Unit 3: States of Matter

Chapter 5: Gases

5.1: Substances That Exist as Gases

Elements that are Gases in Room Temperature: - H₂, N₂, O₂, O₃, F₂, Cl₂ and all Noble Gases.

Compounds that are Gases in Room Temperature:

- some non-metal oxides like NO, NO₂, N₂O, SO₂, CO and CO₂
- other hydrogen-non-metal compounds like HF, HCl, HBr, HI, NH₃, H₂S, HCN, CH₄, C₃H₈ and other light hydrocarbons

Note: Most are colourless except F₂ (pale yellow), Cl₂ (yellowish green), and NO₂ (dark brown)

Properties of Gases:

- 1. Gases take the shape and volume of the container. They have very low boiling points.
- 2. Gases can be compressed much more easily than liquids and solids.
- 3. Gases have much lower densities (g/L) than liquids and solids (g/mL).
- 4. Two or more different gases will mix readily and thoroughly when placed in the same container to form a gaseous mixture.

5.2: Pressure of a Gas

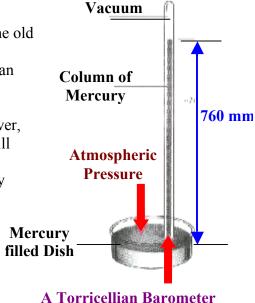
<u>Pressure</u>: - the amount of force per unit of area [1 N/m² = 1 Pascal (Pa)], measured in **kiloPascal** (**kPa**), mm Hg, torr, atmospheric pressure (atm).

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

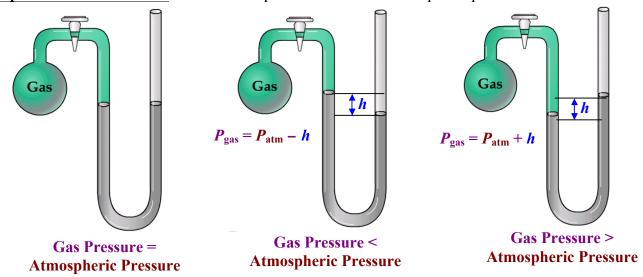
- <u>Barometer</u>: an instrument (invented by Evangelista Torricelli, hence, the old unit of pressure *torr* was named after him) to measure atmospheric pressure using a dish filled with mercury and an inverted glass tube filled with mercury.
 - when the glass tube is placed into the dish filled with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

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

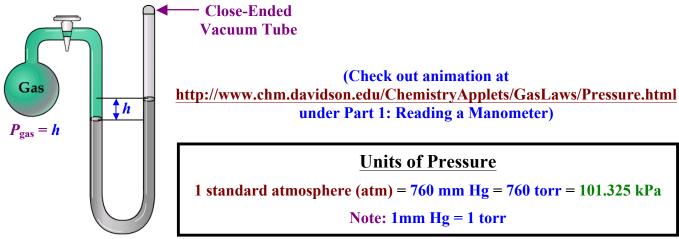
- there are two kinds of manometer: an **open-ended manometer** and a **close-ended manometer**.



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



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



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

525 mm Hg =
$$\frac{525 \text{ torr}}{1 \text{ atm}}$$
 (1 mm Hg = 1 torr)
525 mm Hg × $\frac{1 \text{ atm}}{760 \text{ mm-Hg}}$ = $\frac{0.691 \text{ atm}}{0.691 \text{ atm}}$ 525 mm Hg × $\frac{101.325 \text{ kPa}}{760 \text{ mm-Hg}}$ = $\frac{70.0 \text{ kPa}}{100 \text{ kPa}}$

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

350.
$$\frac{\text{kPa}}{101.325 \text{ kPa}} \times \frac{1 \text{ atm}}{101.325 \text{ kPa}} = 3.45 \text{ atm}$$
350. $\frac{\text{kPa}}{101.325 \text{ kPa}} \times \frac{760 \text{ torr}}{101.325 \text{ kPa}} = 2625.2 \text{ torr} = 2.63 \times 10^3 \text{ torr}$
2.63 × 10³ torr = 2.63 × 10³ mm Hg
(1 mm Hg = 1 torr)

Assignment

5.1 & 5.2 pg. 215–216 #2 to 7, 9, 11, 13 and 14

5.3: The Gas Laws

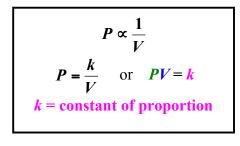
Variables to Describe a Gas:

- 1. <u>Pressure</u> (P): the amount of force per unit of area, measures in kiloPascal (kPa) or standard atmosphere (atm) or mmHg or torr.
- 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).

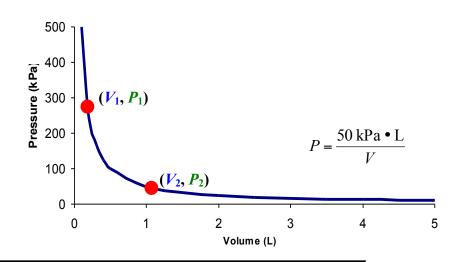
Laws that Relate Gas Variables:

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

Boyle's Law (Constant Temperature)



Volume ↑ Pressure ↓



Boyle's Law

$$P_1V_1 = P_2V_2$$

 P_1 = Pressure at Initial Condition P_2 = Pressure at Final Condition P_2 = Volume at Final Condition P_3 = 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?

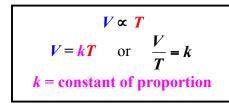
$$P_1 = 101.325 \text{ kPa}$$
 $P_2 = ?$
 $V_1 = 2.50 \text{ L}$
 $V_2 = 6.25 \text{ L}$
 $P_1V_1 = P_2V_2$

$$P_1V_1 = P_2V_2$$

$$P_1V_1 = P_2V_2$$

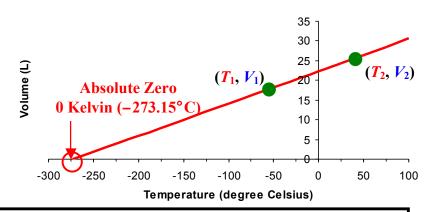
$$P_2 = \frac{(101.325 \text{ kPa})(2.50 \text{ E})}{(6.25 \text{ E})}$$
As Volume ↑, Pressure ↓

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



Temperature ↑ Volume ↑

Charles's Law (Constant Pressure)



Charles's Law

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

 T_1 = Temperature at Initial Condition (in K) T_2 = Temperature at Final Condition (in K)

 V_1 = Volume at Initial Condition

 V_2 = Volume at Final Condition

Example 2: A balloon is 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.

$$V_{1} = 3.25 \text{ L}$$

$$T_{1} = 25.0^{\circ}\text{C} = 298.15 \text{ K}$$

$$V_{2} = ?$$

$$T_{2} = 5.00^{\circ}\text{C} = 278.15 \text{ K}$$

$$\frac{V_{1}}{T_{1}} = \frac{V_{2}}{T_{2}}$$

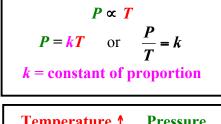
$$\frac{V_{1}T_{2}}{T_{1}} = V_{2}$$

$$\frac{V_{1}T_{2}}{T_{1}} = V_{2}$$

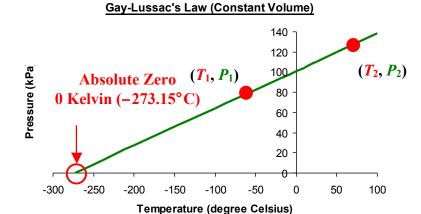
$$\frac{V_{2} = \frac{(3.25 \text{ L})(278.15 \text{ K})}{(298.15 \text{ K})}}{(298.15 \text{ K})}$$

$$As \text{ Temp } \downarrow \text{, Volume } \downarrow$$

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



Temperature 1 Pressure



Gay-Lussac's Law T_1 = Temperature at Initial Condition (in K) P_1 = Pressure at Initial Condition T_2 = Temperature at Final Condition (in K) P_2 = Pressure at Final Condition

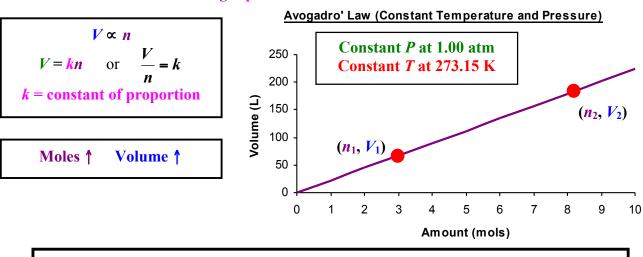
Example 3: A canister is has a pressure of 8.00 atm at 15.0°C. Calculate its pressure if the temperature was to increase to 100.0°C. (**Don't do this at home!**)

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

 $T_1 = 15.0^{\circ}\text{C} = 288.15 \text{ K}$
 $P_2 = ?$
 $T_2 = 100.0^{\circ}\text{C} = 373.15 \text{ K}$
(Change °C to K)
(P can be in atm)
$$P_1 = P_2 \\ T_1 = T_2 \\ T_2 = P_2$$

$$P_2 = \frac{(8.00 \text{ atm})(373.15 \text{ K})}{(288.15 \text{ K})}$$
(288.15 K)
As Temp ↑, Pressure ↑

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



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.

- a. Write a balanced equation for this reaction.
- b. Assuming a complete reaction, what is the volume of phosphorus trichloride produced?

a.
$$P_{4(s)} + 6 Cl_{2(g)} \rightarrow 4 PCl_{3(g)}$$
b.
$$n_{1} = 9.00 \text{ mol } (Cl_{2})$$

$$V_{1} = 223.2 \text{ L}$$

$$n_{2} = 9.00 \text{ mol } Cl_{2} \times \frac{4 \text{ mol } PCl_{3}}{6 \text{ mol } Cl_{2}}$$

$$n_{2} = 6.00 \text{ mol } (PCl_{3})$$

$$V_{2} = ?$$

$$As \text{ Moles } \downarrow, \text{ Volume } \downarrow$$

$$V_{2} = \frac{(6.00 \text{ mol})(223.2 \text{ L})}{(9.00 \text{ mol})}$$

Assignment
5.3 pg. 216 #15 to 26

5.4: The Ideal Gas Law and Combined 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.

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

$$V = 200$$
. L
 $PV = nRT$
 For propane, C_3H_8 , $M = 44.11 g/mol$
 $T = 15.0^{\circ}C = 288.15 \text{ K}$
 $PV = nRT$
 For propane, C_3H_8 , $M = 44.11 g/mol$
 $PV = nRT$
 $PV = nRT$

Standard Mole-Volume Relationships:

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

Example 2: Determine the amount of oxygen gas in a 5.00 L container under STP and SATP.

a. STP

b. SATP

SATP = 24.8 L/mol

$$n = 5.00 \pm \times \frac{1 \text{ mol}}{24.8 \pm}$$
 $n = 0.202 \text{ mol}$

Example 3: Determine the volume of 3.50 g of nitrogen gas under STP and SATP.

a. STP

Page 140.

$$n = \frac{m}{M} = \frac{3.50 \text{ g}}{28.02 \text{ g/mol}} = 0.124910778 \text{ mol}$$

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

$$V = (0.124910778 \text{ mol})(22.4 \text{ L/mol})$$

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

b. SATP

$$n = \frac{m}{M} = \frac{3.50 \text{ g}}{28.02 \text{ g/mol}} = 0.124910778 \text{ mol}$$

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

$$V = (0.124910778 \text{ mol})(24.8 \text{ L/mol})$$

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

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

Combined Gas Law(since
$$R = \frac{PV}{nT}$$
 from the Ideal Gas Law)
$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$
or
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
 (for $n_1 = n_2$) $P_1 =$ Pressure at Initial Condition $P_2 =$ Pressure at Final Condition $V_1 =$ Volume at Initial Condition (in K) $V_2 =$ Volume at Final Condition $T_1 =$ Temperature at Initial Condition (in K) $T_2 =$ Temperature at Final Condition (in K) $n_1 =$ Amount of Moles at Initial Condition $n_2 =$ Amount of Moles at Final Condition

Example 4: A high altitude weather balloon has a volume of 57.2 L at 700. mm Hg and at 25.0°C. Determine its volume at its maximum height when the pressure is 0.365 atm and the temperature is at -45.0°C.

$$n_1 = n_2$$
 (gas amounts did not change)
 $V_1 = 57.2 \text{ L}$
 $P_1 = 700. \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}}$
 $P_1 = 0.9210526316 \text{ atm}$
 $T_1 = 25.0 ^{\circ}\text{C} = 298.15 \text{ K}$
 $V_2 = ?$
 $P_2 = 0.365 \text{ atm}$
 $T_2 = -45.0 ^{\circ}\text{C} = 228.15 \text{ K}$
(P can be in atm or mmHg but change $^{\circ}\text{C}$ to K)
$$\frac{P_1V_1}{T_2} = \frac{P_2V_2}{T_2}$$

$$\frac{P_1V_1T_2}{T_1P_2} = V_2$$

$$\frac{P_1V_1T_2}{T_1P_2} = V_2$$

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

Example 5: A 0.852 mol in a 1.00 L balloon 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 if there was a leak and the amount of xenon reduced to 0.750 mol?

$$n_1 = 0.852 \text{ mol}$$
 $n_2 = 0.750 \text{ mol}$ $T_1 = 23.0^{\circ}\text{C} = 296.15 \text{ K}$ $T_2 = 148.0^{\circ}\text{C} = 421.15 \text{ K}$ $P_1 = 752 \text{ mm Hg}$ $P_2 = 2854 \text{ mm Hg}$ $P_2 = 2854 \text{ mm Hg}$ $V_2 = ?$ $\Delta V = V_2 - V_1 = ?$ $\Delta V = V_2 - V_1 = ?$ $\Delta V = -0.67 \text{ L or a decrease of } 0.67 \text{ L}$ $\Delta V = -0.67 \text{ L or a decrease of } 0.67 \text{ L}$

Example 6: An expandable container is filled with a gas mixture. If the temperature (in Kelvin) of the container is doubled and the pressure is decreased by one-third, how would the new volume compared to the original volume?

 $T_2 = 2T_1$ (temperature doubled)

 $P_2 = \frac{2}{3} P_1$ (P is decreased by a third means new pressure is $1 - \frac{1}{3} = \frac{2}{3}$ of original pressure)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \implies \frac{P_1V_1T_2}{T_1P_2} = V_2$$

$$V_2 = \frac{P_1V_1(2T_1)}{T_1(\frac{2}{3}P_1)} = \frac{P_1V_1(2T_1)}{T_1(\frac{2}{3}P_1)} = \frac{V_1(2)}{(\frac{2}{3})}$$

$$V_2 = 3V_1$$

The new volume will be three times the original volume.

