VAPOR PRESSURE LOWERING

- Described by RAOULT'S LAW
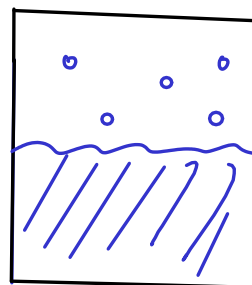
$$P_A = P_A^* \times X_A$$

P_A = partial pressure of the VAPOR of solvent molecules.

mole fraction of component A

vapor pressure of pure component A (depends on temperature)

partial pressure of component A in a solution

... but component "A" above is actually the SOLVENT. If we want to describe this as a colligative property, we want to express Raolt's law in terms of the SOLUTE! Assuming a two-component mixture, we get...

$$\Delta P = P_A^* \times X_B$$

mole fraction of component B (the SOLUTE in a two-component mixture)

Vapor pressure lowering. This is the DECREASE in the vapor pressure of the solvent due to the presence of solute.

BOILING POINT ELEVATION

- Since the vapor pressure is lowered by the presence of a solute, AND since boiling occurs when the vapor pressure of a liquid equals the external pressure - solutes also cause BOILING POINT ELEVATION.

- The equation for boiling point elevation looks almost exactly like the equation for the freezing point depression, and is used in almost the same way.

$$\Delta T_b = K_b \times C_m$$

concentration of solute (molality)

Boiling point elevation constant (for SOLVENT)

Boiling point elevation: The amount the boiling temperature is RAISED by the solute.

What is the boiling point of a solution that contains 2.817 g of molecular sulfur S_8) dissolved in 100.0 grams of acetic acid?

$$T_b = 118.5°C \qquad K_b = 3.08 °C/m \qquad (\text{see p500 for data})$$

$$\Delta T_b = K_b \times C_m \qquad \Big| \qquad C_m = \frac{\text{moles } S_8}{kg\ HC_2H_3O_2}$$

$$\underset{3.08\ °C/m}{\underline{\hspace{2cm}}}$$

$$\underset{100.0g\ =\ 0.1000kg}{\underline{\hspace{2cm}}}$$

We need to calculate delta Tb, but to do that, we must first calculate cm. How?

Find moles of sulfur:

$$2.817_g\ S_8 \times \frac{\text{mol } S_8}{256.56\ g\ S_8} = 0.0109799\ \text{mol } S_8$$

Find cm:

$$C_m = \frac{0.0109799\ \text{mol } S_8}{0.1000kg\ HC_2H_3O_2} = 0.109799\ m\ S_8$$

Find delta Tb

$$\Delta T_b = (3.08\ °C/m)(0.109799\ m\ S_8) = 0.3381\ °C$$

Find Tb by adding the elevation to the original boiling point

$$T_b = 118.5°C + 0.3381\ °C = \boxed{118.8\ °C}$$

OSMOTIC PRESSURE

permits flow of solvent, but not solute particles

- OSMOSIS: the flow of solvent molecules through a SEMIPERMEABLE membrane to equalize concentration of solute on each side of the membrane.

