LIQUID STATE

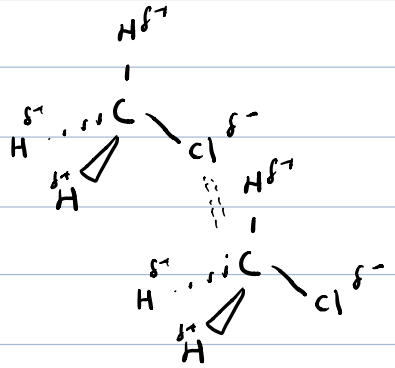
Intermolecular forces: acting between molecules (as opposed to intramolecular forces that act inside the molecule)

DIPOLE-DIPOLE INTERACTIONS

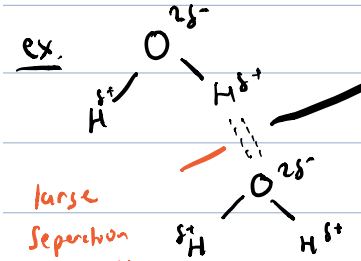
ex. $H^{\delta+} - Cl^{\delta-} \cdots H^{\delta+} - Cl^{\delta-}$

↑ Not real bond, intermolecular forces

ex.



ex.



Large separation of charges

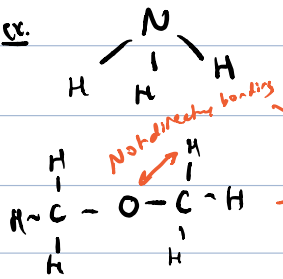
Hydrogen Bond

Special case of dipole-dipole interactions

Requirement

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

ex.



H bonds ✓

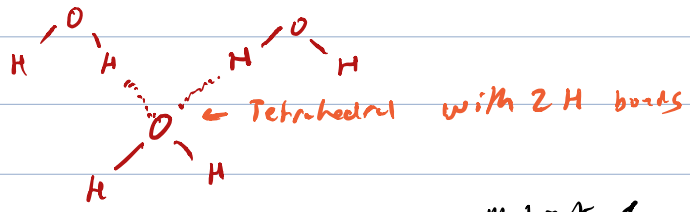
Not directly bonding

No H bonds

LONDON DISPERSION FORCES

(acting between non-polar molecules)

Each O can form a max of 4 H bonds.

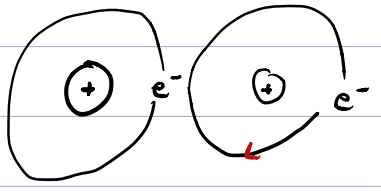


When you add heat, H bonds will break & H_2O molecules will separate and go in the voids. *Bring The Heat

i.e. liquid phase (explanation to why liquids are denser than solids)

LONDON DISPERSION FORCES

(acting between non-polar molecules)



moments of high attraction, followed by moments of weak attraction (moving in sync)

The larger the molecule, the stronger the london force.

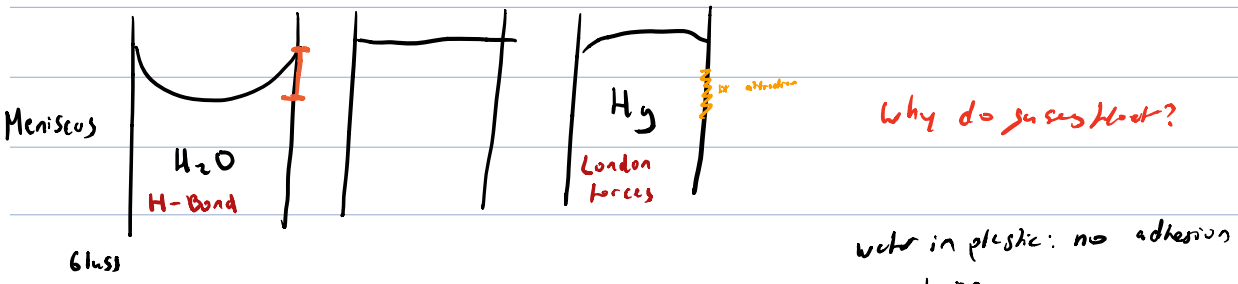
Which will have a higher boiling pt? Molecule with london or H-bonds

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.



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)

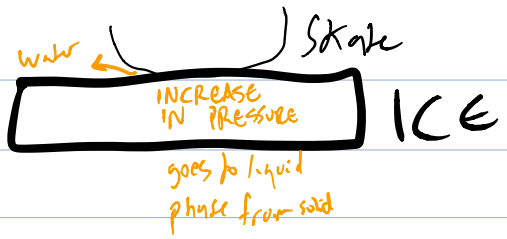
Top plateau (boiling point) --> Heat of vaporization (H_v)
Bottom plateau (melting point) --> Heat of fusion (H_f)

Same diagram applies for London?