Density and Molar Mass Determinations of a Gaseous Substance

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

$$PV = nRT$$

$$PV = \left(\frac{m}{M}\right)RT \qquad \text{(Substitute } \frac{m}{M} \text{ for } n\text{)}$$
Solve for $\frac{m}{V}$ for Density $(D = \frac{m}{V})$ Solve for Molar Mass (M)

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

$$M = \left(\frac{m}{V}\right)\frac{RT}{P} \qquad M = \frac{DRT}{P}$$
Density (g/L)
$$D = \frac{PM}{RT}$$

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

Example 7: 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.

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

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

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

$$R = 8.314 \text{ (L} \cdot \text{kPa) / (K} \cdot \text{mol)}$$
(We use this R because we are given P in kPa)
$$M = \frac{DRT}{P} = \frac{(0.645 \text{ g/E})(8.314 \frac{\text{E} \cdot \text{kPa}}{\text{K} \cdot \text{mol}})(298.15 \text{ K})}{(100.0 \text{ kPa})}$$

$$M = 15.9883832 \text{ g/mol}$$

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

Example 8: Calculate the density in g/L of a sulfur dioxide gas at 724 torr and at -8.47°C.

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

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

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

$$R = 0.0821 \text{ (L • atm) / (K • mol)}$$
For sulfur dioxide, SO₂,
$$M = 64.07 \text{ g/mol}$$

$$D = \frac{PM}{RT} = \frac{(0.9526315789 \text{ atm})(64.07 \text{ g/mol})}{(0.0821 \frac{\text{L*atm}}{\text{K*mel}})(264.68 \text{ K})}$$

$$D = 2.808765065 \text{ g/L}$$

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

5.5: Gas Stoichiometry

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

- 1. Predict the products and balance the chemical equation.
- 2. Put all the information given under the appropriate chemicals.

3. Find the moles of the given chemical:
$$\left(n = \frac{m}{M}\right)$$
 or $\left(n = CV\right)$ or $\left(n = \frac{PV}{RT}\right)$ or $\left(\text{at STP: } n = \text{Volume} \times \frac{1 \text{ mol}}{22.4 \text{ L}}\right)$; at SATP: $n = \text{Volume} \times \frac{1 \text{ mol}}{24.8 \text{ L}}\right)$.

- **4.** 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.
- **5.** Find the mole of the required chemical using mole ratio:

$$\left(\text{mol of require = mol of given} \times \frac{\text{require coefficient}}{\text{given coefficient}}\right)$$

6. Convert mole of the required chemical to its mass, concentration or volume equivalence: (m = nM) or $(C = \frac{n}{V})$ or (PV = nRT) or $(at STP: V = n \times 22.4 \text{ L/mol})$; at $SATP = n \times 24.8 \text{ L/mol})$.

Example 1: 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.

$$2 \text{ Al}_{(s)} + 3 \text{ H}_2 \text{SO}_{4 (aq)} \rightarrow 3 \text{ H}_{2 (g)} + \text{Al}_2 (\text{SO}_4)_{3 (aq)}$$

$$M = 26.98 \text{ g/mol}$$

$$? \text{ g} \qquad \text{STP} = 22.4 \text{ L/mol}$$

$$1 \text{ m}_{H_2} = 5.76 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 0.2571428571 \text{ mol}$$

$$2 \text{ m}_{Al} = 0.2571428571 \text{ mol}_{H_2} \times \frac{2 \text{ mol Al}}{3 \text{ mol}_{H_2}} = 0.1714285714 \text{ mol Al}$$

$$3 \text{ m}_{Al} = nM = (0.1714285714 \text{ mol Al}) (26.98 \text{ g/mol})$$

$$m_{Al} = 4.63 \text{ g}$$

Example 2: 35.24 kg of liquid octane is burned under excess oxygen. Determine the volume of carbon dioxide gas produced at SATP.

Example 3: Ammonia is reacted with oxygen to form nitrogen monoxide and water vapour.

$$4 \text{ NH}_{3(g)} + 5 \text{ O}_{2(g)} \rightarrow 4 \text{ NO}_{(g)} + 6 \text{ H}_{2}\text{O}_{(g)}$$

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

$$4 \text{ NH}_{3 (g)} + 5 \text{ O}_{2 (g)} \rightarrow 4 \text{ NO}_{(g)} + 6 \text{ H}_{2}\text{O}_{(g)}$$

$$50.0 \text{ L} \qquad 30.0 \text{ L}$$

$$25.0^{\circ}\text{C} = 298.15 \text{ K} \qquad 10.0^{\circ}\text{C} = 283.15 \text{ K}$$

$$90.0 \text{ kPa} \qquad ? \text{ kPa}$$

$$0 \text{ } n_{\text{O}_{2}} = \frac{PV}{RT} = \frac{(90.0 \text{ kPa})(50.0 \text{ L})}{(8.314 \frac{\text{kPa*L}}{\text{mol*K}})(298.15 \text{ K})} = 1.815380558 \text{ mol O}_{2}$$

$$2 \text{ } n_{\text{NO}} = 1.815380558 \text{ mol O}_{2} \times \frac{4 \text{ mol NO}}{5 \text{ mol O}_{2}} = 1.452304446 \text{ mol NO}$$

$$3 \text{ } P_{\text{NO}} = \frac{nRT}{V} = \frac{(1.452304446 \text{ mol})(8.314 \frac{\text{kPa*L}}{\text{mol*K}})(283.15 \text{ K})}{30.0 \text{ L}}$$

$$P_{\text{NO}} = 114 \text{ kPa}$$

Example 4: 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.

$$3 \text{ H}_{2 \text{ (g)}}$$
 + $N_{2 \text{ (g)}}$ \rightarrow 2 NH_{3 (g)}
15.25 L 7.85 L; 98.0 kPa; $R = 8.314 \frac{\text{L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}}$? L
STP = 22.4 L/mol $-18.6 ^{\circ}\text{C} = 254.55 \text{ K}$ SATP = 24.8 L/mol

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

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

② $n_{\text{N}_2} = \frac{PV}{RT} = \frac{(98.0 \text{ kPa})(7.85 \text{ L})}{(8.314 \frac{\text{kPa} \cdot \text{L}}{12.2})(254.55 \text{ K})} = 0.3635068598 \text{ mol N}_2$

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

③
$$n_{\text{H}_2} = 0.3635068598 \text{ mol N}_2 \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} = 1.090520579 \text{ mol H}_2 \text{ needed}$$

But we don't have 1.090520579 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 <u>NOT</u> always the chemical with the smaller number of moles. You have to always compare like we did above.)

Now, we calculate the moles of NH₃ formed by using moles of limiting reagent, H₂.

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

$$V_{\rm NH_3} = 11.3 \, \rm L$$

Assignment

5.4 pg. 216-217 #28 to 50 (do even, optional odd); pg. 220 #94

5.5 pg. 217–218 #51 to 60 (do even, optional odd); pg. 219–221 #93, 95, 104, 108, 110

5.6: 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

$$\frac{P_{\text{Total}} = P_1 + P_2 + P_3 + \dots}{V} = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \dots \frac{(\text{Using Ideal Gas Law } P = \frac{nRT}{V})}{(R, T, \text{ and } V \text{ are common to all components in gas mixture})}$$

$$n_{Total} \left(\frac{RT}{V} \right) = \left(\frac{RT}{V} \right) (n_1 + n_2 + n_3 + ...)$$
 (Take out Common Factor $\frac{RT}{V}$ and cancel both sides)

 $n_{\text{Total}} = n_1 + n_2 + n_3 + \dots$ (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 (<u>http://www.mistupid.com/chemistry/aircomp.htm</u>).

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

Example 2: Write the equations for partial pressures for air, which is composed of N₂, O₂, CO₂, Ar, and other trace gases (78.084%, 20.947%, 0.033%, 0.934%, 0.002% by volume respectively). Determine the partial pressures of these gases for 1 atm of air in kPa.

$$\begin{aligned} & \textbf{\textit{P}}_{\text{total}} = \textit{\textit{P}}_{\text{N}_{2}} + \textit{\textit{P}}_{\text{O}_{2}} + \textit{\textit{P}}_{\text{Ar}} + \textit{\textit{P}}_{\text{trace gases}} = \textbf{101.325 kPa} \\ & \textit{\textit{P}}_{\text{N}_{2}} = (0.780\ 804)(101.325\ \text{kPa}) \\ & \textit{\textit{P}}_{\text{O}_{2}} = (0.209\ 47)(101.325\ \text{kPa}) \\ & \textit{\textit{P}}_{\text{CO}_{2}} = (0.000\ 33)(101.325\ \text{kPa}) \\ & \textit{\textit{P}}_{\text{Ar}} = (0.009\ 34)(101.325\ \text{kPa}) \\ & \textit{\textit{P}}_{\text{trace gases}} = (0.00\ 002)(101.325\ \text{kPa}) \end{aligned}$$

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.

$$\frac{\text{Mole Fraction}}{\text{Total Moles in Gas Mixture}} = \frac{\text{Partial Pressure of a Gas Component}}{\text{Total Pressure in Gas Mixture}} = \frac{Partial Pressure of a Gas Component}{P_1}$$

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

 χ = Mole Fraction (χ is pronounced *chi* – like *chi-tea*, not *tai-chi*) has NO UNITS.

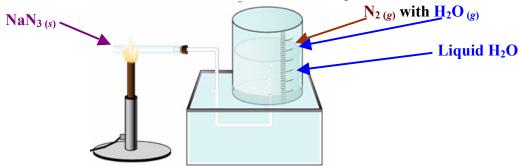
Example 3: Air is composed of 0.20947 oxygen gas. (We would spontaneously combust if air has over 23% oxygen.) Determine the amount, in moles, and the pressure of oxygen if a compressed air tank at 4.50 atm has a total volume of 6.50 L and it is at 18.0°C.

Example 4: Sodium azide, NaN₃, can be electronically ignited to produce nitrogen used in automobile airbags. The reaction is as followed.

$$2 \text{ NaN}_{3(s)} \xrightarrow{\text{heat}} 2 \text{ Na}_{(s)} + 3 \text{ N}_{2(g)}$$

An experiment is set up where the nitrogen produced is bubbled through water for collection and has become saturated with water vapour. Suppose 800 mL of nitrogen gas is collected at 20.0°C and has a total pressure of 105 kPa. (Vapour Pressure of water at 20.0°C is 17.54 torr – the amount of pressure due to evaporation of water into water vapour at a given temperature: a table can be found on pg. 152 of the textbook.)

- a. Determine the partial pressure of the nitrogen gas in this experiment.
- b. Calculate the mass of sodium azide needed to react to produce this amount of nitrogen.



$$P_{\text{water vapour}} = 17.54 \frac{\text{torr}}{760 \text{terr}} \times \frac{101.325 \text{kPa}}{760 \text{terr}}$$

$$P_{\text{water vapour}} = 2.338474342 \text{ kPa}$$

$$P_{\text{nitrogen}} = 2.338474342 \text{ kPa}$$

$$P_{\text{nitrogen}} = 105 \text{ kPa} - 2.338474342 \text{ kPa} = 102.6615257 \text{ kPa}$$

$$P_{\text{nitrogen}} = 103 \text{ kPa}$$

$$V_{\text{Total}} = 800 \text{ mL} = 0.800 \text{ L}$$

$$P_{\text{Total}} = 105 \text{ kPa}$$

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

$$m \text{ NaN}_{3} = ?$$

$$D_{\text{nitrogen}} = \frac{P_{\text{N}_{2}}V}{RT} = \frac{(102.6615257 \text{ kPa})(0.800 \text{ E})}{(8.314 \frac{\text{E·kPa}}{\text{K·mol}})(293.15 \text{ K})} = 0.0336975078 \text{ mol}$$

$$D_{\text{NaN}_{3}} = 0.0336975078 \frac{\text{mol Na}_{3}}{3 \text{ mol Na}_{2}} \times \frac{2 \text{ mol NaN}_{3}}{3 \text{ mol Na}_{3}} = 0.0224759646 \text{ mol NaN}_{3}$$

$$D_{\text{NaN}_{3}} = nM = (0.0224759646 \text{ mol NaN}_{3})(65.02 \text{ g/mol})$$

$$D_{\text{NaN}_{3}} = nM = (0.0224759646 \text{ mol NaN}_{3})(65.02 \text{ g/mol})$$

Example 5: 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?

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

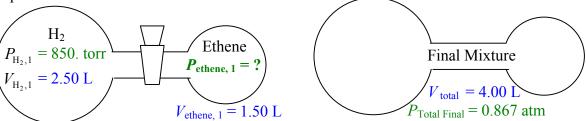
$$P_{\text{oxygen}} = ?$$

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

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

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

Example 6: 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?



$$V_{\rm H_2,1}$$
 = 2.50 L
 $V_{\rm H_2,2}$ = 4.00 L (same as $V_{\rm total}$)
 $P_{\rm H_2,1}$ = 850. torr $P_{\rm H_2,2}$ = ?
($P_{\rm H_2,2}$ is the final partial
pressure of the final mixture;
 $P_{\rm H_2,1}$ is the initial pressure of H₂
before mixing)
 $P_{\rm Total}$ = 0.867 atm × $\frac{760 \, \rm torr}{100 \, \rm torr}$

$$P_{\text{Total}} = 0.867 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}}$$

 $P_{\text{Total}} = 658.92 \text{ torr}$

(Note that P_{Total} is already SMALLER than $P_{H_2,1}$. Total pressure should be greater than partial pressure. This is telling you the H_2 pressure given was at initial conditions).

When the gases are finally mixed, the final pressure of the mixture is the sum of partial pressures of H₂ and ethene.

$$P_{\text{Total Final}} = P_{\text{H}_{2},2} + P_{\text{ethene},2}$$

Calculating final partial pressure of $P_{H_{1,2}}$ using Boyle's Law:

$$P_{\text{H}_{2},2} V_{\text{H}_{2},2} = P_{\text{H}_{2},1} V_{\text{H}_{2},1}$$

 $P_{\text{H}_{2},2} (4.00 \text{ L}) = (850. \text{ torr})(2.50 \text{ L})$ $P_{\text{H}_{2},2} = 531.25 \text{ torr}$

Determine final partial pressure of $P_{\text{ethene, 2}}$:

$$P_{\text{Total Final}} = P_{\text{H}_2, 2} + P_{\text{ethene, 2}}$$

658.92 torr = 531.25 torr + $P_{\text{ethene, 2}}$ $P_{\text{ethene, 2}} = 126.67$ torr

At last, we can calculate the initial pressure of ethene, $P_{\text{ethene, 1}}$, before mixing by using Boyle's Law:

$$V_{\text{ethene, 1}} = 1.50 \text{ L}$$
 $P_{\text{ethene, 1}} = ?$ $V_{\text{ethene, 2}} = 4.00 \text{ L}$ (same as V_{total}) $P_{\text{ethene, 2}} = 126.67 \text{ torr}$ $P_{\text{ethene, 1}} V_{\text{ethene, 1}} = P_{\text{ethene, 2}} V_{\text{ethene, 2}}$ $V_{\text{ethene, 1}} = 338 \text{ torr}$ $P_{\text{ethene, 1}} = 1.50 \text{ L}$ $P_{\text{ethene, 1}} = 1.50 \text{ L}$

5.7: 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 (\overline{u} or u_{rms}): - the average velocity of a single gaseous molecule or atom in a closed system.

