9-3-2024
FRIDAY

CHEMISTRY 4241

Md. Mofazzal Hossain sir

Reversible and equilibrium reactions:

Let's consider the reaction:

$$CuSO_4.5H_2O \xrightarrow{heat} CuSO_4 + 5H_2O$$

blue white

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O$$

It's a reversible and complete reaction.

Whereas,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Ammonia Synthesis

is a reversible and equilibrium reaction

Equlibrium reactions never complete

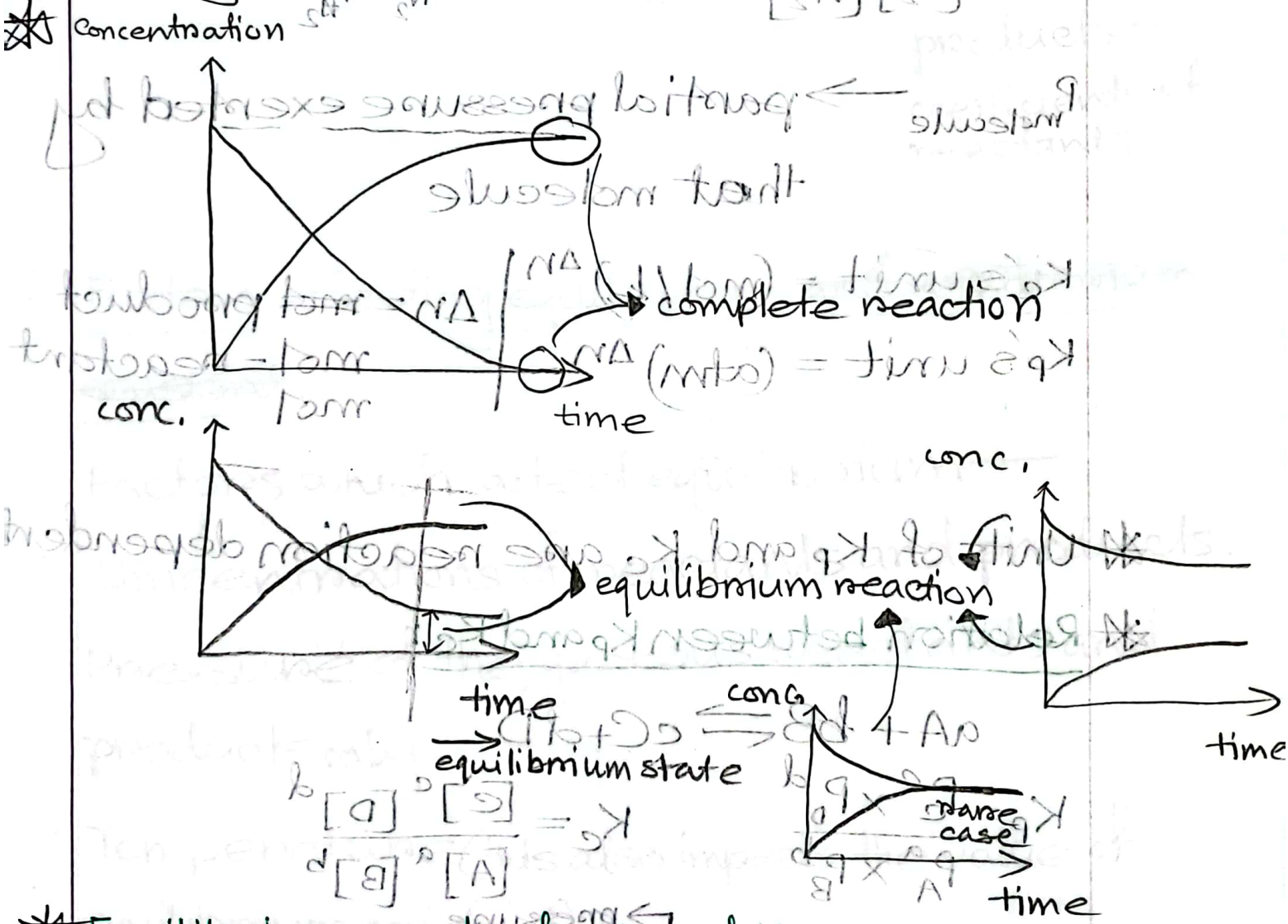
$\rightleftharpoons$ is knowns as Equilibrium Sign.

