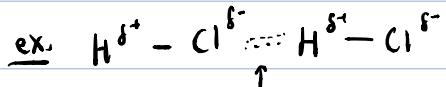


Liquid State

Intermolecular forces: acting between molecules (as opposed to intramolecular forces that act inside the molecule)

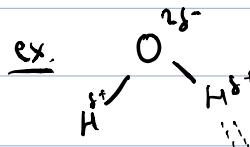
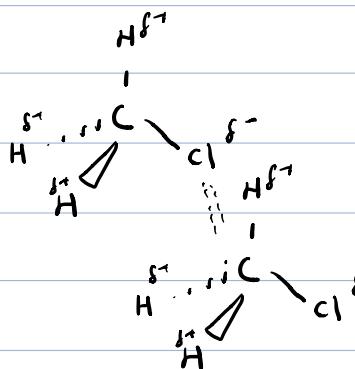
DIPOLE-DIPOLE INTERACTIONS



Atom real bond,
intermolecular forces

LONDON DISPERSION FORCES

(acting between non-polar molecules)



Hydrogen Bond

Special case of dipole-dipole interactions

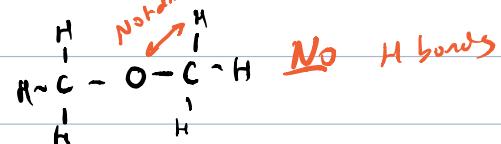
large
separation
of charges



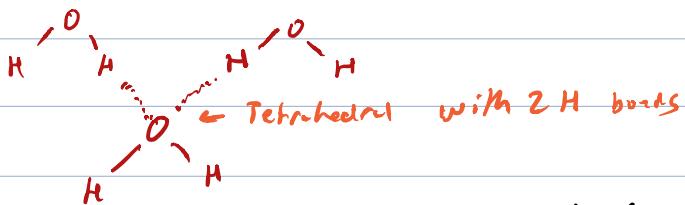
Requirement

An H-atom directly bonded to F, O or N

ex.



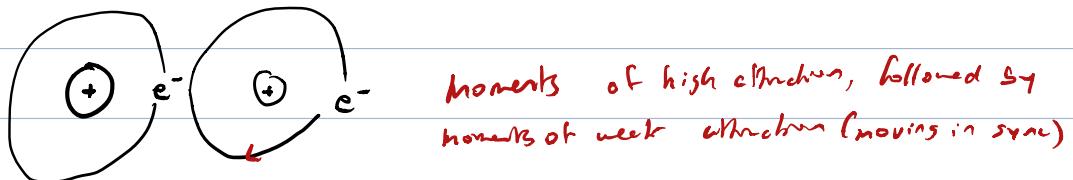
Each O can form a max of 4 H bonds.



When you add heat, H_2O molecules will separate and gain the voids. Bring The Heat
i.e. liquid phase (explanation to why liquids are denser than solids)

LONDON DISPERSION FORCES

(acting between non-polar molecules)



The larger the molecule, the stronger the London force.

Which will have a higher boiling pt? Molecule with London or H-bonds
harder to break