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

Derivation of Pressure as it relates to Average Kinetic Energy

This derivation is a complicated procedure (see http://en.wikipedia.org/wiki/Kinetic_theory#Pressure – if you have background in senior physics!). In any case, the **total pressure** of a gas relates to **kinetic energy** by the formula below.

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

$$N_A(E_k)_{avg} = \text{Average Kinetic Energy per Mole}$$

Relating Temperature and Average Kinetic Energy

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

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

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

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

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

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

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

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

Root Mean Square Velocity

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

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

M = Molar Mass in kg/mol

m = 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.

- a. Determine the average kinetic energy per mole of the gas.
- b. Calculate the root mean square velocity of an argon atom.
- c. Will the average kinetic energy be decreased, increased or remain the same for the following conditions?
 - i. the temperature is increased to 400°C as electricity is applied into the tube.
 - ii. the volume is allowed to double as the argon gas is evacuated into a larger tube.
 - iii. the number of moles is halved as a vacuum is used to draw out some of the argon gas.
- d. 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 atm

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

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

M = 39.95 g/mol M = 0.03995 kg/molR = 8.31 J/ (mol • K) **b.** Since we do not have the mass of Ar, we have the use the first variation of the u_{rms} formula.

$$KE \text{ per mol} = ?$$
 $u_{rms} = ?$

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

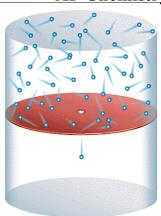
 $u_{rms} = 412 \text{ m/s}$

- c. (i) As *T* ↑, *KE* ↑
- (ii) As $V \uparrow$, 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, $M \downarrow u_{rms} \uparrow$

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 separting 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 effusion rate of a gas is proportional to the square root of its molar mass.

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 2: Calculate the ratio of effusion rates between NH_{3 (g)} and HCl (g) under the same temperature.

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

$$\left(\frac{r_{\rm NH_3}}{r_{\rm HCl}} = 1.463\right)$$

NH₃ effuse about 1.5 times faster than HCl.

Example 3: 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.

$$r_{N_2} = 274 \text{ mL/min}$$

 $M_{F_2} = 38.00 \text{ g/mol}$
 $M_{N_2} = 28.02 \text{ g/mol}$

$$\frac{r_{\rm F_2}}{r_{\rm N_2}} = \frac{\sqrt{M_{\rm N_2}}}{\sqrt{M_{\rm F_2}}}$$

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

 $M_{\rm N_2} = 28.02 \text{ g/mol}$ $r_{\rm F_2} = ?$ Since F₂ is bigger than N₂, $r_{\rm F_2}$ is less than $r_{\rm N_2}$ $r_{\rm F_2} = 235 \text{ mL/min}$

Example 4: Complete the table below and find the molar mass of unknown gas X. (http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/gaslaw/effusion macro.html)

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	$\frac{100\mathrm{mL}}{(5.00/60)\mathrm{min}} = 1200$
O_2	32.00	100 mL	20.0 sec	$\frac{100\mathrm{mL}}{(20.0/60)\mathrm{min}} = 300.0$
Xe	131.29	100 mL	40.6 sec	$\frac{100\mathrm{mL}}{(40.6/60)\mathrm{min}} = 147.8$
Kr	83.80	100 mL	32.4 sec	$\frac{100\mathrm{mL}}{(32.4/60)\mathrm{min}} = 185.2$
Unknown X	?	100 mL	23.5 sec	$\frac{100 \mathrm{mL}}{(23.5/60) \mathrm{min}} = 255.3$

We can use any gas to set up a ratio with r_X . We choose O_2 because its rate is an even number.

$$r_{O_{2}} = 300 \text{ mL/min}$$

$$M_{O_{2}} = 32.00 \text{ g/mol}$$

$$r_{X} = 255.3 \text{ mL/min}$$

$$M_{X} = ?$$

$$r_{O_{2}} = \sqrt{M_{X}} \rightarrow \frac{(r_{O_{2}})\sqrt{M_{O_{2}}}}{(r_{X})} = \sqrt{M_{X}} \rightarrow \frac{(r_{O_{2}})\sqrt{M_{O_{2}}}}{(r_{X})} = \sqrt{M_{X}} \rightarrow \frac{(r_{O_{2}})\sqrt{M_{O_{2}}}}{(r_{X})} = M_{X}$$

$$m_{X} = \frac{(r_{O_{2}})^{2}(M_{O_{2}})}{(r_{X})^{2}} = \frac{(300 \text{ mE/min})^{2}(32.00 \text{ g/mol})}{(255.3 \text{ mE/min})^{2}}$$

$$m_{X} = 44.2 \text{ g/mol}$$
Since r_{X} is less than $r_{O_{2}}$, X is bigger than O_{2} .

- **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 area of High Pressure to an area of very Low Pressure (near vacuum) – like a breach on the hull of a spacecraft or a plane.

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

Assignment
5.6 pg. 218 #61 to 72; pg. 220–221 # 106, 107 and 111
5.7 pg. 219 #73, 74, 78 to 82 (even), 83, 84; pg. 222 #123

5.8: Deviation from Ideal Behaviour

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.

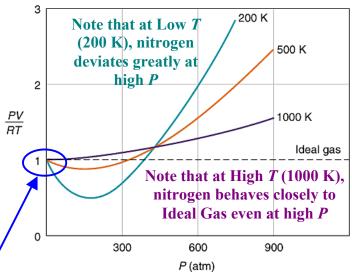
Ideal Gas Low Pressure High Temperature

Real Gas **High Pressure Low Temperature**

Various Gases under High Pressures at 200 K

Strong e- Repulsion between molecules due to Very Small CO, 1.5 Volume Ideal gas $\frac{PV}{RT}$ (1.0 Strong attractions between molecules due to 0.5 Stronger Intermolecular forces (section 10.1) 400 600 800 1000 0 200

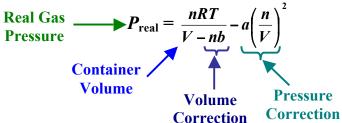
Nitrogen Gas at various Temperatures



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

P (atm)

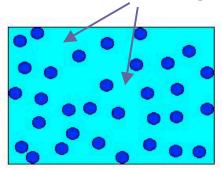
<u>van der Waals Equation</u>: - Johannes van der Waals first proposed <u>correctional factors</u> (volume and pressure due to intermolecular attractions) to correct for real gases under low volume and high pressure.



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

n = number of molesb = van der Waals Volume Constant

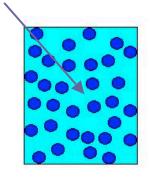
 V_{actual} = Volume of Spaces between Molecules



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

$$V_{\rm actual} \approx V_{\rm container}$$

and $(nb \approx 0)$.



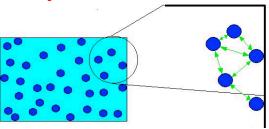
At high pressure, there is a lot less space between molecules and

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

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

n = number of molesa = van der Waals Pressure ConstantV = Volume of Container

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



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.

Gas	M (g/mol)	$a (atm \cdot L^2) / mol^2$	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

van der Waals Constants for Various Gases

Gas	M (g/mol)	$a (atm \cdot L^2) / mol^2$	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*: <u>In general, a >> b</u> (>> 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

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

 $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$ (rearranged to solve for nRT – 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.

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

$$n = 4687.5 \text{ mol}$$

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

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

$$R = 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}$$

$$a = 1.36 \frac{\text{atm} \cdot \text{L}}{\text{mol}^{2}}$$

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

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

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

$$P_{\text{diffe}} = \frac{|P_{\text{ideal}} - P_{\text{real}}|}{|P_{\text{ideal}}|} \times 100\% = \frac{|237 \text{ atm} - 183 \text{ atm}|}{237 \text{ atm}} \times 100\%$$

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

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

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

$$P_{\text{ideal}} = \frac{|P_{\text{ideal}} - P_{\text{real}}|}{P_{\text{ideal}}} \times 100\% = \frac{|237 \text{ atm} - 183 \text{ atm}|}{237 \text{ atm}} \times 100\%$$

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

Assignment
5.8 pg. 219 #86 to 90

Chapter 11: Intermolecular Forces and Liquids and Solids

11.1: Kinetic Molecular Theory of Liquids and Solids

Phase: - is a homogenous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.

Kinetic Molecular Theory of Liquids and Solids:

Liquid: - a phase of matter where it has a *definite volume but takes up the shape of the container*.

- the molecules in this phase have much less space between themselves compared to gas phase molecules. Hence, they are only *slightly compressible*, and resulting in a much higher density compared to densities of gases.
- this phase can still be considered as fluid. Like gas, the *molecules can slide past one another freely*. Therefore, they can be "pour" out of the container.

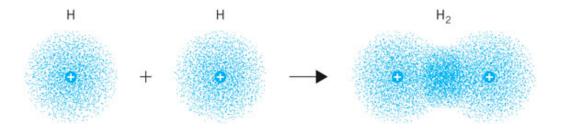
Solid: - a phase of matter where it has a *definite volume and definite shape*.

- the molecules in this phase have much less space between themselves compared to liquid phase molecules (with the exception of water). Hence, they are *not compressible*, and resulting in a very higher density.
- <u>solid is not a fluid</u>. Unlike gas and liquid, the <u>molecules can only vibrate about their fixed</u> <u>positions</u>. Therefore, they cannot be "pour" out of the container. (Even though one can "pour" sand or sugar out of a container, it is not a fluid because the molecules are locked in crystalline form and cannot slide part each other. They can be "pour" out because their crystal sizes are small.)

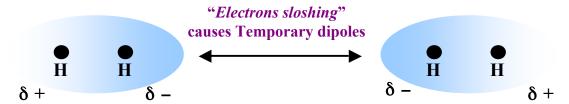
11.2: Intermolecular Forces

Intermolecular Forces: - attraction forces between molecules in a compound

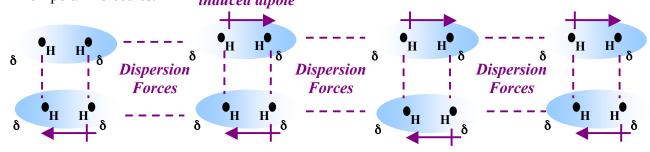
- the strengths of the intermolecular forces <u>explain</u> the <u>physical properties of compounds</u> (solubility, boiling and freezing points).
- **a.** <u>van der Waals Forces</u>: named after Johannes van der Waals who studied real gases and interaction between molecules.
 - there are two kinds of van der Waals forces.
 - they are Dispersion Forces and Dipole-Dipole Interactions.
 - i. <u>Dispersion Forces</u>: also known as <u>London Dispersion Forces</u> (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 <u>temporary dipole</u> that forms within the molecules even in non-polar molecules due 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. induced dipole



- even monoatomic element like Helium has London Forces.
 (Check out animation at 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.

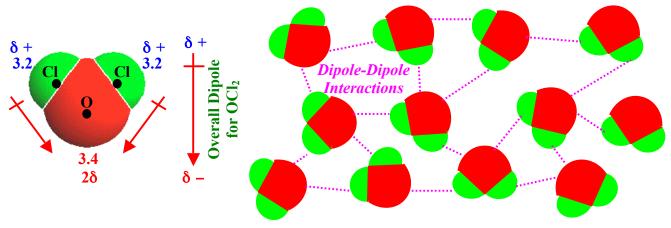
of e- or molar mass in atom or molecule 1, London Dispersion Force 1, Melting and Boiling Point 1

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

Noble Gases	# of <i>e</i> -	Molar Mass (g/mol)	Melting Point	Boiling Point
Не	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)

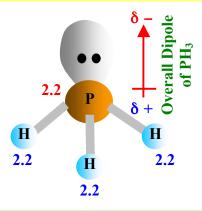
All atoms of noble gases are monoatomic non-polar. The only intermolecular force that governs the melting and boiling points is the London Dispersion Force. As the number of electrons in the noble gases increase, London dispersion force makes the attraction between the atoms greater. This in turn has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

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

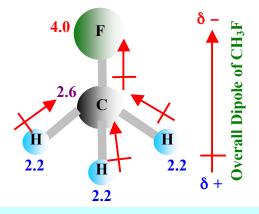


Example 2: Order the boiling points from the least to greatest for the following compounds with similar molar mass. PH₃ (34.00 g/mol), CH₃F (34.04 g/mol), and SiH₄ (32.13 g/mol)

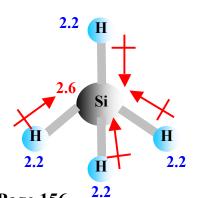
Since PH₃, CH₃F and SiH₄ have similar molar mass; any differences in boiling points cannot be due to London Dispersion forces. Since dipole-dipole interactions exist in polar molecules, we have to examine the molecular geometry and structure of each compound.



PH₃ 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.



CH₃F has a tetrahedral geometry and is very polar. The C-F bond along with the C-H bonds has strong polarity. The overall dipole moment for the molecule has electrons around the F atom.



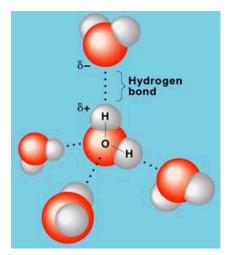
SiH₄ has a tetrahedral geometry with equal dipoles of Si-H bonds cancels out all bond polarities. Hence, SiH₄ is Non-Polar.

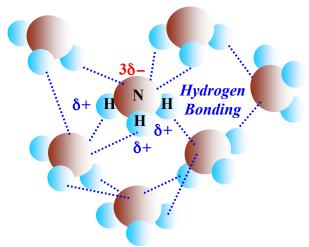
Since non-polar molecules have no dipole interactions, SiH₄ should have the lowest boiling point. PH₃ is less polar than CH₃F due to the difference in electronegativities between P-H bond and C-F with C-H bonds. Therefore, CH₃F must have the highest boiling point.

Boiling Point:

 $SiH_4 < PH_3 < CH_3F$

- **b.** <u>Hydrogen Bonds</u>: 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-Cl and H-F 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 **amongst molecular compounds**.