Characteristics of equilibrium state:

1. It's dynamic (i.e., backward and forward reactions keep running even if they don't bring about any outward changes)
2. Rate of forward reaction = rate of backward reaction

3. Concentrations of reactants and products are constant.

4. The system must be closed.



Equilibrium constants, K_c and K_p:

K → related to time (rate constant)

K → not related to time (equilibrium constant)

For the following reaction, let's figure out K_c and K_p's expressions:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \; L^2 mol^{-2} \qquad K_p = \frac{P_{NH_3}^{\;2}}{P_{N_2} \times P_{H_2}^{\;3}} \; atm^{-2}$$

$P_{molecule}$ → partial pressure exerted by that molecule

K_c's unit = $(mol/L)^{\Delta n}$

K_p's unit = $(atm)^{\Delta n}$

Δn = ~~mol~~ product mol − reactant mol

Units of K_p and K_c are reaction dependent

Relation between K_p and K_c:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_p = \frac{P_C^{\,c} \times P_D^{\,d}}{P_A^{\,a} \times P_B^{\,b}} \qquad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

We know that, $PV = nRT$

P → pressure; V → volume; n → no. of mol; R → molar gas constant; T → temperature in K

$$\Rightarrow P = \frac{n}{V} \times RT = (\text{concentration})RT$$

Then, $$K_p = \frac{\{[C] \times RT\}^c \times \{[D] \times RT\}^d}{\{[A] \times RT\}^a \times \{[B] \times RT\}^b}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)}$$

$$= K_c \times (RT)^{\Delta n}$$; where Δn = coefficients of products − coefficients of reactants

✱ Factors affecting equilibrium ~~and equilibrium constant~~ :

Factors which affect equilibrium —

1. Concentrations of reactants and products.
2. Pressure of the gaseous reactants and products only.
3. Temperature (this also impacts the value of equilibrium constant)

These impacts are explained using La Chatelier principle which states that when a system is at equilibrium, any change in the factors upon which ~~equibri~~ equilibrium depends will change

the equilibrium is such a way that the effect of the change is minimized.

* less (gaseous) molecules = less collisions
  = less pressure

* $\Delta H = -ve \rightarrow$ exothermic reaction
  $= +ve \rightarrow$ endothermic reaction

* Ammonia synthesis is carried out at 450°C and 200 atm (commercially optimum conditions, considerably favourable rate and equilibrium)

* RTP $\rightarrow$ Room Temperature and Pressure

* Ammonia synthesis' reaction rate in rtp is extremely slow (equilibrium is favourable, but rate is not) because its activation energy is huge (due to nitrogen's strong triple bond takes much energy to be broken).

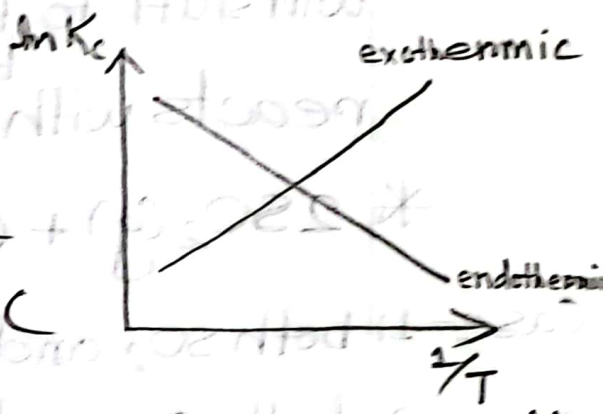
* Position of the equilibrium dictates the partial completion of a reaction, however this doesn't affect the rate of the reaction.

CamScanner

* Very high (or low) pressure and temperature are difficult to maintain, financially and technologically speaking.

* Effect of temperature on K_c and K_p:

$$\boxed{\ln K_c = -\frac{\Delta H}{RT} + \text{constant}}$$



$\Delta H = -ve \longrightarrow$ exothermic

$= +ve \longrightarrow$ endothermic

$\therefore \boxed{\ln K_c = \frac{\Delta H}{RT} + \text{constant}}$ for exothermic reactions

and $\boxed{\ln K_c = -\frac{\Delta H}{RT} + \text{constant}}$ for endother reactions

For exothermic (endothermic) reactions, value of equilibrium constant decreases (increases) with increasing temperature.

* Calculating the value of equilibrium constant at two different temperature shows whether the reaction exothermic or endothermic.

CamScanner

* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If we add HCl here (not directly a reactant or a product here), equilibrium will shift to the right as acidic HCl ~~reactions~~ reacts with basic ~~base~~ NH_3.

* $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

se-1: both SO_2 and SO_3 increase equally ⇒ no impact

se-2: both O_2 and SO_3 increase equally ⇒ equilibriu shifts to the left (as the effect of conc. because of their no. of moles on the right side has risen more due to their ratio).

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{z^2}{x^2 . y}$$

For case-1, $K_c' = \frac{4z^2}{4x^2 . y} = \frac{z^2}{x^2 y} = K_c$

For case-2, $K_c'' = \frac{4z^2}{x^2 . 2y} = \frac{2z^2}{x^2 y} = 2K_c$ (left shift)

To maintain K_c's stability, we must divide

K_c by 2, moving the equilibrium to the left.