π
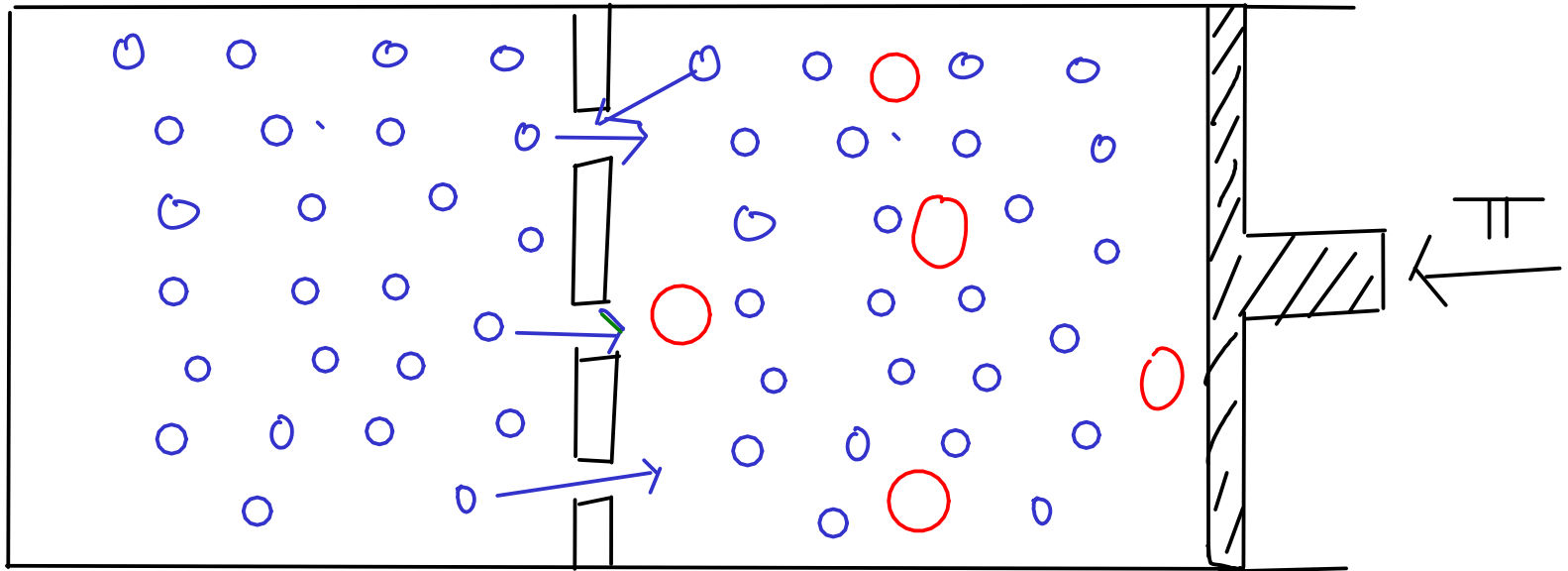
The rate of solvent migration towards the RIGHT is greater than that towards the LEFT.

If you apply enough pressure to the piston, osmosis will not occur. This pressure is called the OSMOTIC PRESSURE
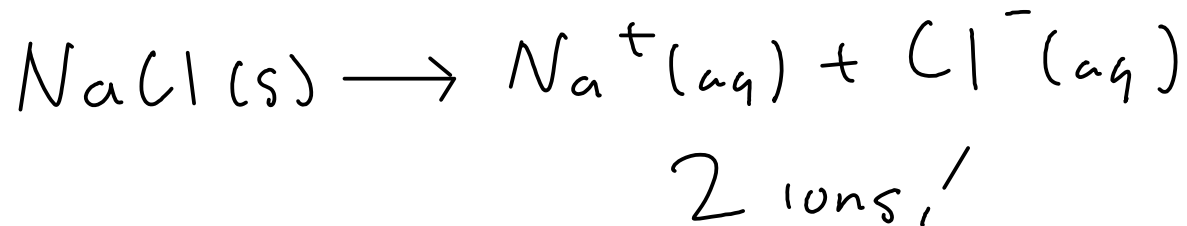
$$\pi = M \times R \times T$$

temperature

ideal gas constant

molar concentration of solute

IONIC COMPOUNDS and colligative properties

- Ionic compounds DISSOCIATE in water into their component ions. Each ion formed can act as a solute and influence the colligative properties!

$$NaCl\,(s) \longrightarrow Na^+(aq) + Cl^-(aq)$$

2 ions!

... so the concentration of IONS here is TWICE the nominal NaCl concentration.

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\,Cl^-(aq)$$

3 ions!
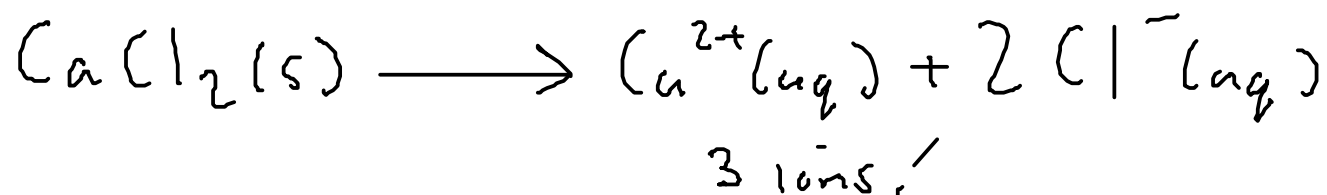
... so the concentration of IONS here is THREE TIMES the nominal calcium chloride concentration.