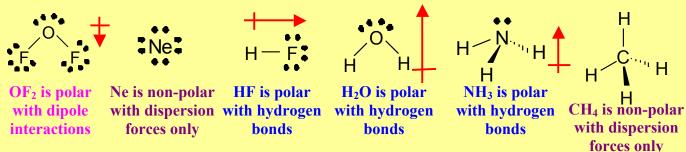


(Check out the Hydrogen Bond Animation at http://www.northland.cc.mn.us/biology/Biology1111/animations/hydrogenbonds.html)

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	✓	X	×	-161°C (112 K)

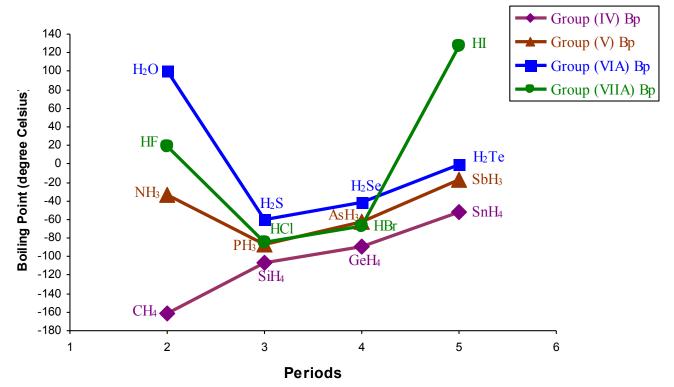
Again, we need to draw the structural formulas of these molecules and compare their polarities.



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

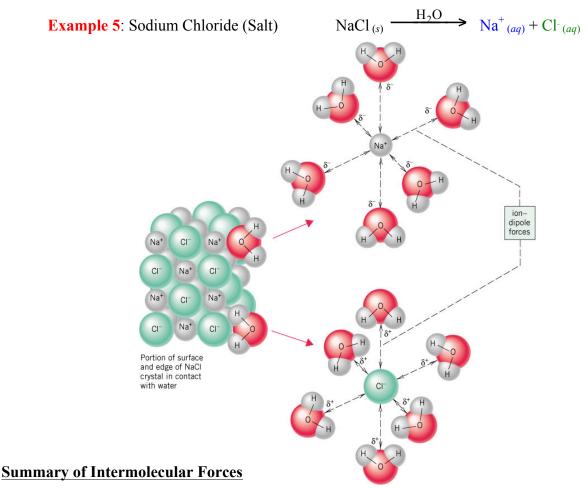




- a. The hydrogen compounds in the Group (VIA) series have higher boiling points than hydrogen compounds in the other series.
- b. The first hydrogen compounds in Groups (VA), (VIA) and (VIIA), namely NH₃, H₂O and HF, have higher boiling points than most other hydrogen compounds in their respective series. 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 most 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.

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

- **c.** <u>Ion-Dipole Force</u>: when ionic compounds dissolve in water, the cation and anion components separate from one another. These ions are then attracted by the polar water molecules.
 - ion-dipole force is the STRONGEST of all intermolecular forces.



- 1. <u>Intermolecular Bonds</u> involve in a compound explain its <u>physical properties</u> such as solubility ("*like dissolves like*"), boiling and melting points (energy involved in physical phase change).
- 2. <u>van der Waals Forces</u> consist of <u>London Dispersion forces</u> (apply to all molecules) and <u>Dipole Interactions</u> (apply to polar molecules).
- 3. Hydrogen Bond is the STRONGEST of the intermolecular bonds amongst molecular compounds
- 4. **Ion-Dipole Force** is the *strongest* of all <u>intermolecular bonds</u>.

Strength of Intermolecular Forces

van der Waals Forces

Ion-Dipole Force > **Hydrogen Bond** > **Dipole Interaction** >> **London Dispersion Force** >> (much stronger than)

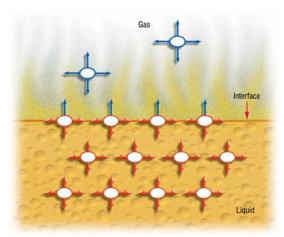
Assignment

11.2 pg. 504-505 #2, 3, 6 to 10, 12 to 20; pg. 508-509 #95, 108, 112, 115, 118

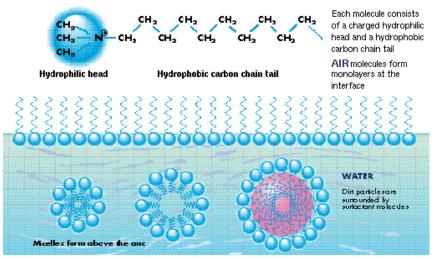
11.3: Properties of Liquids

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

- intermolecular forces from polar molecules cannot attract with molecules in the air, which are nonpolar. Therefore, the higher net force is pushed inward, leaving a stretched surface called surface tension.



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



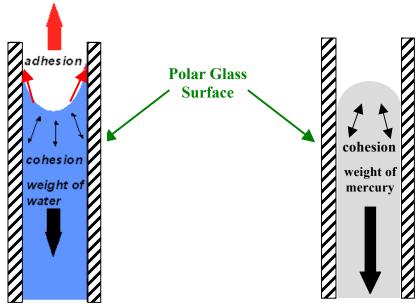
Hydrophobic: - non-polar nature "water fearing". Hydrophilic: - polar nature "water loving".

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

- <u>polar liquids tend to have high viscosity</u> 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.

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**.
- **a.** <u>Cohesive Forces</u>: forces between molecules (intermolecular forces like London Dispersion Force, Dipole interactions, and Hydrogen Bonding).
- **b.** 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.
 - <u>polar liquid molecules</u> with <u>inner surface of the container</u> that are also <u>polar will create a large adhesive force (example: water and glass).</u>
 - <u>non-polar liquid molecules</u> with <u>polar inner surface of the container</u> will create a small adhesive force (example: mercury and glass).



Both adhesion and conesion torces are both strong.

However, adhesion > cohesion.

Therefore, water meniscus is concave.

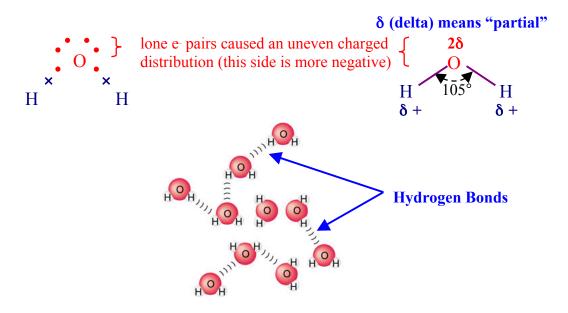
Cohesion forces are weak (Hg is non-polar).

There is no adhesion.

However, <u>cohesion > adhesion</u>.
Therefore, mercury meniscus is <u>convex</u>.

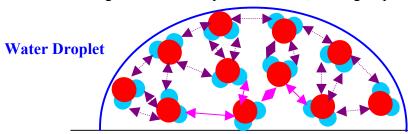
Structural Features of Water:

- 1. V-Shaped: the two O-H bonds form 105° from each other, which leads to its polarity.
- 2. Polar Molecule: unequal charged distribution due to the electron pairs around the oxygen atom.
- **3. Strong O–H Hydrogen Bond**: a type of hydrogen bond that is fairly strong compared to other types of intermolecular bonds (bonds between molecules).



Special Properties of Water:

1. <u>Strong Surface Tension</u> - 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 high surface tension.



Hydrogen Bonds drawn inward and sideways only creating <u>Surface Tension</u>

Water molecules inside the droplets have hydrogen bonds in ALL directions







(Left) Fresh dew drops on a leaf. Note the spherical drop of the water. (Centre) Surface tension of water can support a much denser paper clip. (Right) A water strider is supported by the surface tension of water.

2. High Specific Heat Capacity

Specific Heat Capacity: - the amount of heat it takes to raise the temperature of 1 g of substance by 1°C.
- water has a high specific heat capacity, making it a good storage of solar energy

Specific Heat Capacity of Some Common Substances

Substance	Specific Heat Capacity	Substance	Specific Heat Capacity
Water	4.19 J/(g • °C)	Copper	0.385 J/(g • °C)
Ice	2.00 J/(g • °C)	Iron	0.449 J/(g • °C)
Ammonia	2.06 J/(g • °C)	Oxygen	0.918 J/(g • °C)
Ethanol	2.44 J/(g • °C)	Nitrogen	1.040 J/(g • °C)

3. High Boiling Point and Heat of Vaporization

Boiling Point: - the temperature where the liquid form of a substance evaporates into its gaseous form (or a gaseous form of a substance condenses into its liquid form).

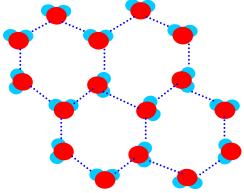
- water has a high boiling point (100°C) due to the strong hydrogen bonds. It takes more energy to break these intermolecular bonds.

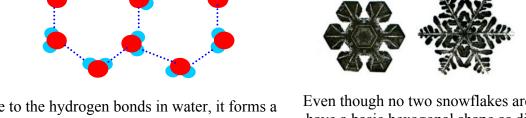
<u>Heat of Vaporization</u>: - the amount of heat to turn 1 mole or 1 gram of liquid substance into its gaseous form.

- water has a molar heat of vaporization of 40.65 kJ/mol or 2.256 kJ/g.
- because it takes an enormous amount of energy to evaporate water, temperatures are regulated on Earth. (Tropical regions are cooled as water absorbs heat. Polar regions are warmed as water vapour condenses to liquid giving off heat).

4. Low Density in Ice compared to Liquid Water

<u>Hexagonal Arrangement of Ice Crystals</u>: - due to the hydrogen bonds in water, it forms a honeycomb shape and expands in volume when it crystallizes into ice.

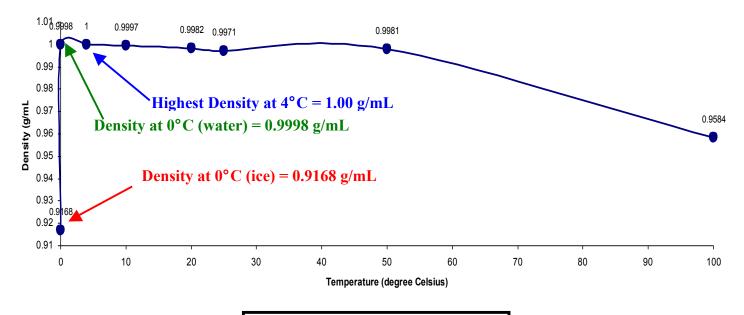




Due to the hydrogen bonds in water, it forms a *honeycomb shape* and expands in volume when it crystallizes into ice.

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

Density of Water



Assignment
11.3 pg. 505 #21 to 25, 27 to 32

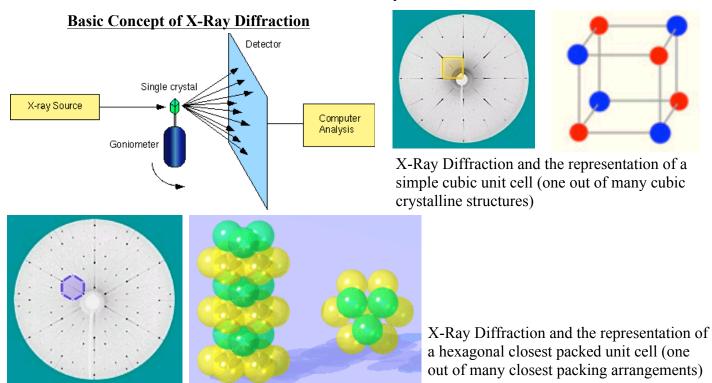
11.6: Types of Crystals

<u>Crystalline Solids</u>: - solids where the arrangemnets of atoms are highly organized.

- the 3-dimensional positions of the atoms in a crystalline solid is called a <u>lattice</u>.
- 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.



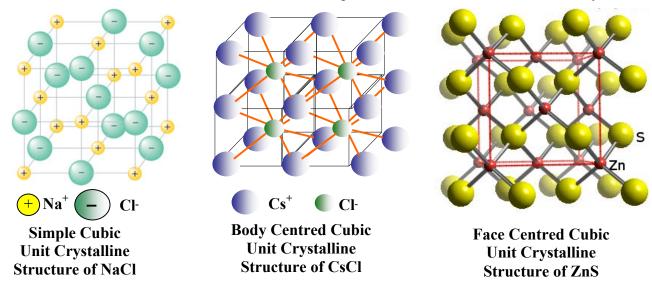
Intramolecular Forces: - attraction forces between atoms WITHIN a molecule.

- the strengths of the intramolecular forces <u>explain</u> the <u>amount of energy</u> involved in a chemical change.

Types of Crystalline Solids

- **a.** <u>Ionic Solids</u>: solids that involved a combination of metal and non-metal elements.
 - atoms are held together by electrostatic attarction of **ionic bonds**.
- **b.** <u>Covalent Solids</u>: solids that involved an <u>extensive 3-dimensional network</u> involving <u>non-metals</u> using their <u>covalent bonds</u>.
- c. <u>Molecular Solids</u>: solids where <u>non-metal atoms</u> are held together by <u>intermolecular forces</u> like dispersion force, dipole-dipole interactions, and/or hydrogen bonds.
- **d.** Metallic Solids: solids that involved metal atoms exclusively using metallic bonds.

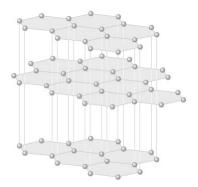
- a. Properties of Ionic Crystalline Solids
- 1. <u>Ionic Compounds have a definite Crystalline Structure and are Poor Conductors of Electricity and Heat in their Solid Form.</u> Conduction of electricity and heat requires ions to move freely within the solid. The lattice structures of the solid ionic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



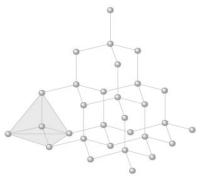
- 2. <u>Ionic solids are generally High Melting Points</u> (typically 300°C to 1000°C). Since a strong force can only shatter the crystal but not bend it as in metals, the energy needed to completely break up the lattice structure (lattice energy) is very large and it is the same energy needed to melt the ionic compounds.
- 3. <u>Ionic solids are Hard and Brittle</u>. 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.** <u>Ionic solids can be Melted to form Liquids that are Electrical Conductors</u>. 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.
- b. Properties of Covalent Crystalline Solids
- **1.** <u>Metalloids</u>: 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).
- 2. Three-Dimensional Network Solids as they form giant molecules by directional covalent bonding (contains no discrete molecular units where an array or network of atoms are held together by conventional covelent bonds, which are directional with dipoles of neighboring atoms.
- **3.** Covalent Compounds are Hard and have High Melting Points. This is due to a more organized crystalline structure and covalent bonds are strong intramolecular bonds.

4. Covalent Compounds are Relatively Poor Heat and Electric Conductors (or Good Heat or Electric Insulators). Covalent compounds do not have any charge particles like ions. Therefore, they cannot conduct heat and electricity well. *An exception is silicon elements*. (Silicon has smaller networks than diamonds, allowing some electrons to pass through. Hence, silicon is called a semiconductor.)