* $3Fe_{(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 4H_2(g)$

CHEMISTRY 4241

Md. Sofiul Alom sir

-1-2024 WEDNESDAY

* Covalent bonds' formation due to the outermost half-filled orbitals' overlapping is explained by Valence Bond Theory.

* Types of atomic orbital overlapping:

i. s-s overlap (direction less as s doesn't have any directional property)

ii. s-p overlap ($s-p_x = s-p_y = s-p_z$ as s doesn't have any directional property)

iii. p-p head on overlap (p_x-p_x, p_y-p_y, p_z-p_z)

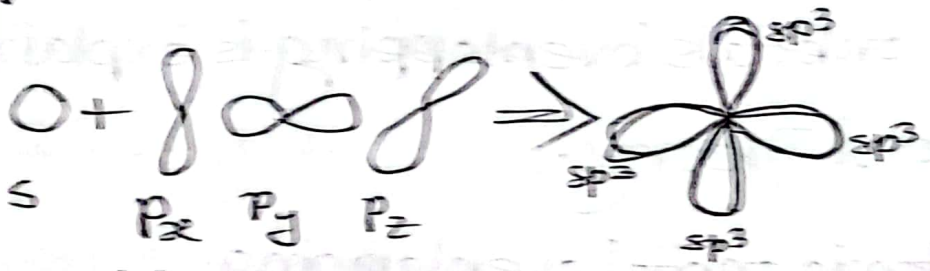
iv. p-p sideways /lateral overlap (orbital symmetry should be same)

* s can only create sigma bonds. s-s, s-p, p-p head on create sigma bonds; whereas p-p sideways overlapping creates pie bonds.

CamScanner

* Electrons situated at atomic orbitals don't participate in hybridization, rather they go on to live in the hybrid orbitals as usual.

* Hybrid orbitals tend to maintain maximum possible distance.

* 

* Hybrid orbitals are always identical in all respects.
* The energy of hybrid orbitals lies somewhere between the participating orbitals. For example in terms of energy: $s < sp^3 < p$.

* Types of hybridizations:

i. sp^2 hybridization (the other p orbital can participate in creating pi bonds or remain unused.)

ii. sp hybridization

iii. sp^3d hybridization

iv. sp^3 hybridization

v. sp^3d^2 hybridization

CamScanner

* No. of hybrid orbitals = $\frac{1}{2}$ [no. of valence electrons in the core atom + no. of sigma bonds + anion charge − cation charge]

* Molecular Orbital Theory, so far, has been the best explainer for the formation of covalent bonds

* No. of molecular orbitals = no. of atomic orbitals taking part

* If the atomic orbitals combine in phase, they create Bonding Orbital (due to constructive interference). Otherwise, out of phase orbitals will cause destructive interference to make Anti-Bonding Orbital. The contributing atomic orbitals must belong to similar energy levels and have symmetrical directionalities.

* Bond order = $\frac{1}{2}[N_B - N_A]$

$N_B \rightarrow$ no. of electrons in bonding orbitals

$N_A \rightarrow$ no. of electrons in antibonding orbitals

$[N_B - N_A] > 0 \Rightarrow B > 0 \rightarrow$ stable Bond

CamScanner

* no. of bonding orbitals = no. of antibonding orbitals

* Bond order expresses the no. of bonds present in certain molecule.

Chapter
Solutions

* A solution is a homogeneous mixture of two or more substances, ions and molecules. Here, a solute is dissolved into solvent.

* Dissolving CO_2 into sugar water creates carbonated water.

* Expressions for concentration of a solution

i. Mass percentage of solute $= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100\%$

ii. Mole fraction, $X_A = \frac{\text{Moles of A}}{\text{Total moles of solution}} = \frac{\text{Moles of A}}{\text{Moles of solute} + \text{Moles of solvent}}$

iii. Molarity, $M = \frac{\text{Moles of solute}}{\text{liters of solution}}$ (mol/L)

iv. Molality, $m = \frac{\text{Moles of solute}}{\text{kilogram of solvent}}$ (mol/kg)

v. Normality, $N = \frac{\text{gram equivalent of solute}}{\text{liters of solution}}$ (g/L)

* Mole percentage = Mole fraction × 100%

* equivalent of solute = $\frac{\text{mass}}{\text{gram equivalent of solute}}$

gram equivalent of solute = $\frac{\text{molecular weight}}{\text{no. of effective substance ion/atom}}$

* 1 kg of water ≅ 1 L of water (water's density is ~0.997 g/mL)

* moles = $\frac{\text{given mass}}{\text{molecular mass}}$

* Solubility is the maximum quantity of solute which can be dissolved in a certain solvent/solution at a particular temperature or pressure.

* A solution can be saturated (equilibrium state), unsaturated or supersaturated.