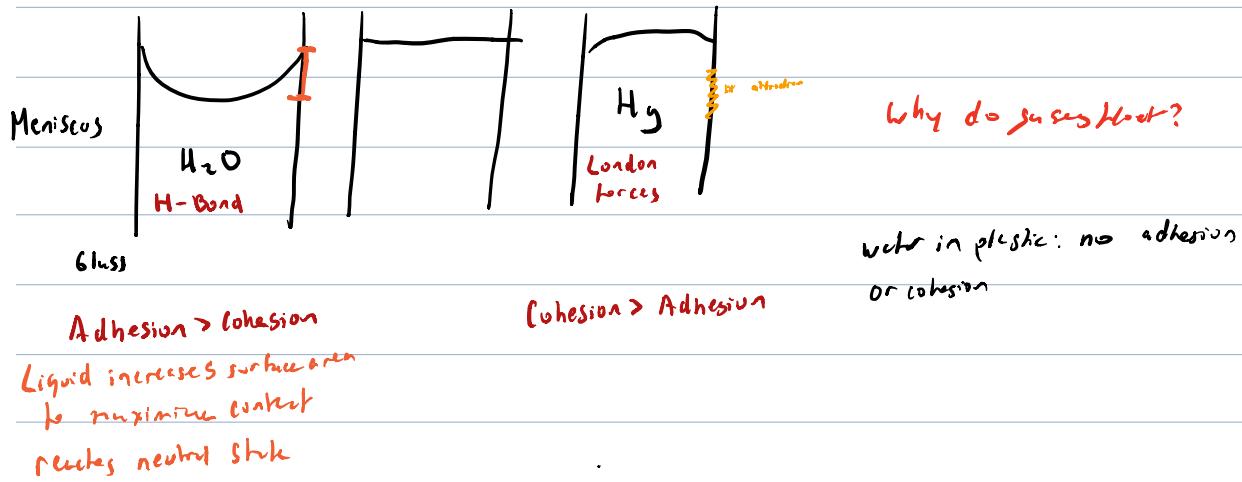
• "like" dissolves "like"

→ polar and polar mix polar molecules with polar solvent ✓

→ non-polar " non-polar "

SURFACE TENSION

= energy required to increase the surface area of a liquid.



water in plastic: no adhesion or cohesion

Adhesion vs Cohesion

Adhesion: intermolecular forces acting between the liquid and solid

Cohesion: intermolecular forces acting within the liquid

Viscosity

= The resistance to flow

The stronger the intermolecular forces, the higher the resistance to flow (i.e. higher viscosity); other factor is size

Vapour Pressure

Depends on size (smaller = easier to evaporate) and intermolecular forces (weaker molecular forces = easier to evaporate, higher vapour pressure). Plus temperature.

Boiling point: temp at which the vapor pressure of the liquid equals 1 atm (normal boiling point; traditional boiling point measures depend on altitude --> which influence the pressure in the atmosphere)

Phase Changes

breaking the 10% of hydrogen bonds explains why when we add heat to water at 0°C (melting point) there will be a plateau. At 100°C (boiling point), breaking of the remaining of the hydrogen bond (now water is a complete gas)

Top plateau (boiling point) --> Heat of vaporization (H_v)

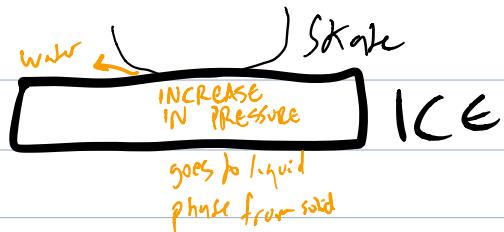
Bottom plateau (melting point) --> Heat of fusion (H_f)

*Same diagram
applies for Latent?*

November 18, 2016

Critical point: temp at which a gas can never go back to liquid regardless of pressure

Solid --> Gas = sublimation (Don't get to see it for water at 1 atm)



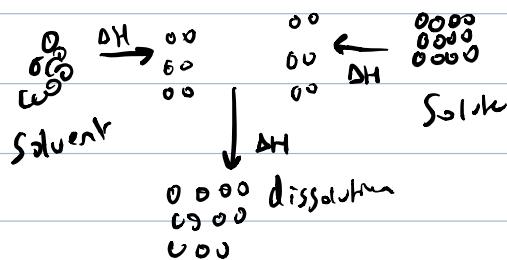
Energetics of Dissolution

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Want the sum to be negative (=more attraction=more stable)

If $\Delta H < 0$ dissolution

$\Delta H > 0$ Most times, no dissolution



Factors for Dissolution

1. Structure

"Like dissolves like"