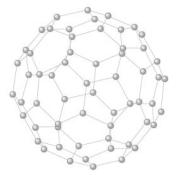
Example: Alloptropes of Carbon



Carbon as <u>Graphite</u> has <u>weak</u> <u>layered with delocalized bonding</u> <u>network</u> (only some carbon atoms are connected – for each layer is $2sp^2$ hybridized which explains its hardness and brittleness). The layers are connected by weak van der Waal forces and hence, graphite can be slippery to the touch. For this reason, we can use it as a lubricant.



Carbon as <u>Diamond</u> has <u>strong</u> <u>tetrahedral network</u> (2sp³) where all four bonding sites of each carbon atoms are connected. Hence, diamond is the hardest material known, and it has an extremely high melting point (3550°C).



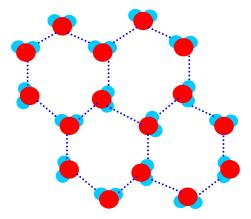
Carbon Network as C_{60} , <u>Buckminsterfullerene</u>, was discovered in 1985. <u>Fullerenes</u> are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane.

Example: Quartz crystal (SiO₂) has a hexagonal network structure. For a 3-D look, (http://earthsci.terc.edu/content/investigations/es0506/es0506page06.cfm)

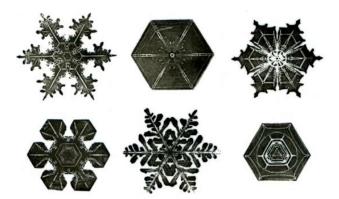


- c. Properties of Molecular Crystalline Solids
- 1. Molecular Compounds tend to have much Lower Boiling and Melting Points than ionic compounds. This is because solid molecular compounds use weak intermolecular forces to form their lattice structures, which does not take much energy to break them. Their boiling points are lower than ionic compounds because there are no ion interactions in liquid state, only intermolecular forces.
- 2. <u>Molecular Compounds are Soft.</u> Again, molecular compounds have a weak lattice structure made of intermolecular bonds that makes them soft.
- 3. Some Molecular Compounds and Elements tend to be More Flammable than ionic compound. This is due to the some non-metals like sucrose and sulfur, which combine readily with oxygen in combustion reactions.
- **4.** Most Molecular Compounds are Insoluble in Water. Because water is very polar, and it has lots of hydrogen bonds, it can only dissolve molecular compounds that are polar as well "Like Dissolves Like". Since most molecular compounds are fairly non-polar, they do not dissolve in polar water well.

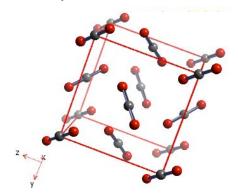
- **5.** Molecular Compounds do NOT Conduct Electricity in their Solid States due to a lack of delocalized electrons.
- **6.** Soluble Molecular Compounds do NOT Conduct Electricity in Water. This is simply due to the fact that molecular compounds do not dissociate into ions or electrolytes like soluble ionic compounds do.



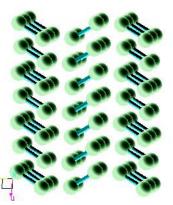
Due to the hydrogen bonds in water, it forms a *honeycomb shape* and expands in volume when it crystallizes into ice.



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, CO_{2 (s)}, is a covalent compound that has a crystalline structure.

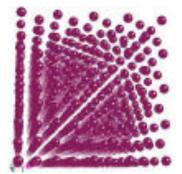


Even a halogen like $I_{2(s)}$ has a crystalline structure.

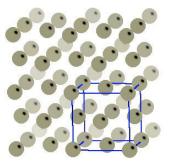


Phosphorus, P_{4 (s)} can form crystalline structure.

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



Solid Ne Crystal Structure

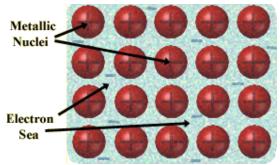


Solid Ar Crystal Structure

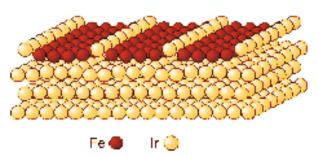
- d. Properties of Metallic Crystalline Solids
- 1. <u>Metals and Alloys</u>: characterized by <u>delocalized non-directional covalent bonds</u> (can be pictured as a bunch of positive charged nuclei floating in a "sea of valence electrons").
 - These valence electrons have not been ionized, but they are usually so far remove from the nucleus that they can be viewed as ionized (hence the word *delocalized*). There is no dipole interactions involved in metallic bonds (therfore the term *non-directional*), but they do *exhibit small covalent properties* due to their close proximity to each other.

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

- 2. <u>Metallic Solids and Alloys are Very Good Conductors of Electricity</u> since the metal atoms are in a sea of valence electrons.
- 3. Metallic Solids and Alloys are Very Good Conductors of Heat since the metal atoms are arranged in closest packing (atoms are packed in layers to minimize spaces in between). This also explains that metallic solids have high densities.
- 4. Metallic Solids 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

General Strength of Different Types of Crystalline Solids

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

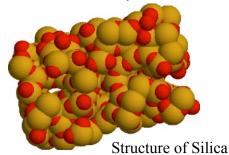
Intramolecular Bonds >> Intermolecular Bonds

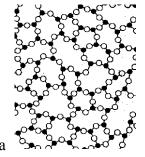
*Ionic Bonds can be Stronger than some Metallic Bonds (depending on the metal / alloy)

11.7: Amorphous Solids

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

Examples: glass (heated silica), quartz glass – SiO₂ (different than quartz crystal, which has a crystalline structure), Pyrex (SiO₂, B₂O₃ and Al₂O₃), soda-lime glass (SiO₂, Na₂O, CaO)





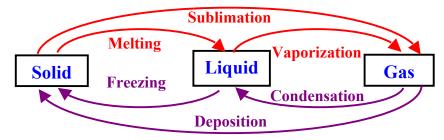
There is no regular molecular arrangement in a quartz glass

Assignment

11.6 pg. 506 #51 to 56; pg. 508 #98, 106 11.7 pg. 506 #57

11.8 & 11.9: Phase Changes & Phase Diagrams

Phase Changes



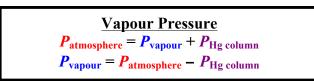
Sublimation: - when a solid becomes a gas directly without undergoing a liquid phase in between.

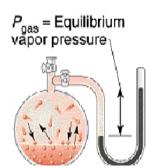
Example: Dry ice (Solid Carbon Dioxide) sublimates from solid to gas directly, skipping the liquid phase.

<u>Deposition</u>: - the phase change from gas to solid directly without undergoing a liquid phase in between.

<u>Vapour Pressure</u>: - 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 equal rates of a two-way process.

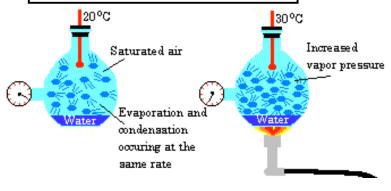


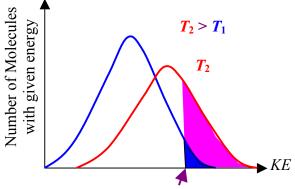


- in general, for a particular compound, as temperature increases, the vapour pressure increases.
- This is because the **higher the temperature**, **kinetic energy increases** and **more lquid molecules** will overcome the **intermolcular forces** to become a gas. Thereby, **increasing vapour presuure**.

Temperature ↑, Vapour Pressure ↑

Note that at higher temperature, more molecules can overcome the intermolecular forces to be in gaseous state.





Minimum energy needed to overcome any intermolecular forces.

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.

Molar Heat of Vaporization (ΔH_{vap}): - amount of heat needed to boil 1 mole of a compound from liquid to gas at its boiling point.

Intermolecular Force \uparrow , ΔH_{vap}

- the stronger the intermolecular force, the higher the molar heat of vaporization.

Calculating Vapour Pressure

$$P_{\text{vap}}$$
 = Vapour Pressure (torr) ΔH_{vap} = Heat of Vaporization (J/mol) T = Temperature in K R = Gas Constant (8.31 J/ (K • mol))

A = Constant Factor relating to Vapour Pressure of a Particular Liquid

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

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

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

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

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

 (P_{vap}) is an exponential function of the reciprical 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)]

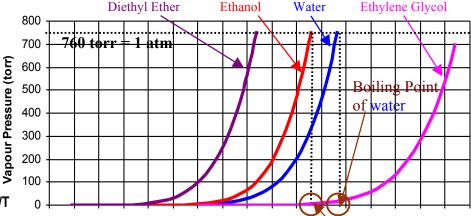
$$[\ln (e^x) = x]$$
 and let $\ln (A) = C$

[Now, $\ln (P_{\text{vap}})$ has a <u>linear relationship</u> with (1/T)] **Vapour Pressure of Various Substances**

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_{va}

In (Vapour Pressure) vs. 1/T Ethanol

Diethyl Ether



140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 Temperature (K) Boiling Point for ethanol

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

10 0.d01 0.d02 0.d03 0.d04 0.005 0.006 0.007 -10 ylene Glyc - 15

1/T (K)

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

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

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

(Check out Animation at

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

Water

- **Example 1**: The following data is collected for octane. Using your TI-83 Plus Calculator,
 - a. graph P_{vap} versus T.
 - b. linearized the previous graph by graphing $ln(P_{vap})$ versus (1/T).
 - c. obtain the equation of the linearized graph.
 - d. calculate the ΔH_{vap} of octane.
 - e. 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:







Check if you entered the **Correct Number of Data Values**

To plot Scatter Plot on TI-83 Plus Calculator:

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









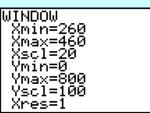
3. Graph Scatter Plot



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

WINDOW

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

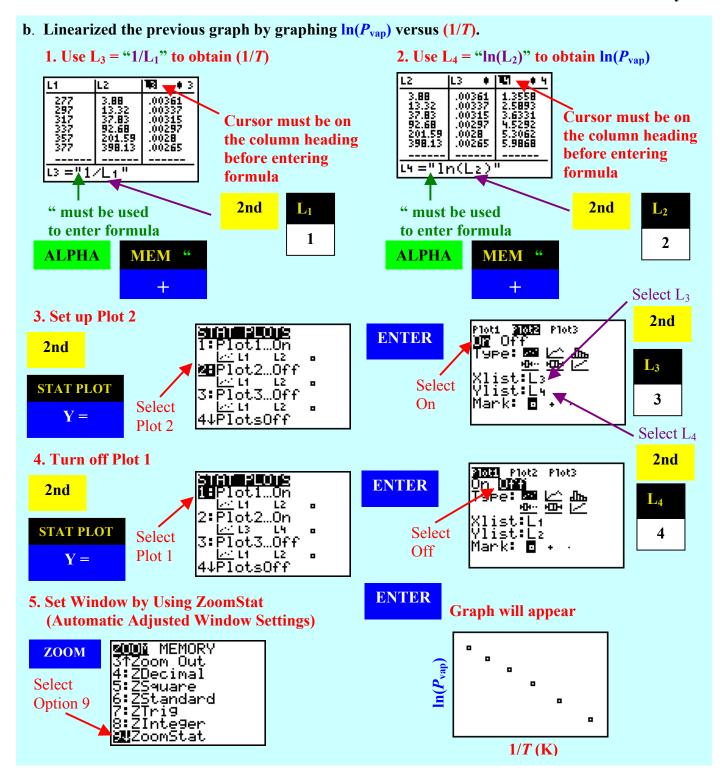


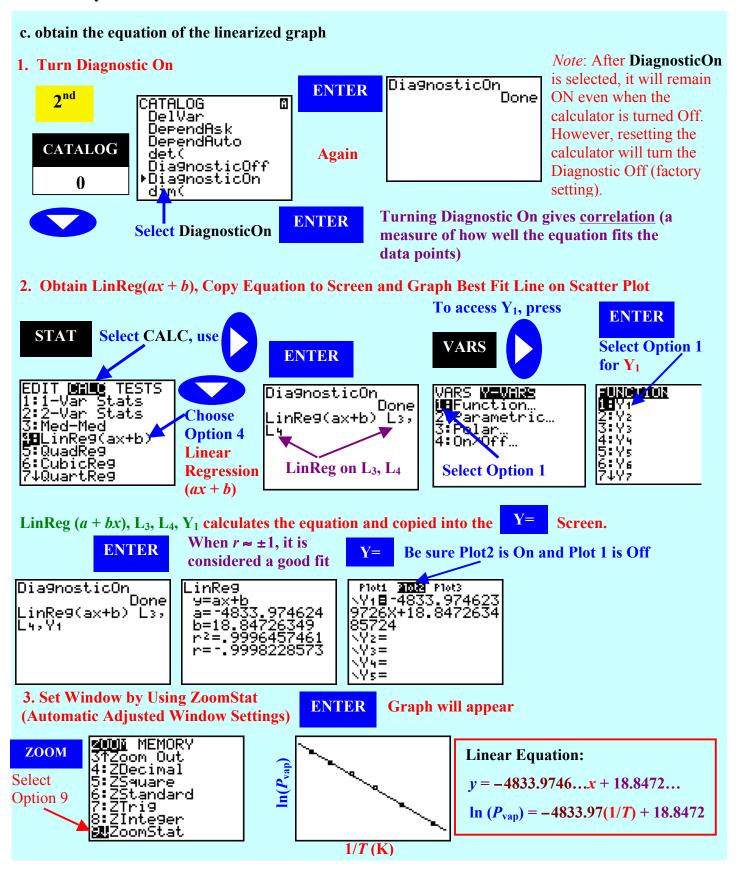
P_{vap} (torr) 400

800 460 T (K) 0 360 260

GRAPH

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





d. Calculate the $\Delta H_{\rm vap}$ of octane

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

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

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

$$-\Delta H_{\text{vap}} = -4833.97 \text{ K} (8.31 \text{ J/ (K} \bullet \text{ mol)})$$

$\Delta H_{\rm vap} = 4.02 \times 10^4 \text{ J/mol} = 40.2 \text{ kJ/mol}$

e. Determine the normal boiling point at 760. torr.

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

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

$$R = 8.31 \text{ J / (K • mol)}$$

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

$$C = 18.8472$$

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

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

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

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

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

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

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

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

$$\ln\left(P_{vap,T_1}\right) - \ln\left(P_{vap,T_2}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2}\right) - \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1}\right) \qquad \text{(Bring both } P_{vap} \text{ and } T \text{ on either side)}$$

$$\ln\left(\frac{P_{vap,T_1}}{P_{vap,T_2}}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{[Using Logarimic Law } \ln(M) - \ln(N) = \ln\left(\frac{M}{N}\right)\text{]}$$

Clausius-Clapeyron Equation of Vapour Pressures

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

$$P_{vap,T_1} = P_{vap} \text{ (torr) at } T_1 \qquad \Delta H_{vap} = \text{Heat of Vaporization (J/mol)}$$

$$P_{vap,T_2} = P_{vap} \text{ (torr) at } T_2 \qquad T_1 \text{ and } T_2 = \text{Different Temperatures (K)}$$

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 vaprization 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.