- Ions interact with each other in solution, so unless an ionic solution is DILUTE, the effective concentrations of ions in solution will be less than expected. A more advanced theory (Debye-Huckel) covers this, but we'll assume that our solutions are dilute enough so that we can use the concentration of the ions in solution to determine the colligative properties!

If you are at an altitude high enough for the boiling point of water to be 95.00 C, what amount of sodium chloride would you need to add to 1.000 kg of water to raise the boiling point to 100.00 C?

$$K_b = 0.512 \,°C/m \qquad NaCl: 58.443 \, g/mol$$

$$\Delta T_b = K_b \times C_m \quad\Bigg|\quad C_m = \frac{moles\ ions}{Kg\ H_2O}$$

$$\underbrace{}_{0.512\,°C/m}$$

$$\underbrace{}_{1.000\ kg}$$

$$= 100.00\,°C - 95.00\,°C = 5.00\,°C$$
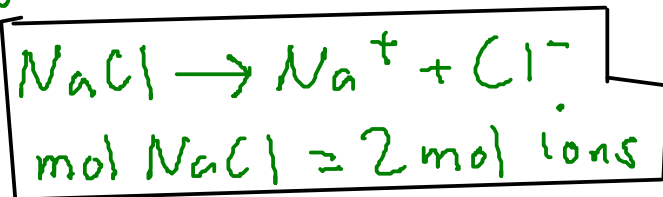
Find cm (molal concentration of ions):

$$\Delta T_b = K_b \times C_m : (5.00\,°C) = (0.512\,°C/m) \times C_m$$

$$C_m = 9.765625 \, m \ \underline{ions}$$

Find moles ions:

$$C_m = \frac{moles\ ions}{Kg\ H_2O} : 9.765625 \, m \ \underline{ions} = \frac{moles\ ions}{1.000\ kg\ H_2O}, \ moles\ ions = 9.765625 \, mol$$

$$\boxed{\begin{array}{l} NaCl \rightarrow Na^+ + Cl^- \\ mol\ NaCl = 2\ mol\ ions \end{array}}$$
One mole of NaCl dissociates into 2 moles of ions!

Find mol NaCl, then mass NaCl:
$$9.765625 \, mol\ ions \times \frac{mol\ NaCl}{2\ mol\ ions} = 4.8828125 \, mol\ NaCl$$

$$4.8828125 \, mol\ NaCl \times \frac{58.443\ g\ NaCl}{mol\ NaCl} = 285 \, g\ NaCl$$

<u>EXTERNAL FACTORS AFFECTING SOLUBILITY</u>

- There are a few external factors that affect the solubility. (By external, we mean other than the chemical identity of the solute and solvent).

① TEMPERATURE

-For gases dissolved in liquids, the solubility DECREASES as the temperature INCREASES

- This is why THERMAL POLLUTION is bad! Hot water holds less oxygen than cooler water.

- For solids dissolved in liquids, solubility USUALLY increases with temperature. This is not true for ALL solid/liquid solutions.

② PRESSURE

- For gases dissolved in liquids, solubility INCREASES when the partial pressure of the solute gas over the solution INCREASES.

- Consider soft drinks. They go flat after opening because the pressure of carbon dioxide over the liquid goes down.

- No significant pressure effects for solid/liquid solutions.

KINETICS

- the study of the RATE of chemical reactions. Or, the study of the factors affecting how fast chemical reactions proceed.

DEFINING RATE

- RATE is defined as the change in the molar (M) concentration of a reactant or product over time. Usually, rate is defined in terms of one of the REACTANTS

$$A + B \longrightarrow C$$

...Let's look at a simple combination

$$Rate = \frac{-\Delta [A]}{\Delta t}$$

$[A]$ = "molar concentration of substance "A".

Square brackets ( ) are used to denote MOLAR concentration

$$Rate = \frac{\Delta [C]}{\Delta t}$$

change in time

You could ALSO define the rate in terms of the disappearance of B or the appearance of C over time! Our choice of A was arbitrary,

Negative sign because we define the rate as a POSITIVE number, and (A) will decrease over time!

