed to be isotonic with human blood at the osmotic pressure of 8.01 atm at 37.0°C.

$$T = 37.0^{\circ}\text{C} = 310.15 \text{ K}$$

$$\Pi = 8.01 \text{ atm}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm)/(mol} \cdot \text{K)}$$

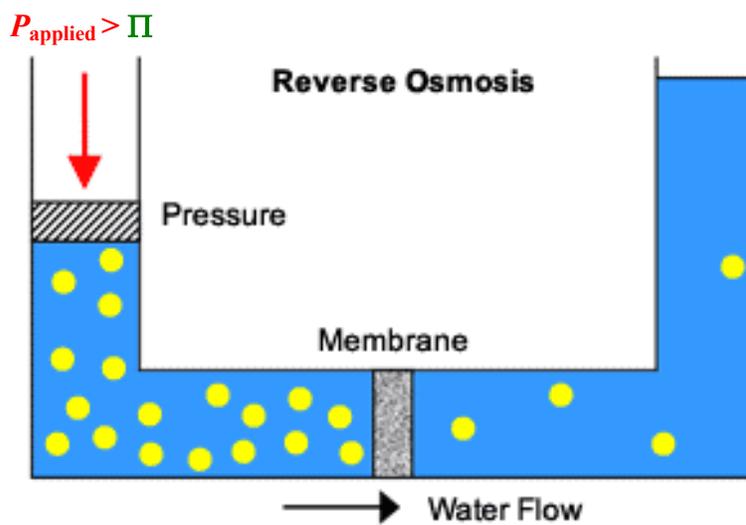
$$C = ?$$

$$\Pi = CRT$$

$$C = \frac{\Pi}{RT} = \frac{(8.01 \text{ atm})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(310.15 \text{ K})} = 0.3147235331 \text{ mol/L}$$

$$[\text{glucose}] = 0.315 \text{ mol/L}$$

Hypertonic Solutions: - when solutions have greater osmotic pressure than pure solvent (**reverse osmosis**).
- the main principle used in **desalination (removal salt from salt water)**.



Assignment

11.5 pg. 550 #57 to 64

11.6 pg. 550 #65 to 67

11.7: Colligative Properties of Electrolytic Solutions

Because ionic solutes form electrolytes when they dissociate in solutions, we must account for the total moles of solute ions form.

van't Hoff Factor (i): - is a factor that relates the number of moles of all ions in a solution per mole of solutes dissolved.
- because non-electrolytic solutions do not form ions, **$i = 1$ for all non-ionic solutions.**

Colligative Properties of Electrolytic Solutions	
van't Hoff Factor (i) = $\frac{n_{ions}}{n_{solute}}$	
Boiling Point Elevation:	$\Delta T_b = iK_b \times \text{Molality}_{solute}$
Freezing Point Depression:	$\Delta T_f = iK_f \times \text{Molality}_{solute}$
Osmotic Pressure:	$\Pi = iCRT = \frac{nRT}{V} i$

Example 1: Calculate the concentration of an aqueous potassium carbonate solution needed to be isotonic with human blood at the osmotic pressure of 8.01 atm at 37.0°C.

$$\text{K}_2\text{CO}_3(s) \rightarrow 2\text{K}^+(aq) + \text{CO}_3^{2-}(aq) \quad \Pi = iCRT$$

$$i = 2 \text{ mol K}^+ + 1 \text{ mol CO}_3^{2-} = 3 \quad C = \frac{\Pi}{iRT} = \frac{(8.01 \text{ atm})}{(3) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (310.15 \text{ K})} = 0.1049078444 \text{ mol/L}$$

$$T = 37.0^\circ\text{C} = 310.15 \text{ K}$$

$$\Pi = 8.01 \text{ atm}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm)/(mol} \cdot \text{K)}$$

$$[\text{K}_2\text{CO}_3] = ? \quad \text{[K}_2\text{CO}_3] = 0.105 \text{ mol/L}$$

Example 2: Determine the freezing point of a saturated salt solution (35.7 g / 100 g H₂O) if the K_f for pure water is 1.86 °C • kg/mol.

$$K_f = 1.86^\circ\text{C} \cdot \text{kg/mol}$$

$$m_{\text{water}} = 100 \text{ g} = 0.100 \text{ kg}$$

$$n_{\text{NaCl}} = \frac{35.7 \text{ g}}{58.443 \text{ g/mol}}$$

$$n_{\text{NaCl}} = 0.610851599 \text{ mol}$$

$$i = 2$$

$$(1 \text{ mol Na}^+ \text{ and } 1 \text{ mol Cl}^-)$$

$$\Delta T_f = ?$$

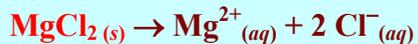
$$\Delta T_f = iK_f \times \text{Molality}_{\text{NaCl}} = iK_f \times \frac{n_{\text{NaCl}}}{\text{kg of water}}$$

$$\Delta T_f = (2)(1.86^\circ\text{C} \cdot \text{kg/mol}) \left(\frac{0.610851599 \text{ mol}}{0.100 \text{ kg}} \right) = 22.72367948^\circ\text{C}$$

$$\text{New Freezing Point} = 0^\circ\text{C} - 22.72367948^\circ\text{C} \quad T_f(\text{soln}) = -22.7^\circ\text{C}$$

Ion Pairing: - a phenomenon that happens when not all electrolytes from an ionic solute dissociate completely.
 - this usually results in a lower than expected van't Hoff factor and thereby lowering the osmotic pressure.

Example 3: In an experiment to determine the van't Hoff value of MgCl_2 , 5.00 mmol/L of solution is used inside a tube consisting of a semi-permeable membrane. The measured osmotic pressure is 247 torr and the temperature in the lab is 18.0°C . Compare the expected and observed value of the van't Hoff factor.



$$i(\text{expected}) = 2 \text{ mol K}^+ + 1 \text{ mol CO}_3^{2-}$$

$$i(\text{expected}) = 3$$

$$C = 5.00 \text{ mmol/L} = 0.00500 \text{ mol/L}$$

$$T = 18.0^\circ\text{C} = 291.15 \text{ K}$$

$$\Pi = 247 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.325 \text{ atm}$$

$$R = 0.08206 \text{ (L} \cdot \text{atm)/(mol} \cdot \text{K)}$$

$$i = ?$$

$$\Pi = iCRT$$

$$i = \frac{\Pi}{CRT} = \frac{(0.325 \text{ atm})}{(0.00500 \text{ mol/L}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (291.15 \text{ K})}$$

$$i(\text{observed}) = 2.55 \text{ due to ion pairing}$$

Assignment

11.7 pg. 550–551 #68 to 75