2. Pressure

Henry's Law:

$$C \propto P$$

Henry's constant

$$C = kP$$

partial pressure
of the gas above
the sol'n

Gas concentration
in the liquid

Ex. When a certain soft drink was bottled, the partial pressure of the CO₂ over the liquid was 5.0 atm at 25°C. Assuming the partial pressure of CO₂ in the atmosphere is 4.0 × 10⁴ atm, calculate the concentration of CO₂ in the soda before and after the bottle is opened ($k = 0.03125 \text{ (mol)/(L} \cdot \text{atm})$)

BEFORE: $C = k \cdot P = 0.03125 \frac{\text{mol}}{\text{L} \cdot \text{atm}} \times 5.0 \text{ atm} = 0.156 \frac{\text{mol}}{\text{L}}$

AFTER: $C = 0.03125 \frac{\text{mol}}{\text{L} \cdot \text{atm}} \times 4.0 \times 10^{-4} \text{ atm} = 1.3 \times 10^{-5} \frac{\text{mol}}{\text{L}}$

3. Temperature

Solids

In general: increase in temp --> solubility increases

(For some solids, dissolution is exothermic, and by Le Chatelier, promoting reverse dissolution so solubility decreases)

Gases

Always: Solubility decreases with an increase in temperature

(Bubbles that form before boiling point are due to solubility)

$$\text{Molality (m)} = \frac{\text{moles of solute}}{\text{kg's of solvent}} \left[\frac{\text{mol}}{\text{kg}} \right]$$

Ex. A sol'n is prepared by mixing 1.00 g of Ethanol ($\text{C}_2\text{H}_5\text{OH}$) with 100.0 g of water to give a final volume of 101.0 mL. Calculate the molarity, molality, mole fraction and % by mass of ethanol.

$$1.00 \text{ g } \text{C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 2.17 \times 10^{-2} \text{ mol } \text{C}_2\text{H}_5\text{OH}$$

$$M = \frac{\text{mol}}{\text{L}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.215 \text{ M}$$

$$m = \frac{\text{mol}}{\text{kg}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.100 \text{ kg}} = 0.217 \text{ m}$$

can form H-bonds
 Similar b.c.
 Solute concentration
 is small

$$\% \text{ By MASS} = \frac{1.0 \text{ g}}{101.0 \text{ g}} \cdot 100 = 0.99 \%$$

$$\chi_{\text{C}_2\text{H}_5\text{OH}} = \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{n_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{H}_2\text{O}}} = \frac{2.17 \times 10^{-2}}{2.17 \times 10^{-2} + 5.56} = 0.00389$$

$$101.0 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 5.56 \text{ mol } \text{H}_2\text{O}$$

N.B. $\chi_{\text{C}_2\text{H}_5\text{OH}} + \chi_{\text{H}_2\text{O}} = 1$
 Mole fractions have to add up to 1

ex. The electrolyte in automobile lead storage batteries is 3.75 M H_2SO_4 that has a density of 1.230 g/mL. Calculate the mass %, molality and mole fraction of H_2SO_4 .

N.B. When density is given, assume $V=1$

$$\text{Mass of sol'n} = 1230 \text{ g}$$

$$3.75 \text{ mol } \text{H}_2\text{SO}_4 \times \frac{98.1 \text{ g}}{1 \text{ mol}} = 368 \text{ g } \text{H}_2\text{SO}_4$$