THE RATE LAW

- We express the rate of reaction using an equation called the RATE LAW.

$$A + B \rightarrow C$$
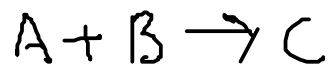
$$Rate = -\frac{\Delta[A]}{\Delta t} = k \times [A]^p \times [B]^q$$

This is the RATE CONSTANT. It depends on TEMPERATURE, but does not depend on the CONCENTRATION of any reactant or product.

"p" and "q" are called REACTION ORDERS. They indicate the effect a particular reactant or catalyst has on the rate of a reaction. Reaction orders may be positive, zero (in which case the substance has NO effect on rate) and negative (in which case the substance actually slows the reaction down).

- Rate laws depend on CONCENTRATION of reactants. Since the concentrations of reactants CHANGE throughout the course of the reaction, so does the rate!

- RATE CONSTANTS and REACTION ORDERS are determined experimentally. If you do experiment 13 (the iodine clock reaction), you will see how this can be done in the lab via the INITIAL RATES METHOD.

INITIAL RATES METHOD

- To determine the rate constant and reaction orders in a reaction, it's possible to monitor the rate of a reaction starting from time zero to a short time later where the concentrations of the reactants haven't changed much. In other words, we look at the INITIAL RATE.

- To determine the rate constant and orders, we need to perform several experiments - one for each order to determine and one baseline experiment to determine the rate constant.

Example:

$$A + B \rightarrow C + D$$

$$Rate = k [A]^q [B]^r$$
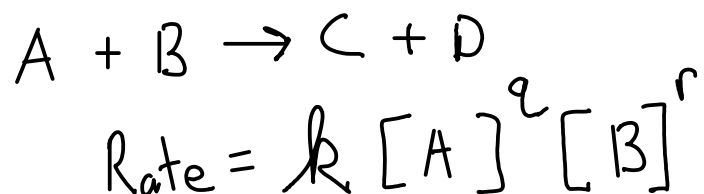
... we want to find the rate constant 'k', and the orders 'q' and 'r'.

Trial	$[A]$	$[B]$	Rate $\dfrac{\Delta [A]}{sec}$	
1	0.156	0.150		Baseline experiment
2	0.300	0.156		Double (A) to find 'q'
3	0.150	0.300		Double (B) to find 'r'

Trial	[A]	[B]	Rate	$\frac{\Delta [A]}{sec}$	
1	0.150	0.150		0.0016875	Baseline experiment
2	0.300	0.150		0.0033750	Double (A) to find 'q'
3	0.150	0.300		0.0067500	Double (B) to find 'r'

$$Rate = k [A]^q [B]^r$$

... so how do we use the data above to find out the values of 'k', 'q', and 'r'?

We observe that in the second trial ((A) doubled), the rate has doubled!

$$(2 \times [A])^q = 2 \times Rate \; ; \; so \; q = 1$$

We observe that in the third trial ((B) doubled), the rate has quadrupled.

$$(2 \times [B])^r = 4 \times Rate \; ; \; so \; r = 2$$

$$\boxed{Rate = k [A][B]^2}$$

Now, we'd like to know the value of 'k'. Solve rate law for 'k'.

$$Rate = k[A][B]^2$$

$$k = \frac{Rate}{[A][B]^2}$$

Plug in each set of data to this equation and calculate 'k'!

Trial	$[A]$	$[B]$	Rate $\frac{\Delta[A]}{sec}$	Calculated 'k'
1	0.156	0.150	0.0016875	0.500
2	0.300	0.150	0.0033750	0.500
3	0.150	0.300	0.0067500	0.500

The average of these calculated 'k' values equals the rate constant.
(For real data, expect some experimental error in these numbers!)

$$Rate = 0.500[A][B]^2$$

FACTORS THAT AFFECT REACTION RATE

① CONCENTRATION OF REACTANTS

② SURFACE AREA OF CONTACT BETWEEN REACTANTS

③ CONCENTRATION OF / PRESENCE OF A CATALYST

④ TEMPERATURE

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Fe

6m HCl

Fe powder

6m HCl