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

$$T_{1} = 100^{\circ}\text{C} = 373.15 \text{ K}$$

$$P_{vap,T_{2}} = 253 \text{ torr}$$

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

$$= 40650 \text{ J/mol}$$

$$R = 8.31 \text{ J/ (K • mol)}$$

$$T_{2} = ?$$

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

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

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

$$T_{2} = \frac{1}{\frac{(8.31 \frac{1}{\text{K-mol}})}{(40650 \text{ J/mol})} \ln \left(\frac{760. \text{ torr}}{253 \text{ torr}} \right) + \frac{1}{373.15 \text{ K}}} = \frac{1}{0.0029048655 \text{ K}^{-1}}$$

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?

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

$$= 80.3 \text{ torr}$$

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

$$T_2 = -120.^{\circ}\text{C} = 153.15 \text{ K}$$

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

$$= 6820 \text{ J/mol}$$

$$R = 8.31 \text{ J/ (K • mol)}$$

$$\ln\left(\frac{80.3 \text{ torr}}{P_{vap,T_2}}\right) = \frac{6820 \text{ J/mel}}{(8.31 \text{ J/ (K • mol)})} \left(\frac{1}{153.15 \text{ K}} - \frac{1}{73.15 \text{ K}}\right)$$

$$\ln\left(\frac{80.3 \text{ torr}}{P_{vap,T_2}}\right) = -5.860598995$$

$$\ln\left(\frac{80.3 \text{ torr}}{P_{vap,T_2}}\right) = e^{5.860598995}$$

$$e^{\ln\left(\frac{80.3 \text{ torr}}{P_{wp,T_2}}\right)} = e^{5.860598995}$$

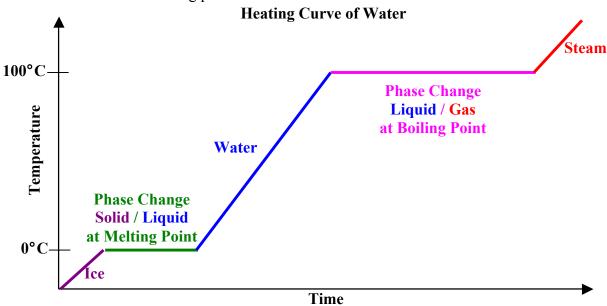
$$e^{10.3 \text{ torr}}$$

$$e^{10.3$$

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 aquired enough energy to overcome the intermoelcular forces nexessary. 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 refered 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 $T < Melting Point, P_{vap} Solid > P_{vap} Liquid$. 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 >Melting Point, P_{vap} Liquid $> P_{\text{vap}}$ Solid. As such, any solid's vapour pressure will be used by the liquid to equilibrate its own vapour pressure. Therfore, solid will slowly become a liquid above its melting point.

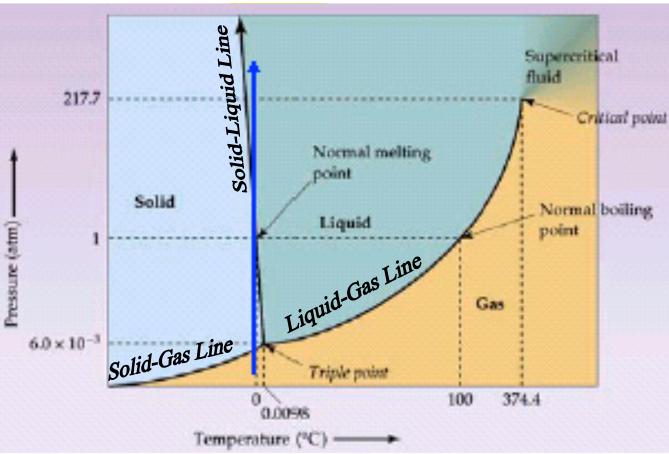
- Normal Boiling Point: the temperature where vapour pressures of liquid is equaled to that of a gas under normal atmospheric condition of 1 atm.
 - when temperature is at the normal boiling point, both liquid and gas can coexist.
 - when T < Boiling Point, P_{vap} Liquid $< P_{\text{vap}}$ Gas. Hence, 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 > Boiling Point, P_{vap} Gas $< P_{\text{vap}}$ Liquid. As such, any liquid's vapour pressure will be used by the gas to equilibrate its own vapour pressure. Therfore, liquid will slowly become a gas above its boiling point.

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

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

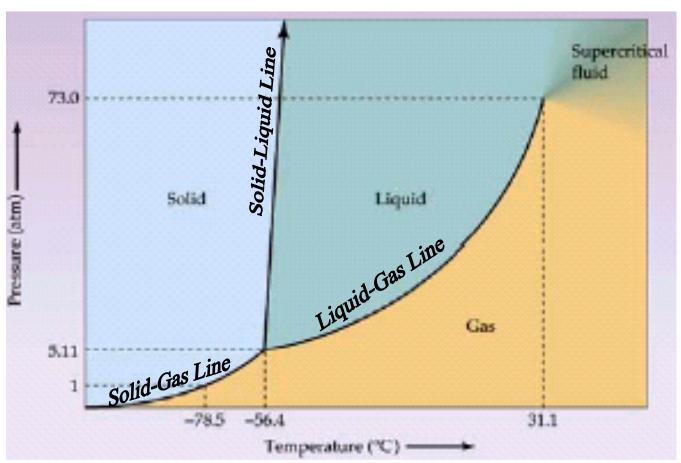
- **Supercooled Liquid:** when a liquid is cooled too rapidly, its temperature is below the melting point.
 - happens because molecules need time rearrange themselves for recrystallization to become a solid.
- **Superheated Liquid**: when a liquid is heated too rapidly, its temperature is above the boiling 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 preessure.
- **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 a 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 in **dynamic equilibrium** (a state where the rate of forward process is exactly balanced by the reverse process).
 - used to find the **melting point** of a substance at any given pressure.
- <u>Liquid-Gas Line</u>: a line that outlines the temperatures and the corresponding pressures where liquid and gas phases coexist in dynamic equilibrium.
 - used to find the **boiling point** of a substance at any given pressure.
- <u>Solid-Gas Line</u>: a line that outlines the temperatures and the corresponding pressures where solid and gas phases coexist in dynamic equilibrium.
 - used to find the **sublimation point** of a substance at any given pressure.
- <u>Triple Point</u>: 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** in dynamic equilibrium.
- <u>Critical Point</u>: a point at the end of the liquid-gas line which indicates an intermediate "fluid" region where liquid can be coverted 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 withoutout going through a change of state.

Phase Diagram of Water



Notes 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 illustates 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 instantenously.



Phase Diagram of Carbon Dioxide

Notes 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 illustates 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 11.8 pg. 506–507 #59 to 61, 64, 66, 68 to 74, 76, 79, 81, 82, 85 to 88; pg. 508–510 #96, 103, 121, 133 11.9 pg. 507–508 #89 to 94; pg. 508–510 #99, 101, 131, 134, 139

Chapter 12: Physical Properties of Solutions

12.1: Types of Solutions

Solution: - a homogeneous mixture of two or more substances.

Solute: - the substance that is being dissolved or the smaller component of the solution.

Solvent: - the substance that is doing the dissolving or the larger component of the solution.

Different Types of Solutions in Various Phases:

Phases		es		
Solute	Solvent	Solution	Examples	
Solid	Solid	Solid (Alloys)	Steel (97% Fe; 3% C), Common Brass (63% Cu; 37% Zn)	
Solid	Liquid	Liquid	NaCl (aq), Sugar Drinks	
Liquid	Liquid	Liquid	Alcoholic Cocktails (ethanol in water)	
Gas	Liquid	Liquid	Carbonated Beverages (Soda Water – CO ₂ in water)	
Gas	Solid	Solid	H ₂ gas in palladium	
Gas	Gas	Gas	Air (78% N ₂ ; 21% O ₂ ; 1% CO ₂ , Ar and trace gases)	

<u>Crystallization</u>: - the process in which solid solute comes out of the solution and form well-developed crystals over a long period of time.

- happens when a supersaturated solution (see below) is disturbed either by adding a solid matter (seeding the crystal) or scratching the side of the container.

<u>Precipitation</u>: - the process in which dissolved solute comes out of the solution and form small particles over a relative short period of time.



(Left) Lead iodide precipitate from the reaction between lead chlorate and potassium iodide

(Right) Home-grown alum crystals



General Descriptions of Solutions at Various Levels of Concentration:

- 1. <u>Unsaturated Solution</u>: when a solvent can still dissolve more solute at a particle temperature.
- **2.** Saturated Solution: when a solvent cannot dissolve anymore solute.
 - the rate of solvation is the same as the rate of crystallization.
- **3.** <u>Supersaturated Solution</u>: when a saturated solution is heated and more solute is dissolved, which is then followed by a slow cooling without any recrystallization.
 - the density and the viscosity of a supersaturated solution is higher than a saturated solution. (Example: Sugar Syrup Supersaturated Sugar Water)

12.2: A Molecular View of the Solution Process

The Dissolving Process:

- 1. Solute Molecules need to overcome their Intermolecular Forces or the Break-up of Ionic Crystal Lattice. (ΔH_1 or $\Delta E_{lattice}$ is Endothermic Input Energy)
- 2. Solvent Molecules need to overcome their Intermolecular Forces.

 $(\Delta H_2 \text{ is Endothermic} - \text{Input Energy})$

3. The Molecules of Solute and Solvent interact to Create New Intermolecular Forces.

(ΔH_3 is Exothermic –Energy is Released as new bonds form)

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).

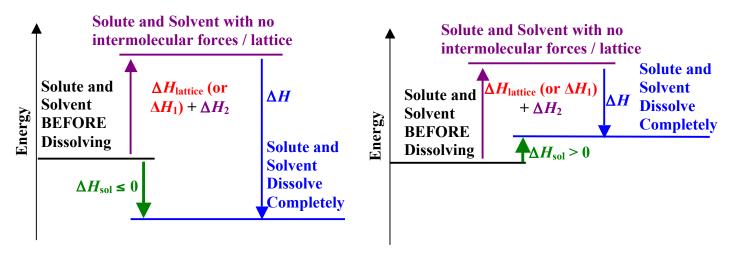
$$\Delta H_{\text{hyd}} = \Delta H_2 + \Delta H_3$$

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

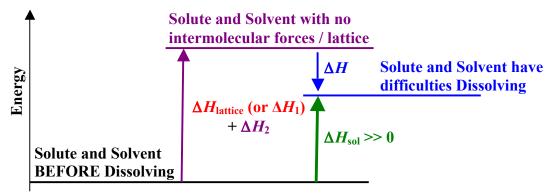
$$\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} (\text{or } \Delta H_1) + \Delta H_{\text{hyd}}$$

- "Like-Dissolves-Like": a dissolving rule that states *polar solutes tend to dissolve in polar solvents* and *non-polar solutes tend to 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 initial energies involve in the dissolving process ($\Delta H_{lattice}$ and ΔH_2) are too large (endothermic) for solution to form spontaneously.

When "Like Dissolves Like", ΔH_{sol} is Exothermic or Slightly Endothermic (Solute can easily dissolve in Solvent)



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.

$$\Delta H_{\text{lattice}} = 905 \text{ kJ/mol}$$

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

$$\Delta H_{\text{sol}} = 905 \text{ kJ/mol} + (-757 \text{ kJ/mol})$$

$$\Delta H_{\text{sol}} = 905 \text{ kJ/mol} + (-757 \text{ kJ/mol})$$

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

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.

$$\Delta H_{\text{lattice}} = 2526 \text{ kJ/mol}$$

$$\Delta H_{\text{sol}} = -74 \text{ kJ/mol}$$

$$\Delta H_{\text{hyd}} = 2526 \text{ kJ/mol}$$

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

$$\Delta H_{\text{hyd}} = (-74 \text{ kJ/mol}) - 2526 \text{ kJ/mol}$$

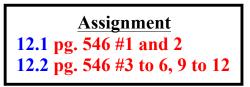
$$\Delta H_{\text{hyd}} = -2600 \text{ kJ/mol}$$

Solubility: - the amount of solute that can dissolve in a given amount of solvent at a specific temperature. - usually measures in g / 100 g of solvent.

General Descriptions of Solutions with Various Solubilities:

- 1. <u>Miscible</u>: when two liquids can dissolve each other completely with infinite solubility. (Example: Vinegar-Water Solution Both have polar bonds.)
- Partially Miscible: when two liquids are slightly soluble in each other.
 (Example: Anaesthetic Diethyl ether-Water Solution weak polar versus strong polar bonds.)
- **3.** <u>Immiscible</u>: when two liquids cannot dissolve in each other, which result in a mechanical or heterogeneous mixture.

(Example: Italian Salad Dressing – Vinegar and Oil: polar versus non-polar bonds.)



12.3: Concentration Units

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

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

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

<u>Percent by Solutions</u>: - concentration of solution expressed in % volume/volume or % mass/volume.

$\frac{\text{Percent by Solutions}}{\text{\% Solution by Volume (\% (v/v))}} = \frac{\text{Volume of Solute}}{\text{Total Volume of Solution}} \times 100\%$ (Same Unit for Both Volumes) $\text{\% Solution by Mass (\% (m/v))} = \frac{\text{Mass of Solute (g)}}{\text{Total Volume of Solution (mL)}} \times 100\%$

Example 1: Calculate the percent by solutions of the following.

a. 1.32 g of salt in 325 mL of water

b. 45.0 mL of pure vinegar with 250. mL of water

% (m/v) =
$$\frac{\text{Mass of Solute (g)}}{\text{Total Volume of Solution (mL)}} \times 100\%$$
% (m/v) =
$$\frac{1.32 \text{ g salt}}{325 \text{ mL water}} \times 100\%$$

$$0.406\% \text{ salt (m/v)}$$

% (v/v) =
$$\frac{\text{Volume of Solute}}{\text{Total Volume of Solution}} \times 100\%$$

% (v/v) = $\frac{45.0 \text{ mL vinegar}}{(250. \text{ mL H}_2\text{O} + 45.0 \text{ mL solute})} \times 100\%$

Example 2: What is the mass of solute required to make a 3.75 L of a 22.5% (m/v) sugar solution?