$$\text{Mass of H}_2\text{O} = 1230 - 368 = 862 \text{ g H}_2\text{O}$$

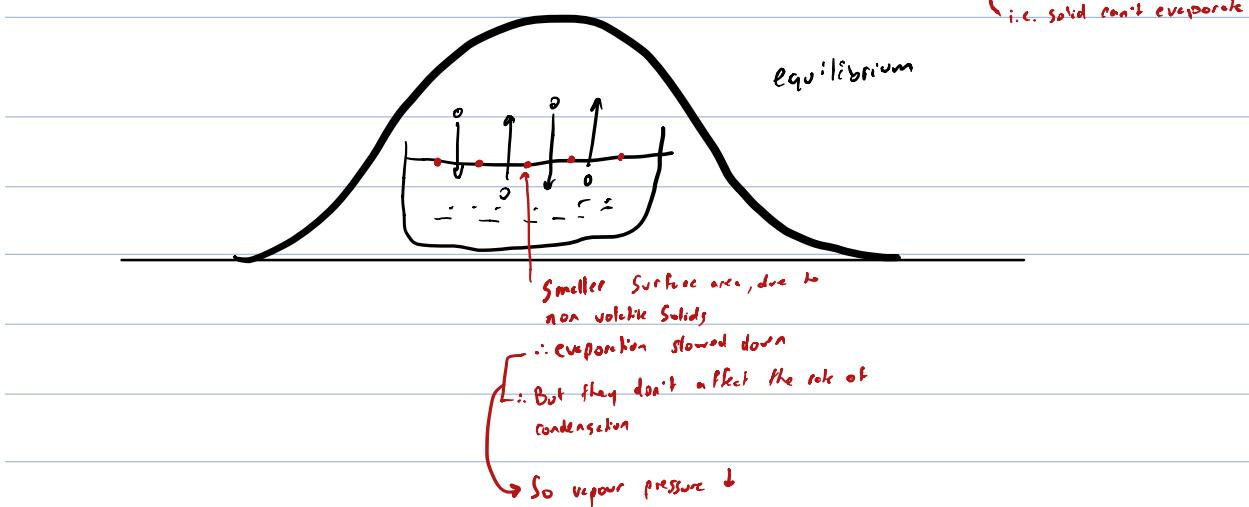
$$862 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.05} = 47.1 \text{ mol}$$

$$\% \text{ by Mass} = \frac{368}{1230} \cdot 100 = 29.9\%$$

$$M = \frac{\text{mol H}_2\text{SO}_4}{\text{kg's H}_2\text{O}} = \frac{3.75 \text{ mol}}{0.862 \text{ kg}} = 4.35 \text{ m}$$

$$X_{\text{H}_2\text{SO}_4} \approx \frac{\text{mol H}_2\text{SO}_4}{\text{total mol.}} = \frac{3.75}{3.75 + 47.9} = 0.0726$$

VAPOR PRESSURE OF SOLUTIONS CONTAINING NON-VOLATILE SOLIDS



R A OULT'S LAW

Vapour pressure \rightarrow

$$P_{\text{sol'n}} = P_{\text{solvent}}^0 \cdot X_{\text{solvent}}$$

If $X_s = 1$, then all solution

Solutions (in class problems)

- 1) A sol'n is prepared by mixing 1.00 g of ethanol (C_2H_5OH) with 100 g of water to give final volume of 101 mL. Calculate the molarity, molality, % by mass and mole fraction of ethanol in this sol'n.
- 2) The electrolyte in automobile lead storage battery is 3.75 M sulfuric acid that has a density of 1.230 g/mL. Calculate the molality, % by mass and mole fraction of sulfuric acid in this sol'n.
- 3) Calculate the expected vapor pressure at 25 °C for a sol'n prepared by dissolving 158.0 g of sucrose (M.M.= 342.3 g) in 643.5 mL of water. At 25 °C the density of water is 0.9971 g/mL and the vapor pressure is 23.76 torr.
- 4) A sol'n was prepared by adding 20.0 g of urea to 125.0 g of water at 25 °C, at which pure water has a vapor pressure of 23.67 torr. The observed vapor pressure of the sol'n was found to be 22.67 torr. Calculate the molar mass of urea.
- 5) Predict the vapor pressure of sol'n prepared by mixing 35.0 g of solid Na_2SO_4 (M.M.= 142 g) with 175 g of water at 25 °C. The vapor pressure of pure water at 25 °C is 23.76 torr.