* Solubility ∝ Temperature (not always though)

* To make a supersaturated solution, first make a saturated solution. Then heat it up to add more solute. Finally, cool it down slowly to not let the excess solute precipate. After this operation, however, if even a single grain of solute is added,

CamScanner

all the excess solute will precipitate.

* For gaseous solutes, solubility drops at increased temperatures. Generally, the opposite case is true for liquid or solid solutes.

* Dissolution generates heat, breaking of bonds requires heat.

* Henry's Law describes the effect of pressure on solutions (effective only on gaseous solutes). It states that at a particular temperature, the solubility of a gas or the concentration of the gas dissolved in a liquid is directly proportional to its partial pressure.

$C \propto P \Rightarrow \boxed{C = K_H P}$

K_H → Henry's law constant (g/atm.L)

* C_2H_2 ⇒ Acetylene

CHEMISTRY 4242

Mofazzal Hossain sir

* **Ionic equilibrium:** Similar to chemical equilibrium, but exists in aqueous systems. Particularly applicable for weak acids and weak alkali.

Examples

$$CH_3COOH \xrightleftharpoons{H_2O} CH_3COO^-(aq) + H^+(aq); \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$NH_4OH \xrightleftharpoons{H_2O} NH_4^+(aq) + OH^-(aq); \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$K_{a/b} \rightarrow$ acid/base disassociation constant

* $H_2O \rightleftharpoons H^+ + OH^-$

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \Rightarrow [H^+][OH^-] = K_c \times [H_2O]$$

$= \text{const.} \times \text{const.}$

[$\because H_2O$ is a solvent and must be present in large excess]

$\Rightarrow K_w$ = ionic product of water

$K_w = 10^{-14}$ at 25°C
mol^2/L^2

* $[H^+]^2 = 10^{-14}$

$\Rightarrow [H^+] = 10^{-7} mol/L = [OH^-]$

$\therefore pH = pOH = 7$

* pH of pure water at higher temperature is lower. The reason for this is that the disassociation process of water is endothermic. Then, K_w will be $> 10^{-14} mol^2/L^2$.

Still, it will remain neutral as pOH will decrease as well and the ~~entri~~ entire range of the pH scale will compress ($0^+ - 14^-$)

* Practically, it's not possible for the water to have pH 0. Theoretically, such high temperature are possible.

* Calculation of pH:

i. Strong acid

ii. Strong alkali
iii. Weak acid
iv. Weak alkali
v. Buffer solution

* Calculate pH of —

0.01 $mol L^{-1}$ of HCl / H_2SO_4 / CH_3COOH $[K_a = 1.7 \times 10^{-5}]$ / $NaOH$ / NH_4OH $[K_b = 1.8 \times 10^{-5}]$

For NH_4OH, we know that, $\boxed{[OH^-] = \sqrt{K_b [alkali]}}$

[Similar formula for acids is $\boxed{[H^+] = \sqrt{K_a [acid]}}$]

$$\therefore [OH^-] = \sqrt{K_b [NH_4OH]} = \sqrt{1.8 \times 10^{-5} \times 0.01}$$

$$= 4.24 \times 10^{-4} \, mol L^{-1}$$

$$\therefore \boxed{[H^+] = \frac{K_w}{[OH^-]}} = \frac{10^{-14}}{4.24 \times 10^{-4}} \longrightarrow \text{at } 25°C$$

$$= 2.35 \times 10^{-11} \, mol L^{-1}$$

$$\therefore pH = -\log(2.35 \times 10^{-11}) = 10.6$$

* **Buffer solutions:** A buffer solution resists the change of its pH after the addition of small amount of acid or alkali.

Buffer solutions can be made in 2 ways:

i. Weak acid and its conjugate base [example: $CH_3COOH + CH_3COONa$]

ii. Weak alkali and its conjugate acid [example: $NH_4OH + NH_4Cl$]

* $\underbrace{NH_4^+}_{\text{weak acid}} + \underbrace{NH_3}_{\text{conjugate base}}$ makes a buffer solution (an acidic one)

* $\underbrace{H_2PO_4^-}_{\text{weak acid}} + \underbrace{HPO_4^{2-}}_{\text{conjugate base}}$ makes an acidic buffer mixtur

* **Mechanism of buffer solutions:**

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \text{ [partial disassociation]}$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na \text{ [full disassociation]}$$

If extra H^+ is added, only a trace amount of excess CH_3COO^- reacts with H^+ and shifts the equilibrium to the left.