% (m/v) =
$$\frac{\text{Mass of Solute (g)}}{\text{Total Volume of Solution (mL)}} \times 100\%$$

22.5% (m/v) = $\frac{m_{solute}}{3750 \text{ mL water}} \times 100\%$
3.75 L = 3750 mL $m_{solute} = 844 \text{ g of sugar}$

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

$$\chi_{A} = \frac{n_{A}}{n_{Total}}$$

$$n_{A} = \text{moles of component A}$$

$$n_{Total} = \text{Total Moles of Solution} = n_{A} + n_{B} + n_{C} + \dots$$

Molarity (Concentration): - moles of solute per Litre of solution (M = mol/L).

Molarity (Concentration)

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

C = Concentration (M = mol/L) n = moles of Solute

V =Total Volume of Solution

Molality: - moles of solute per kilogram of solvent (m = mol/kg).

Molality

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

Molality = m (mol/kg)

n =moles of Solute

 $m_{solvent}$ = Mass of Solvent in kg

Example 3: 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

- a. molarity
- b. molality
- c. percent by mass
- d. mole fraction

a. Molarity

$$n = \frac{40.0 \,\mathrm{g}}{60.11 \,\mathrm{g/mol}} = 0.6654466811 \,\mathrm{mol} \,\mathrm{C}_3\mathrm{H}_7\mathrm{OH}$$

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

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

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

$$[C_3H_7OH] = \frac{0.6654466811 \text{ mol}}{0.1998132005 \text{ L}}$$
 $\boxed{[C_3H_7OH] = 3.33 \text{ M}}$

b. Molality

$$n = \frac{40.0 \,\mathrm{g}}{60.11 \,\mathrm{g/mol}} = 0.6654466811 \,\mathrm{mol}\,\,\mathrm{C_3H_7OH}$$

$$m_{\text{solvent}} = 150 \text{ g} = 0.150 \text{ kg}$$
 (1 g ≈ 1 mL H₂O)

Molality =
$$\frac{n_{solute}}{m_{solute}} = \frac{0.6654466811 \,\text{mol}}{0.150 \,\text{kg}}$$

Molality =
$$4.44 m$$

c. Percent by Mass

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

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

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

Percent by Mass =
$$\frac{m_{solute}}{m_{sol}} \times 100\%$$

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

Percent by Mass = 21.1%

d. Mole Fraction

$$n = \frac{40.0 \,\mathrm{g}}{60.11 \,\mathrm{g/mol}} = 0.6654466811 \,\mathrm{mol}\,\,\mathrm{C}_3\mathrm{H}_7\mathrm{OH}$$

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

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

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

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

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

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

Example 4: Alcoholic beaverages have labels indicating alcoholic content (C_2H_5OH) using (% v/v). Suppose a Canadian whiskey has a 35.0% (v/v) alcohol content, and the density of pure ethanol is 0.789 g/cm³, determine the composition of the whiskey by

- a. molarity
- b. molality
- c. percent by mass
- d. mole fraction

a. Molarity (Assume 100. mL of whiskey)
$$35.0\% (v/v) = \frac{35.0 \text{ mL C}_2 \text{H}_5 \text{OH}}{100 \text{ mL Tota}}$$
 $m_{\text{ethanol}} = 0.789 \text{ g/em}^3 \times 35.0 \text{ mL} = 27.615 \text{ g}$
 $n = \frac{27.615 \text{ g}}{46.08 \text{ g/mol}} = 0.5992838542 \text{ mol C}_2 \text{H}_5 \text{OH}$
 $V_{\text{Total}} = 100. \text{ mL} = 0.100 \text{ L}$
 $[C_2 \text{H}_5 \text{OH}] = \frac{0.5992838542 \text{ mol}}{0.100 \text{ L}}$

Molarity (Assume 100. mL = 27.615 g)
 V_{so}
 $V_{\text{so$

b. Molality (Assume 100. mL of whiskey) $n = 0.5992838542 \text{ mol } C_2H_5OH$ $V_{\text{solvent}} = V_{\text{Total}} - V_{\text{ethanol}}$ $V_{\text{solvent}} = 100. \text{ mL} - 35.0 \text{ mL} = 65.\text{mL}$ $m_{\text{solvent}} = 65. \text{ g} = 0.065 \text{ kg}$ (1 g ≈ 1 mL H₂O) Molality = $\frac{n_{solute}}{m_{solvent}} = \frac{0.5992838542 \text{ mol}}{0.065 \text{ kg}}$ Molality = 9.22 m

c. Percent by Mass

$$m_{\text{ethanol}} = 27.615 \text{ g}$$
 $m_{\text{solution}} = m_{\text{ethanol}} + m_{\text{water}}$
 $m_{\text{solution}} = 27.615 \text{ g} + 65. \text{ g} = 92.615 \text{ g}$

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

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

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

d. Mole Fraction $n_{\text{ethanol}} = 0.5992838542 \text{ mol C}_2\text{H}_5\text{OH}$

$$n_{\text{water}} = \frac{65 \text{ g}}{18.02 \text{ g/mol}} = 3.607103219 \text{ mol H}_2\text{O}$$

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

$$n_{\text{mol}} = 0.5002838542 \text{ mol} + 3.607103210 \text{ mol}$$

$$n_{\text{Total}} = 0.5992838542 \text{ mol} + 3.607103219 \text{ mol}$$

 $n_{\text{Total}} = 4.206387073 \text{ mol}$

$$\chi_{\text{ethanol}} = \frac{n_{\text{ethanol}}}{n_{Total}} = \frac{0.5992838542 \text{ mol}}{4.206387073 \text{ mol}}$$

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

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

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

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

Example 5: 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.

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

 $N = Equivalence \times Molarity(C)$

Example 6: 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

- a. percent by mass
- b. molality
- c. normality

a. Percent by Mass

 $[Ba(OH)_2] = 0.327 \text{ mol/L}$ In 1 L of solution, $m = 0.327 \text{ mol} \times 171.35 \text{ g/mol}$ $m = 56.03145 \text{ g Ba}(OH)_2$

In 1 L of solution, $m_{\text{total}} = 2.18 \text{ g/mL} \times 1000 \text{ mL}$ $m_{\text{total}} = 2180 \text{ g}$

Percent by Mass =
$$\frac{m_{solute}}{m_{solution}} \times 100\% = \frac{56.03145 \,\text{g}}{2180 \,\text{g}} \times 100\%$$

Percent by Mass = 2.57%

b. Molality (Assume 1 L of solution)

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

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

 $m_{\text{solvent}} = 2180 \text{ g} - 56.03145 \text{ g}$

 $m_{\text{solvent}} = 2123.96855 \text{ g} = 2.12396855 \text{ kg}$

Molality =
$$\frac{n_{solute}}{m_{solvent}}$$
 = $\frac{0.327 \text{ mol}}{2.12396855 \text{ kg}}$

Molality = 0.154 m

c. Normality

$$Ba(OH)_{2(s)} \rightarrow Ba^{2+}_{(aq)} + 2OH_{(aq)}$$

Since there are 2 moles of OH- for every 1 mole of $Ba(OH)_2$ dissolves, the equivalence = 2.

Normality = 2×0.327 M

Normality = 0.654 *N*

Assignment

12.3 pg. 546-547 #13, 15 to 24

12.4: The Effect of Temperature on Solubility

Solubility verus Temperature:

- as **temperature** <u>increases</u>, solubility of <u>some solid solutes generally increases</u>. (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 dissoliving process. Therby, solubility increases. (Examples: KNO₃ and NaNO₃)
- 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: Na₂SO₄ and Ce₂(SO₄)₃)
- as **temperature** <u>increases</u>, <u>the solubility of gas solutes</u> <u>decreases</u>. (The increase temperature causes gas solute particles to move faster, breaking the intermolecular bonds they established with the molecules of the liquid solvent.)

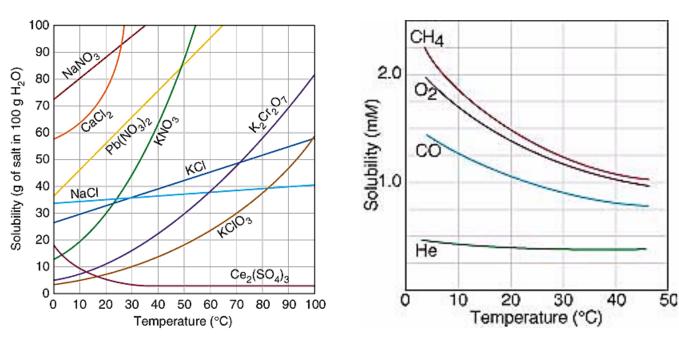
Temperature ↑ Solid S

Solid Solute Solubility ↑

Gas Solute Solubility ↓

Solubility of some Solid Solutes

Solubility of some Gaseous Solutes



Example 1: A maximum 6.70 g of carbon dioxide gas is dissolved in 2000 g of water at 0°C under normal atmosphere pressure (101.3 kPa). Calculate the solubility of carbon dioxide gas in g / 100 g of H₂O.

Solubility =
$$\frac{\text{Mass of Solute}}{100 \text{ g of Solvent}}$$
Solubility =
$$\frac{6.70 \text{ g CO}_2}{2000 \text{ g water}} = \frac{x \text{ g CO}_2}{100 \text{ g water}}$$
 (cross-multiply)
$$2000x = (6.70)(100)$$

$$x = \frac{(6.70)(100)}{2000}$$

$$x = 0.335 \text{ g CO}_2$$
 Solubility = 0.335 g CO₂ / 100 g of water

Example 2: The solubility of sucrose (cane sugar) is 230.9 g / 100 g of H₂O. Determine the amount of solvent needed to dissolve 3.00 kg of cane sugar.

Solubility =
$$\frac{230.9 \text{ g sucrose}}{100 \text{ g H}_2\text{O}} \times \frac{3000 \text{ g sucrose}}{x \text{ g H}_2\text{O}} \times \frac{3.00 \text{ kg} = 3000 \text{ g}}{(\text{cross-multiply})}$$

 $230.9x = (100)(3000)$
 $x = \frac{(100)(3000)}{230.9}$
 $x = 1299.263751 \text{ g water} \times = 1.30 \text{ kg of H}_2\text{O}$

12.5: The Effect of Pressure on Solubility of Gases

Solubility versus Pressure:

- as **pressure** <u>increases</u>, <u>solubility</u> <u>of gas solutes generally increases</u>. (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.

Pressure † Gas Solute Solubility †

<u>Henry's Law</u>: - 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 a gas in solution with the pressure above the solution.
- dependant on temperature and the identity of the gas solute.

```
Henry's Law

C = kP

C = \text{Concentration of Gas in Solution (mol/L)}

P = \text{Pressure above the solution (atm)}

k = \text{Henry's Law Constant [mol / (L • atm)]}
```

- **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.
 - a. Calculate the concentration of oxygen in this beverage.
 - b. 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.

```
a. k = 0.001322 \text{ mol } / \text{ (L } \bullet \text{ atm)} k = 0.001322 \text{ mol } / \text{ (L } \bullet \text{ atm)} P = 7.50 \text{ atm} P = 0.20947 \text{ atm} C = ? C = kP = (0.01322 \text{ mol } / \text{ (L } \bullet \text{ atm)}) (7.50 \text{ atm}) C = kP = (0.01322 \text{ mol } / \text{ (L } \bullet \text{ atm)}) (0.20947 \text{ atm}) C = 0.000 \text{ 277 mol/L}
```

- 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).

```
Agitation ↑ Solid Solute Solubility ↑
Size of Solute ↑ Rate of Solubility ↓
"Like Dissolves Like"
```

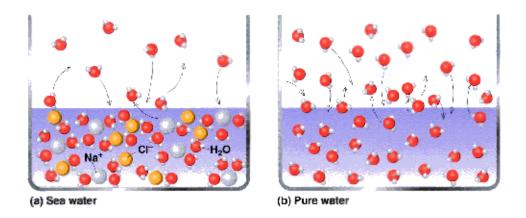
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Assignment
12.4 pg. 547 #25, 27 to 29
12.5 pg. 547 #30 to 38
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12.6: Colligative Properties of Nonelectrolye Solutions

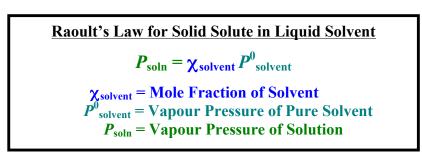
<u>Vapour Pressure of Solution</u>: - in general, vapour pressure of solution tends to decrease as more solutes is dissoved into the solvent.

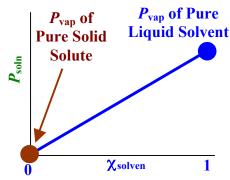


- this is because the presence of solutes molecules create more intermolecular bonds that hinder the vaporization of the solvent.



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.





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 dissoved in 150. mL of water at 10°C.

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

$$n_{\text{glucose}} = \frac{5.00 \text{ g}}{180.18 \text{ g/mol}} = 0.0277500278 \text{ mol } \text{C}_{6}\text{H}_{12}\text{O}_{6}$$

$$n_{\text{water}} = \frac{\left(150 \cdot \text{mL}\right)\left(0.9997 \text{ g/mL}\right)}{18.02 \text{ g/mol}} = 8.321587125 \text{ mol } \text{H}_{2}\text{O}$$

$$n_{\text{total}} = 0.0277500278 \text{ mol} + 8.321587125 \text{ mol}$$

$$n_{\text{total}} = 8.349337153 \text{ mol}$$

$$\sum_{\text{water}} \frac{n_{\text{water}}}{n_{\text{Total}}} = \frac{8.321587125 \text{ mol}}{8.349337153 \text{ mol}}$$

$$\sum_{\text{water}} P_{\text{water}}^{0}$$

$$\sum_{\text{water}} P_{\text{water}}^{0}$$

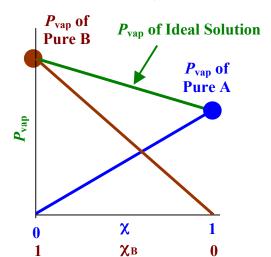
$$\sum_{\text{water}} P_{\text{water}}^{0}$$

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

Note that Pvap 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 silimiar intermolecular forces between solute-solute, solventsolvent, and solute-solvent molecules



Ideal Solution of Liquid-Solute and Liquid-Solvent

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

χ_A = Mole Fraction of Component A $P_A^0 = Vapour Pressure of Pure A$

χ_B = Mole Fraction of Component B P⁰_B = Vapour Pressure of Pure B

 P_{Total} = Total Vapour Pressure of Solution

Example 2: Carbon tetrachloride (CCl₄) is commonly used to dissolve many non-polar liquid or solid solutes. At 20°C, pure CCl₄ has a vapour pressure of 91.0 kPa. An 2.50 g of unknown solid solute is dissolved in 90.0 g of CCl₄. The resulting vapour pressure was determined to be 84.1 kPa. Assuming the solution is ideal, calculate the molar mass of this unknown solid solute.