3.

$$643 \text{ mol H}_2\text{O} \times \frac{0.99713}{1} = 641.6 \text{ g}$$

$$641.6 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.015} = 35.63 \text{ mol}$$

$$150 \text{ g Suc} \times \frac{1 \text{ mol}}{342.3} = 0.4616 \text{ mol}$$

$$\chi_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{Suc}}} = \frac{35.63}{35.63 + 0.4616} = 0.9872$$

$$\begin{aligned} P_{\text{Solv}} &= P_{\text{saturation}}^{\circ} \times \chi_{\text{solvent}} \\ &= 23.76 \text{ bar} \times 0.9872 \\ &= 23.46 \text{ bar} \end{aligned}$$

$$4. P_{\text{Solv}} = P_{\text{H}_2\text{O}}^{\circ} \times \chi_{\text{H}_2\text{O}}$$

$$\chi_{\text{H}_2\text{O}} = \frac{P_{\text{Solv}}}{P_{\text{H}_2\text{O}}} = \frac{23.46}{23.76} = 0.9578$$

$$0.9578 = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{urea}}} \quad \left| \begin{array}{l} n_{\text{H}_2\text{O}} : 125.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.015} = 6.94 \\ \hline \end{array} \right.$$

$$\begin{aligned} \text{So } \frac{6.94}{0.9578} &= 6.94 + n_{\text{urea}} \\ 0.9578 &\approx 6.94 + n_{\text{urea}} \end{aligned}$$

$$n_{\text{urea}} = 0.305 \text{ mol}$$

$$MM = \frac{20.05}{0.305 \text{ mol}} = 65.6 \text{ g/mol}$$

For soln's where both A & B can evaporate:

Variable Solids:

$$P_{\text{sol'n}} = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$$

- 6) At 30.0 °C the vapor pressure of pure benzene is 125 mm Hg, while that of toluene is 39.0 mm Hg. Solutions of benzene and toluene are ideal. A sol'n is prepared by mixing 0.300 mol of benzene with 0.300 mol of toluene. Calculate the partial pressures of benzene and toluene in the vapor phase at equilibrium with this sol'n. What is the vapor pressure of this sol'n?
- 7) A sol'n was prepared by dissolving 18.0 g of glucose in 150.0 g of water ($K_b = 0.51 \text{ } ^\circ\text{C kg/mol}$) The resulting sol'n was found to have a boiling point of 100.34 °C. Calculate the molar mass of glucose.
- 6) What mass of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, M.M.= 62.1g), the main component of antifreeze, must be added to 10.0 kg of water to produce a sol'n for use in a car's radiator that freezes at – 10 °F (-23.3 °C)?
- 8) Thyroxine is a human hormone that control metabolism. A sample of thyroxin weighing 0.546 g was dissolved in 15.0 g of benzene, and the freezing point depression was determined to be 0.24 °C. Calculate the molar mass of thyroxine.
- 9) To determine the molar mass of a certain protein, 1.00×10^{-3} g of it was dissolved in enough water to make 1.00 ml of sol'n. The osmotic pressure of this sol'n was found to be 1.12 torr at 25 °C. Calculate the molar mass of the protein.

$$6. \chi_{\text{Benz}} = \frac{0.300}{0.3+0.3} = 0.50$$

$$\chi_{\text{tot}} = 0.50$$

N.B. Soln with 0.5 % are

Called equimolar solns

$$P_{\text{soln}} = \underbrace{125 \text{ mm Hg} \cdot 0.5}_{62.5 \text{ mm Hg}} + \underbrace{34.0 \text{ mm Hg} \cdot 0.5}_{17.0 \text{ mm Hg}}$$

Partial Pressure

N.B. Concentration of vapour will be higher in Benzene to achieve an equilibrium

COLLIGATIVE PROPERTIES

depend on # of particles, not on their nature

Freezing pt depression:

$$\Delta T_f = k_f m \rightarrow \text{molality}$$

freezing
 pt depression molal freezing
 depression constant

$$8. 23.3^\circ\text{C} = 1.86 \frac{\text{K}^\circ\text{C}}{\text{mol}} \cdot m$$

$$m = \frac{23.3^\circ\text{C}}{1.86 \frac{\text{K}^\circ\text{C}}{\text{mol}}} = 12.5 \text{ mol / kg H}_2\text{O}$$

$$n_{\text{C}_2\text{H}_4\text{O}_2} = \frac{12.5 \text{ mol}}{1 \text{ kg H}_2\text{O}} \cdot 10 \text{ kg H}_2\text{O} = 125 \text{ mol}$$

$$125 \text{ mol} \cdot \frac{62.1 \text{ g}}{\text{mol}} = 7.8 \times 10^3 \text{ g} = 7.8 \text{ kg}$$