If OH^- is added, it reacts with CH_3COOH to create CH_3COO^- and H^+. $[CH_3COO^-]$ remains largely unchanged due to its vast volume.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\Rightarrow -\log K_a = -\log[H^+] - \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

generates mostly from the salt

$$\Rightarrow pK_a = pH - \log\frac{[Salt]}{[Acid]}$$

$$\Rightarrow \boxed{pH = pK_a + \log\frac{[Salt]}{[Acid]}}$$

Henderson-Hasselbalch equation

Salt Hydrolysis: $NaCl + H_2O \longrightarrow NaCl(aq)$; this is not a reaction, rather it's dissolution process

$(Na^+_{(aq)} + Cl^-_{(aq)})$

$$CH_3COONa + H_2O \longrightarrow CH_3COOH + Na^+ + OH^-$$

$$\Rightarrow CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

[removing all the spectator ions]

this is salt hydrolysis in basic medium

$NH_4^+ + H_2O \rightarrow NH_4OH + H^+$ [in acidic solution]

* Salts made by weak (strong) acid and strong (weak) alkali undergoes hydrolysis in basic (acidic) solution

* $A^- + H_2O \rightarrow AH + OH^-$

$$K_h = \frac{[AH]([OH^-][H^+])}{[A^-][H^+]} = \frac{K_w}{K_a}$$

multiplied both the numerator and the denominator by $[H^+]$

If the salt A^- undergoes hydrolysis, then $[AH] = [OH^-]$

$$\therefore \frac{[OH^-]^2}{[A^-]} = \frac{K_w}{K_a}$$

$$\Rightarrow [OH^-]^2 = \frac{K_w}{K_a} \times [A^-]$$

$$\Rightarrow \left(\frac{K_w}{[H^+]}\right)^2 = \frac{K_w}{K_a} \times [A^-] \quad \left[\because [OH^-] = \frac{K_w}{[H^+]}\right]$$

$$\Rightarrow [H^+] = \sqrt{\frac{K_w \times K_a}{[A^-]}}$$

$$\Rightarrow -\log[H^+] = \frac{1}{2}\{-\log K_w - \log K_a + \log[A^-]\}$$

$$\Rightarrow \boxed{pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log[A^-]}$$

2024
NESDAY

CHEMISTRY 4241
Md. Sofiul Alom sir

* **Nernst's Distribution Law**: If two solvents can get mixed together, they're called Miscible Solutions; otherwise they're Immiscible Solutions.

$$\boxed{\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = \frac{C_1}{C_2} = K_D}$$

* Nernst's distribution law is an equilibrium law.
It is applicable in ideal conditions only.

* $X + X \longrightarrow X_2 \Rightarrow$ Association

$X \longrightarrow A + B \Rightarrow$ Dissociation

* Higher concentration of solutes increase the chances

of association among the molecules of the solute

* Equilibria (plural) ≡ Equilibrium

* $\boxed{nX = X_n}$ Mass Law

K_p and K_c are derived from mass law

$$\rightarrow \boxed{\frac{[X_n]}{[X]^n} = K_c}$$

* Nernst's distribution law can be modified ~~into~~ to factor in the association and dissociation of the solute.

* Degree of Dissociation denotes the amount of dissociation 1 mol of solid solute undergoes.

22-4-2024
MONDAY

CHEMISTRY 4241
Md. Mofazzol Hossain sir

* Calculation of K_p and K_c:

example

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Initial Conditions: 0.4 mol, 0.4 mol, 0.2 mol, 0.2 mol

If the value of K_c is 0.64, calculate the no. of moles for each component.

← Let's consider that x mol of CO react at

equilibrium.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

At equilibrium: $0.4-x$ $0.4-x$ $0.2+x$ $0.2+x$

$$\therefore 0.64 = \frac{(0.2+x)^2}{(0.4-x)^2} \Rightarrow x = \frac{1}{15} \text{ mol/L}$$

$$\therefore [CO] = [H_2O] = 0.4 - x = \frac{1}{3} \text{ mol/L and}$$

$$[CO_2] = [H_2] = \frac{4}{15} \text{ mol/L}$$

Finding K_p using mole fraction:

Example

$$P \rightleftharpoons 2Q + R$$

Initial: 0.2 mol 0 mol 0 mol

equilibrium: $(0.2-x)$ mol $2x$ mol x mol

(Q was halved i.e., 2Q was reduced in x mol): $(0.2-\frac{x}{2})$ mol x mol $\frac{x}{2}$ mol

Colligative Properties of Dilute Solutions:

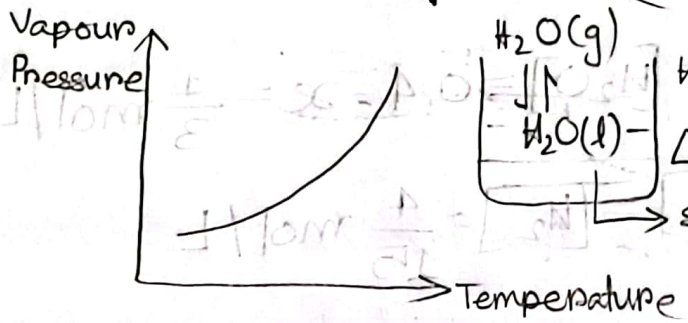
Colligative properties are the ones which depend on the number of particles not on the nature of the substance. The four colligative properties are:

1. Lowering of vapour pressure
2. Elevation of boiling point

iii. Depression of freezing point

iv. Osmotic pressure

* **Vapour Pressure** is the pressure exerted by vapour that remains in equilibrium in liquid state. It's an endothermic process (i.e., temperature ↑ pressure ↑).