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

$$n_{\text{CCI}_4} = \frac{90.0 \text{ g}}{153.81 \text{ g/mol}} = 0.5850880558 \text{ mol CCI}_4 \qquad \chi_{\text{CCI}_4} = ? \qquad \chi_{\text{unknown}} = ? \qquad n_{\text{unknown}} = ? \qquad M_{\text{unknown}} = ?$$

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

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

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

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

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

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

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

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

$$n_{\text{unknown}} = \frac{m_{\text{unknown}}}{-0.9241758242} \qquad n_{\text{unknown}} = 0.0480036574 \text{ mol}$$

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

$$M_{\text{unknown}} = 52.1 \text{ g/mol}$$

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.

$$P_{\text{toluene}}^{0} = 384 \text{ torr} \\ P_{\text{toluene}}^{0} = 133 \text{ torr} \\ P_{\text{Total}} = 200. \text{ torr}$$

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

$$P_{\text{toluene}}^{0} = ?$$

$$\text{χ-benzene} = ?$$

$$\text{χ-toluene} = 1.5 \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = 1.5 \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = 1.5 \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

$$\text{χ-toluene} = ?$$

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$$\text{χ-toluene} = ?$$

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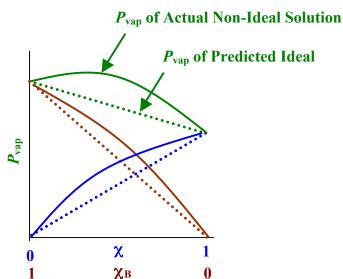
$$\text{χ-toluene} = ?$$

$$\text{χ-toluene} = 1.5 \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

$$\text{χ-toluene} = 1.5 \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

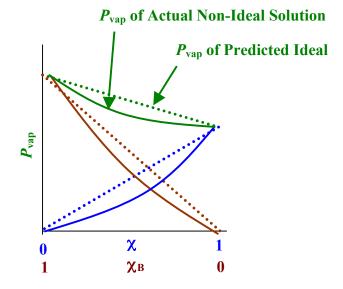
$$\text{χ-toluene} = 1.5 \text{ then } (1 - \chi_{\text{benzene}}) = \chi_{\text{toluene}}$$

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



Positive Deviation Non-Ideal Solution

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



Negative Deviation Non-Ideal Solution

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

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 you answer mathematically.

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

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

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

$$P_{\text{hexane}}^{0} = 24.0 \text{ g}$$

$$P_{\text{hexane}}^{0} = 15.0 \text{ g}$$

$$P_{\text{actual}}^{0} = 54.4 \text{ kPa}$$

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

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

$$P_{\text{Total}}^{0} = 0.5162467143 \text{ mol} + 0.1740611721 \text{ mol}$$

$$P_{\text{hexane}}^{0} = 0.5162467143 \text{ mol} + 0.1740611721 \text{ mol}$$

$$P_{\text{total}}^{0} = 0.5162467143 \text{ mol}$$

$$P_{\text{total}}^{0} = 0.7478499442$$

$$P_{\text{total}}^{0} = 0.2521500558$$

$$P_{\text{Total}}^{0} = P_{\text{total}}^{0} = P_{\text{total}}^{0} = P_{\text{hexane}}^{0}$$

$$P_{\text{total}}^{0} = P_{\text{total}}^{0} = P_{\text{total}}^{0} = P_{\text{total}}^{0} = 0.7478499442$$

$$P_{\text{total}}^{0} = P_{\text{total}}^{0} = 0.2521500558)(130 \text{ kPa})$$

$$P_{\text{predicted}}^{0} = 38.6 \text{ kPa}$$

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.

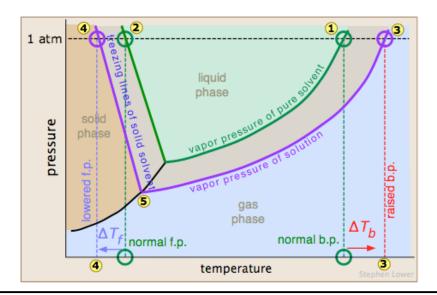
Colligative Properties: - changes in physically properties of a pure substance as it is mixed with a solute.

- 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.

<u>Molal Boiling-Point Elevation Constant</u> (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 Depression 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

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

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

$$\Delta T_b = \text{Change in Boiling Point Elevation (°C)}$$

$$\Delta T_f = \text{Change in Freezing Point Depression (°C)}$$

$$K_b = \text{Molal Boiling-Point Constant (°C • kg/mol)}$$

$$K_f = \text{Molal Freezing-Point Constant (°C • kg/mol)}$$

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

- **Example 5**: Antifreeze, ethylene glycol (CH₂OHCH₂OH), is commonly used to prevent water from freezing in the engine in cold temperature as well as overheating. The maximum temperature a radiater 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°C kg/mol and 1.86 °C kg/mol,
 - a. determine the volume of antifreeze needed to add to 10.0 L of water to sustain the maximum radiater temperature.
 - b. what is the freezing point of the solution?

a.

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

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

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

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

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

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

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

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

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

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

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

$$\Delta T_f = K_f \times \text{Molality}_{\text{antifreeze}} = \frac{24340.94117 \text{ g}}{1.11 \text{ g/mL}} = 21928.77583 \text{ mL}$$

$$V_{\text{antifreeze}} = 22 \text{ L}$$
b.

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

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

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

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

$$\Delta T_f = ?$$
New Freezing Point = 0°C - 72.94117646^{\circ}\text{C}
$$T_f(\text{soin}) = -72.9^{\circ}\text{C}$$

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Example 6: 20.0 g of a newly synethsized enzyme can lower the freezing point of 100.0 g CCl₄ by 4.70°C. Given that K_f for CCl₄ is 30.0°C • kg/mol, calculate the molar mass of this new enzyme.

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

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

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

$$m_{\text{enzyme}} = 20.0 \text{ g}$$

$$m_{\text{enzyme}} = ?$$

$$M_{\text{enzyme}} = ?$$

$$M_{\text{enzyme}} = ?$$

$$\Delta T_f = K_f \times \text{Molality}_{\text{enzyme}} = K_f \times \frac{n_{enzyme}}{\text{kg of CCl}_4}$$

$$kg \text{ of CCl}_4$$

$$(30.0^{\circ}\text{C} \cdot \text{kg/mol}) = 0.0156666667 \text{ mol}$$

$$M_{\text{enzyme}} = ?$$

$$M_{\text{enzyme}} = \frac{m_{enzyme}}{n_{enzyme}} = \frac{20.0 \text{ g}}{0.0156666667 \text{ mol}} = 1276.595745 \text{ g/mol}$$

$$M_{\text{enzyme}} = 1.30 \times 10^3 \text{ g/mol} = 1.30 \text{ kg/mol}$$

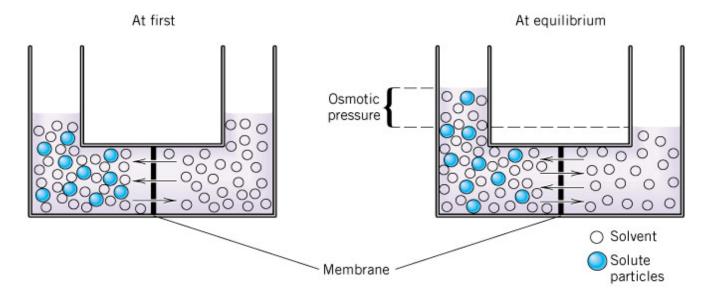
<u>Semipermeable Membrane</u>: - a fine flter that allows solvent molecules to pass through but solute molecules are left behind the filter.

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
$$\Pi = CRT = \frac{nRT}{V}$$

$$R = Gas Constant = 0.0821 (L • atm)/(mol • K)$$

$$C = Molarity (mol/L)$$

$$T = Temperature (K)$$

Example 7: Calculate the molar mass of a newly synthezied progesterone (pregnancy hormone) if its osmotic pressure at 37.0°C is 41.2 torr when 22.0 mg is dissolved in 50.0 mL of water.

$$T = 37.0^{\circ}\text{C} = 310.15 \text{ K}$$

$$\Pi = 41.2 \frac{1}{60 \text{ torr}} \times \frac{1}{60 \text{ torr}} = 0.0542105263 \text{ atm}$$

$$m_{\text{progesterone}} = 22.0 \text{ mg} = 22.0 \times 10^{-3} \text{ g}$$

$$V = 50.0 \text{ mL} = 0.0500 \text{ L}$$

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

$$M_{\text{progesterone}} = 207 \text{ g/mol}$$

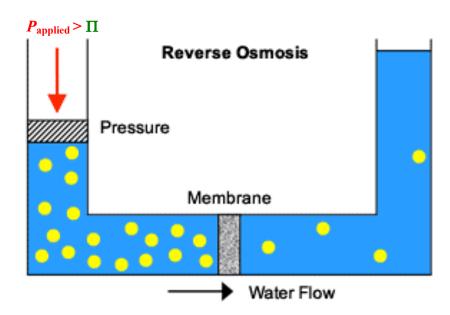
$$M_{\text{progesterone}} = 207 \text{ g/mol}$$

Isotonic Solutions: - when solutions have exactly the same osmotic pressures.

Example 8: 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.

$$T = 37.0^{\circ}\text{C} = 310.15 \text{ K}$$
 $\Pi = 8.01 \text{ atm}$
 $R = 0.0821 \text{ (L • atm)/(mol • K)}$
 $C = \frac{\Pi}{RT} = \frac{(8.01 \text{ atm})}{(0.0821 \frac{\text{L•atm}}{\text{mol•K}})(310.15 \text{ K})} = 0.3145701964 \text{ mol/L}$
[glucose] = 0.315 mol/L

<u>Hypertonic Solutions</u>: - when solutions have greater osmotic pressure than pure solvent (reverse osmosis). - the main priciple used in desalination (removal salt from salt water).



12.7: 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.

<u>van't Hoff Factor</u> (i): - is a factor that relates the <u>total number of moles of ions</u> 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) =
$$\frac{n_{ions}}{n_{solute}}$$

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

Raoult's Law (Lowering Vapour Pressure): $P_{\text{soln}} = i\chi_{\text{solvent}} P_{\text{solvent}}^0$ Boiling Point Elevation: $\Delta T_b = iK_b \times \text{Molality}_{\text{solute}}$ Freezing Point Depression: $\Delta T_f = iK_f \times \text{Molality}_{\text{solute}}$

Osmotic Pressure: $\Pi = iCRT = i \frac{nRT}{V}$

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 of magnesium chloride is dissolved in 150 mL of water at 10°C.

chloride is dissolved in 150 mL of water at 10°C.

Since MgCl₂ is an ionic solute, the dissociation equation is $MgCl_{2(s)} \rightarrow Mg^{2+}_{(aq)} + 2 Cl_{(aq)}$

 $P_{\text{water}}^{0} = 9.23 \text{ torr}$ $n_{\text{ions}} = 3 \times \frac{5.00 \text{ g}}{95.20 \text{ g/mol}} = 0.1575630252 \text{ mol Mg}^{2+} \text{ and Cl- ions}$

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

$$n_{\text{water}} = \frac{(150 \text{ mE})(0.9997 \text{ g/mE})}{18.02 \text{ g/mol}} = 8.321587125 \text{ mol H}_2\text{O}$$

 $n_{\text{total}} = 0.1575630252 \text{ mol} + 8.321587125 \text{ mol}$

 $n_{\text{total}} = 8.47915015 \text{ mol}$

$$\chi_{\text{water}} = \frac{n_{\text{water}}}{n_{Total}} = \frac{8.321587125 \text{ mol}}{8.47915015 \text{ mol}}$$

$$\chi_{\text{water}} = 0.9814175923$$

$$R_{\text{obs}} = \chi_{\text{obs}} = 0.9814175923$$

 $P_{\text{soln}} = \chi_{\text{water}} P_{\text{water}}^{0}$ $P_{\text{soln}} = (0.9814175923)(9.23 \text{ torr})$ $P_{\text{soln}} = 9.06 \text{ torr}$

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

Example 2: 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.

$$K_2CO_3 (s) → 2 K^+ (aq) + CO_3^2 (aq)$$
 $i = 2 \text{ mol } K^+ + 1 \text{ mol } CO_3^2 = 3$
 $T = 37.0 ° C = 310.15 K$
 $Π = 8.01 \text{ atm}$
 $R = 0.0821 (L • atm)/(mol • K)$
 $[K_2CO_3] = ?$
 $Π = iCRT$

$$C = \frac{Π}{iRT} = \frac{(8.01 \text{ atm})}{(3)(0.0821 \frac{L • \text{atm}}{\text{mol}•K})(310.15 \text{ K})} = 0.1048567321 \text{ mol/L}$$

Example 3: Determine the freezing point of a saturated salt solution (35.7 g / 100 g H_2O) if the K_f for pure water is 1.86 °C • kg/mol.

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

$$m_{\text{water}} = 100 \text{ g} = 0.100 \text{ kg}$$

$$n_{\text{NaCl}} = \frac{35.7 \text{ g}}{58.44 \text{ g/mol}}$$

$$n_{\text{NaCl}} = 0.6108829569 \text{ mol}$$

$$i = 2 \text{ (1 mol Na}^{+} \text{ and 1 mol Cl})$$

$$\Delta T_{f} = ?$$

$$\Delta T_{f} = iK_{f} \times \text{Molality}_{\text{NaCl}} = iK_{f} \times \frac{n_{\text{NaCl}}}{\text{kg of water}}$$

$$\frac{n_{\text{NaCl}}}{\text{kg of water}} = 22.724846^{\circ}\text{C}$$

$$\frac{n_{\text{NaCl}}}{0.100 \text{ kg}} = 22.724846^{\circ}\text{C}$$

$$T_{f}(\text{soln}) = -22.7^{\circ}\text{C}$$

Ion Pairing: - a phenomenon that happens when not all electrolytes from an ionic solute dissociate completely.
- this usually results in a lower than expected vant's Hoff factor and therby lowering the osmotic pressure.

Example 4: In an experiment to determine the van't Hoff value of MgCl₂, 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.

MgCl_{2 (s)} → Mg²⁺_(aq) + 2 Cl-_(aq)

$$i \text{ (expected)} = 2 \text{ mol } K^+ + 1 \text{ mol } CO_3^{2-} \qquad i \text{ (expected)} = 3$$

$$C = 5.00 \text{ mmol/L} = 0.00500 \text{ mol/L}$$

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

$$\Pi = 247 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ terr}} = 0.325 \text{ atm}$$

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

$$i = ?$$

$$i \text{ (expected)} = 2 \text{ mol } K^+ + 1 \text{ mol } CO_3^{2-} \qquad i \text{ (expected)} = 3$$

$$i \text{ (expected)} = 2 \text{ mol } K^+ + 1 \text{ mol } CO_3^{2-} \qquad i \text{ (expected)} = 3$$

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