Since there is so much ethylene, ethylene must be very soluble in water, so must be able to form H-bonds

$$9. M = \frac{T_f}{K_b} = \frac{0.24^\circ C}{5.12} = 4.69 \times 10^{-2} \text{ mol/kg benzene}$$

$$\Delta T_{\text{hydrazine}} = 4.69 \times 10^{-2} \frac{\text{mol}}{\text{kg benzene}} \times 0.015 \text{ kg benzene} = 7.04 \times 10^{-4} \text{ mol hydrazine}$$

$$MM = \frac{0.5463}{7.04 \times 10^{-4} \text{ mol}} = 776 \text{ g/mol}$$

Boiling pt elevation:

$$\Delta T_b = k_b M \rightarrow \text{molality}$$

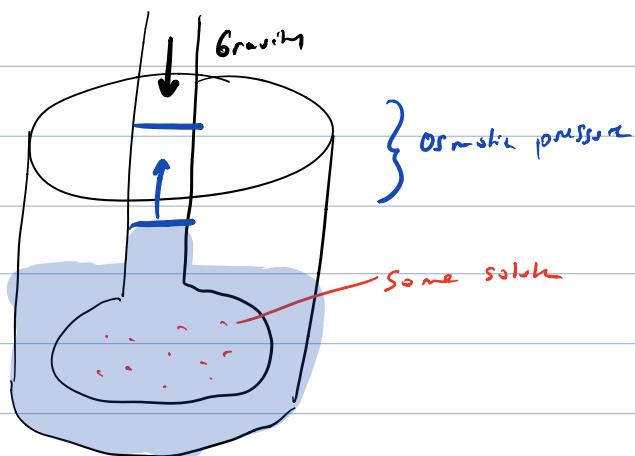
↓ ↓
 boiling pt depression molar boiling
 depression constant

$$7. M = \frac{\Delta T_b}{k_b} = \frac{0.34^\circ C}{0.51 \frac{^\circ C \cdot kg}{mol}} = 0.67 \text{ mol/kg H}_2\text{O}$$

$$\Delta T_{\text{glucose}} = \frac{0.67 \text{ mol}}{M \text{ H}_2\text{O}} \times 0.150 \text{ kg H}_2\text{O} = 0.10 \text{ mol glucose}$$

$$MM = \frac{18.0 \text{ g}}{0.10 \text{ mol}} = 180 \text{ g/mol}$$

Osmotic Pressure:



$$\Pi = M \cdot R \cdot T$$

↗ OSMOTIC PRESSURE ↗ MOLARITY ↗ GAS CONSTANT ↗ ABS. TEMP

$$10. \quad \Pi = 1.12 \frac{\text{bar}}{\text{atm}} \times \frac{1 \text{ atm}}{760 \text{ bar}} = 1.47 \times 10^{-3} \text{ atm}$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{1.47 \times 10^{-3} \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \cdot 298 \text{ K}} = 6.01 \times 10^{-5} \text{ M}$$

$$\Pi_{\text{protein}} = \frac{6.01 \times 10^{-5} \text{ mol}}{4} \times 0.001 \text{ L} = 6.01 \times 10^{-8} \text{ mol protein}$$

$$M = \frac{1.0 \times 10^{-3} \text{ g}}{6.01 \times 10^{-8} \text{ mol}} = 1.66 \times 10^4 \text{ g}$$

N.B. for ionic compounds

$$\Pi = i M \cdot R \cdot T$$