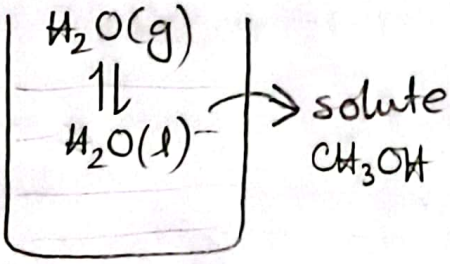
$H_2O(l) \rightleftharpoons H_2O(g)$

$\Delta H_{vap} = (+)$ve

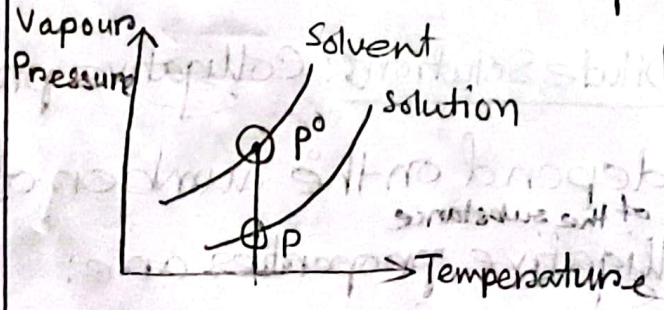
Vapour pressure increases exponentially.

* Temperature ↑ ⇒ Kinetic Energy ↑

*



If CH_3OH (solute) is added, less water molecules will be present because some will react with the solute. As the volume of the solution increases, vapour pressure will decrease



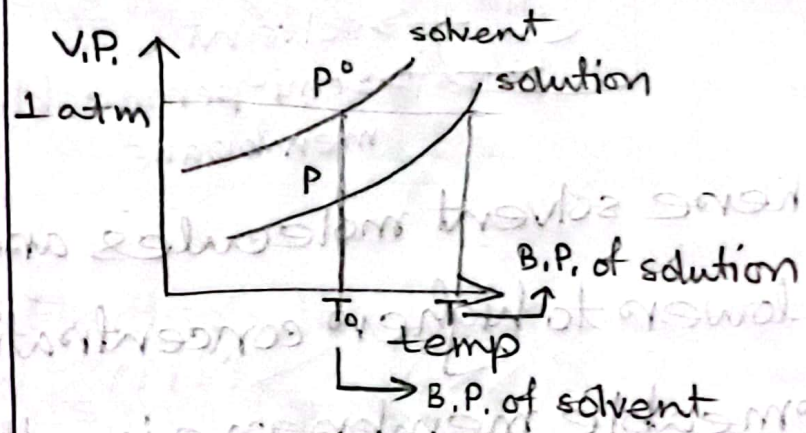
$P^o - P$ = lowering of vapour pressure at any temperature

* **Boiling Point**, the temperature at which liquid turns into vapour, increases upto the saturation

point. ⇒ Solute ↑ → Boiling Point ↑

* At boiling point, the vapour pressure of a liquid is equal to the atmospheric pressure.

* Boiling point of solution is always higher than that of the solvent.

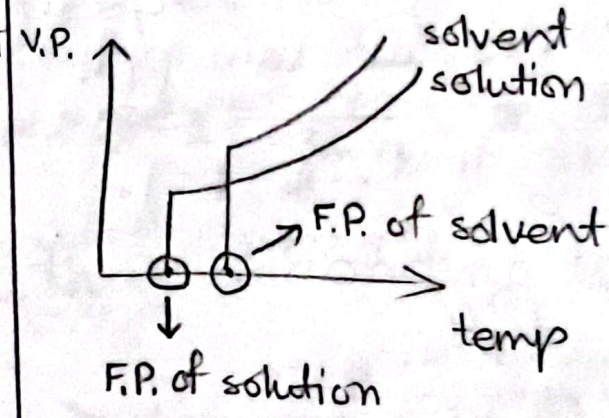


Solution's V.P. is lower, so to make it equal to atmospheric pressure, more temperature is required.