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)



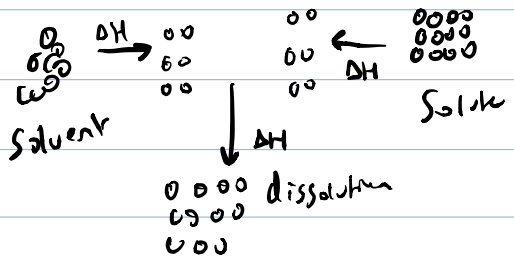
Energetics of Dissolution

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

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: $C \propto P$

$C = kP$

- k: Henry's constant
- P: partial pressure of the gas above the soln
- C: Gas concentration in the liquid

Ex. When a certain soft drink was bottled, the partial pressure of the CO_2 over the liquid was 5.0 atm at 25°C. Assuming the partial pressure of CO_2 in the atmosphere is 4.0×10^4 atm, calculate the concentration of CO_2 in the soda before and after the bottle is opened (k = 0.03125 (mol)/(L•atm))

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

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

3. Temperature

Solids

In general: increase in temp --> solubility increases

(For some solids, dissolution is exothermetic, 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)

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 (C_2H_5OH) 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.

can form H-bonds

$$1.00\,g\,C_2H_5OH \times \frac{1\,mol}{46.07\,g} = 2.17 \times 10^{-2}\,mol\,C_2H_5OH$$

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

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

Similar b.c. solute concentration is small

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

$$\chi_{C_2H_5OH} = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{H_2O}} = \frac{2.17 \times 10^{-2}}{2.17 \times 10^{-2} + 5.56} = 0.00389$$

$$101.0\,g\,H_2O \times \frac{1\,mol}{18.0\,g} = 5.56\,mol\,H_2O$$

N.B. $\chi_{C_2H_5OH} + \chi_{H_2O} = 1$

Mol 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 L

mass of sol'n = 1230 g

$$3.75\,mol\,H_2SO_4 \times \frac{98.1\,g}{1\,mol} = 368\,g\,H_2SO_4$$

Mass of H_2O = 1230 − 368 = 862 g H_2O

$$862\ g\ H_2O \times \frac{1\ mol}{18.0\ g} = 47.9\ mol$$

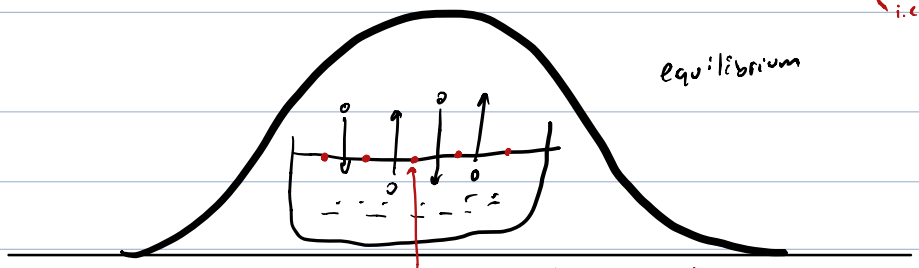
$$\%\ By\ Mass = \frac{368\ g}{1230\ g} \cdot 100 = 29.9\%$$

$$m = \frac{mol\ H_2SO_4}{kg's\ H_2O} = \frac{3.75\ mol}{0.862\ kg} = 4.35\ m$$

$$\chi_{H_2SO_4} = \frac{mol\ H_2SO_4}{total\ mol's} = \frac{3.75}{3.75 + 47.9} = 0.0726$$

VAPOR PRESSURE OF SOLUTIONS CONTAINING NON-VOLATILE SOLIDS

i.e. solid can't evaporate



Smaller surface area, due to non volatile solids

∴ evaporation slowed down

∴ But they don't affect the rate of condensation

So vapour pressure ↓

RAOULT'S LAW

Vapour pressure → $P_{sol'n} = P^{\circ}_{solvent} \cdot \chi_{solvent}$

If $\chi_s = 1$, 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 ^oC 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 ^oC 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 ^oC, 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 ^oC. The vapor pressure of pure water at ^oC 25 is 23.76 torr.

3.