* no. of particles ↑ ⇒ B.P. ↑

Hence, B.P. : ~~$CH_3CH_2OH > CH_3COOH > NaCl$~~ [let all of them be of the same concentration ($0.01\ mol\ L^{-1}$)]

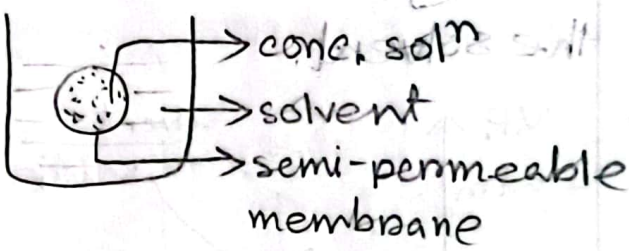
$NaCl > CH_3COOH > CH_3CH_2OH$

* 

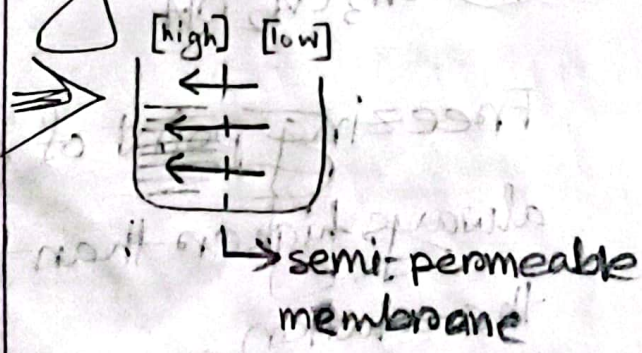
Freezing point of solvent is always higher than that of the solution.

* The temperature at which solid solute ~~remain~~ remains in equilibrium with pure solvent or solution is known as Freezing Point/Melting Point.

* **Osmotic Pressure:**



The process where solvent molecules are migrated from lower to higher concentrations through semi-permeable membrane is called Osmosis. The external pressure exerted by a highly concentrated solution just to stop the in-flow/migration of solvent molecules from lower to higher concentration is called Osmotic Pressure.



CHEMISTRY 1241

Md. Mutazzil Hossain sir

* Lowering of vapour pressure:

Vapour pressure of solvent $= P^\circ$

" " " solution $= P$

$\therefore$ lowering of vapour pressure $= P^\circ - P$ and

the relative lowering of vapour pressure $= \frac{P^\circ - P}{P^\circ}$

* Raoult's law of lowering of vapour pressure: $\boxed{\frac{P^\circ - P}{P^\circ} = x_2}$

* Electrolytes undergo some level of dissociation, changing its mole number

* x_2 = mole fraction of the solute

x_1 = mole fraction of the solvent

$\therefore x_1 + x_2 = 1$

Let n and N be the no. of mol of solute and solvent, respectively

$\therefore x_1 = \frac{N}{N+n}$, $x_2 = \frac{n}{N+n}$

thus, according to Raoult's law, $\boxed{\frac{P^\circ - P}{P^\circ} = \frac{n}{N+n} = x_2}$

$\Rightarrow 1 - \frac{P^\circ - P}{P^\circ} = 1 - \frac{n}{N+n} \Rightarrow \boxed{\frac{P}{P^\circ} = \frac{N}{N+n} = x_1} \Rightarrow \boxed{P = x_1 P^\circ}$

$\therefore P \propto x_1$

* Ideal solutions obey the Raoult's law at all temperatures and compositions.

* From the formula of relative lowering of vapour pressure, we can determine the molecular mass of a substance.

$$\frac{p^\circ - p}{p^\circ} = \frac{n}{N+n}$$

For dilute solutions, $n \ll N \Rightarrow N+n \approx N$

$$\therefore \frac{p^\circ - p}{p^\circ} = \frac{n}{N} = \frac{w_2/M_2}{w_1/M_1}$$

(w_2, M_2 → for solutes; w_1, M_1 → for solvents)

$$\Rightarrow \boxed{M_2 = \frac{p^\circ \times w_1}{w_2 \times M_2 (p^\circ - p)}}$$

* Elevation of boiling point: Raoult's law applies here as well which dictates that $\Delta T_b = T - T_0$

(T → elevation of b.p.; T → b.p. of solute; T_0 → b.p. of solvent)

$\Delta T_b \propto m$

$$\Rightarrow \boxed{\Delta T_b = k_b m}$$

(m → molal concentration; k_b → ebullioscopic constant (depends only on

the solvent)

* Elevation of boiling point is a colligative property.
* Raoult's law is applicable for depression of f.p. as well.
* Thermodynamic derivation of b.p. elevation:

$$\boxed{\ln\frac{P_2}{P_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$ Clapeyron-Clausius equation