$643 \text{ mL } H_2O \times \frac{0.9971 \text{ g}}{\text{mL}} = 641.6 \text{ g}$

$641.6 \text{ g } H_2O \times \frac{1 \text{ mol}}{18.01 \text{ g}} = 35.63 \text{ mol}$

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

$\chi_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{sucr}} = \frac{35.63}{35.63 + 0.4616} = \boxed{0.9872}$

$P_{sol'n} = P^\circ_{solvent} \cdot \chi_{solvent}$

$= 23.76 \text{ torr} \times 0.9872$

$= 23.46 \text{ torr}$

4. $P_{sol'n} = P^\circ_{H_2O} \times \chi_{H_2O}$

$\chi_{H_2O} = \frac{P_{sol'n}}{P_{H_2O}} = \frac{22.67}{23.67} = 0.9578$

$0.9578 = \frac{n_{H_2O}}{n_{H_2O} + n_{urea}}$ | $n_{H_2O} = 125.0 \text{ g } H_2O \times \frac{1 \text{ mol}}{18.01 \text{ g}} = 6.94$

So

$0.9578 = \frac{6.94}{6.94 + n_{urea}}$

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

$MM = \frac{20.0 \text{ g}}{0.305 \text{ mol}} = 65.6 \text{ g/mol}$

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

Volatile solids:

$$P_{soln} = P_A^\circ \cdot \chi_A + P_B^\circ \cdot \chi_B$$

6) At 30.0 ^{o}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 ^{o}C kg/mol)The resulting sol'n was found to have a boiling point of 100.34 ^{o}C. Calculate the molar mass of glucose.

6) What mass of ethylene glycol ($C_2H_6O_2$, 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 ^{o}F (-23.3 ^{o}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 ^{o}C. Calculate the molar mass of thyroxine.

9) To determine the molar mass of a certain protein, 1.00 x 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 ^{o}C. Calculate the molar mass of the protein.

6. $\chi_{benz} = \frac{0.300}{0.300} = 0.50$

$\chi_{tol} = 0.50$

N.B. Soln with 0.5 χ are called equimolar soln's

$P_{soln} = \underbrace{125\ mm\ Hg \cdot 0.5}_{62.5\ mm\ Hg} + \underbrace{34.0\ mm\ Hg \cdot 0.5}_{19.3\ mm\ Hg}$

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:

$$\Delta T_f = k_f\ m$$

ΔT_f: freezing pt depression; k_f: molal freezing depression constant; m: molality

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

$m = \frac{23.3^\circ C}{1.86 \frac{^\circ C\ kg}{mol}} = 12.5\ mol / kg\ H_2O$

$n_{C_2H_6O_2} = \frac{12.5\ mol}{kg\ H_2O} \cdot 10\ kg\ H_2O = 125\ mol$

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

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

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

$n_{thyroxine} = 4.69 \times 10^{-2} \frac{mol}{kg\ benz} \times 0.015\ kg = 7.04 \times 10^{-4}$ mol thyroxine

$MM = \frac{0.546\ g}{7.04 \times 10^{-4} mol} = 776$ g/mol

Boiling pt elevation:

$\Delta T_b = K_b \cdot m$ → molality

boiling pt depression

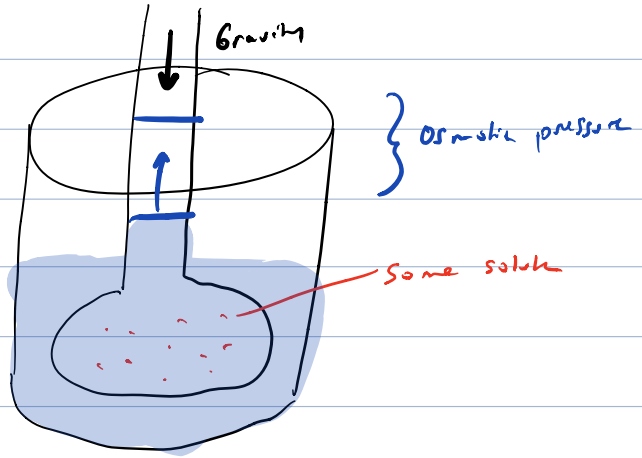
molal boiling depression constant

7. $m = \frac{\Delta T_b}{K_b} = \frac{0.34^\circ C}{0.51 \frac{^\circ C\ kg}{mol}} = 0.67$ mol/kg H_2O

$n_{glucose} = \frac{0.67\ mol}{kg\ H_2O} \times 0.150\ kg\ H_2O = 0.10$ mol glucose

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

Osmotic Pressure:



$$\pi = M \cdot R \cdot T$$

- π: OSMOTIC PRESSURE
- M: MOLARITY
- R: GAS CONSTANT
- T: ABS. TEMP

10. $\pi = 1.12 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.47 \times 10^{-3} \text{ atm}$

$\pi = MRT$

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

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

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

N.B. for ionic compounds

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

i = # ionic compounds produced

$NaCl \rightarrow Na^+ + Cl^- \quad i = 2$

$Na_2SO_4 \rightarrow 2\,Na^+ + SO_4^{2-} \quad i = 3$