For elevation of b.p., $\ln\frac{P}{P^\circ} = -\frac{\Delta H}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)$

$$= -\frac{\Delta H}{R}\left(\frac{T-T_0}{TT_0}\right)$$

$$= -\frac{\Delta H}{R}\times\frac{\Delta T_b}{T_0^2}$$ [for dilute solutions, $T \approx T_0$]

$$\Rightarrow \ln x_1 = -\frac{\Delta H}{R}\times\frac{\Delta T_b}{T_0^2}$$ [$\because x_1 = 1-x_2 = P/P^\circ$]

$$\Rightarrow \ln(1-x_2) = -\frac{\Delta H}{R}\times\frac{\Delta T_b}{T_0^2}$$

When x_2 is very small (for dilute solutions), we can infer that $\ln(1-x_2) \approx -x_2$

$$\therefore -x_2 = -\frac{\Delta H}{R}\times\frac{\Delta T_b}{T_0^2} \Rightarrow \boxed{\Delta T_b = \frac{RT_0^2}{\Delta H}x_2} = \frac{RT_0^2}{\Delta H}\cdot\frac{n}{N}$$ [$\because N-n \approx N$]

$$= \frac{RT_0^2}{\Delta H} \frac{W_2/M_2}{W_1/M_1}$$

$$= \underbrace{\frac{RT_0^2}{\frac{\Delta H}{M_1} \times 1000}}_{k_b} \times \underbrace{\frac{W_2/M_2}{W_1} \times 1000}_{\text{Molal Concentration}}$$

$$\therefore \Delta T_b = k_b . m$$

* Depression of f.p.: Raoult's law here states that-

$$\boxed{\Delta T_f = K_f . m}$$

$m \rightarrow$ molal concentration

$K_f \rightarrow$ cryoscopic constant

* Depression of f.p. and elevation of b.p. have similar mathematic properties
* equimolar $\neq$ equimolecular
* Osmotic Pressure and Osmosis: Osmosis is a process or a phenomenon. Osmotic pressure is a colligative properties and it abides by 3 laws.
* Vant Hoff law for Osmotic Pressure: $\boxed{\pi \propto C}$ [T => constant]

$\pi \rightarrow$ osmotic pressure

$\Rightarrow \boxed{\pi \propto \frac{1}{V}}$ $\left[\because C = \frac{1}{V}\right]$

$\boxed{\pi \propto T}$ [P => constant]

$\boxed{\pi \propto n}$

Summarizing all these eq^n's gives us — $\pi = \frac{nRT}{V}$

$\Rightarrow \boxed{\Pi = CRT}$ (C → molar concentration)

* Colligative properties are used to determine the molecular mass of an unknown solute.

CHEMISTRY 4241

Md. Sofiul Alom sir

* Phase Rule is used to predict qualitatively by means of a diagram effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium. William Gibb's phase rule is expressed mathematically as—

$$\boxed{F = C - P + 2}$$

(C → no. of components; P → no. of phases; F → degree of freedom)

* Heterogeneous systems have more than one phase (ice cube (solid) floating on water (liquid)) and homogeneous systems feature only one phase (chemical solutions (for the most part))

* Pure substances, mixtures of gases, aqueous solutions and miscible liquids make homogeneous systems.

* Phase $\neq$ state $\neq$ Component

* To be of the same phase, the physical and chemical properties match.

* Degrees of Freedom is defined as the least number of variable factors which must be specified so that other variable factors are automatically fixed and the system is completely defined.

* For a pure gas, F=2 as it follows PV=nRT

For mixtures of gases, F=3 (composition, temperature and pressure)

↳ liquids aren't affected much by their volume

For water $\rightleftharpoons$ water vapour equilibrium, F=1 (temperature or pressure).

↳ vapour pressure is fixed at a temperature

For ice-water-vapour system, F=0 (vapour pressure of water is fixed at the triple point of water). It's called an Invariant System.

* Phase rule for a one-component system is

$\boxed{F=3-P}$

* Phase Diagram depicts the relationship between pressure and temperature for different phases of a component.
* Melting point and boiling point are calculated at 1 atm.
* Triple-point of water ⇒ 0.0078°C, ~~4.68mm(Hg)~~
  4.68 mm(Hg)
* For each line of the water system's phase diagram, degree of freedom is 1 (temperature or pressure). Each region's degree of freedom is, however, 2 (temperature and pressure). At the triple point, degree of freedom drops to 0 for water (Invariant Point).
* Supercooled water is in a volatile stability, known as a metastable state.
* Only unsaturated compounds' pi bonds undergo addition reaction. Its opposite is elimination reaction.
* Condensation reaction separates a water molecule to combine two compounds.
* Combustion reaction is a type of oxidizing reaction where the oxidizing reagent is O_2.

* Esterification reaction needs an acid catalyst.
* $R-\overset{O}{\overset{\|}{C}}-O-R \Rightarrow$ Ester

CHEMISTRY 1241

Md. Mufazzal Hossain sir

Electrolysis

- Anions are oxidized at anodes and cathodes are reduced at cathodes for electrolytic cells.
- Faraday's law for electrolysis:

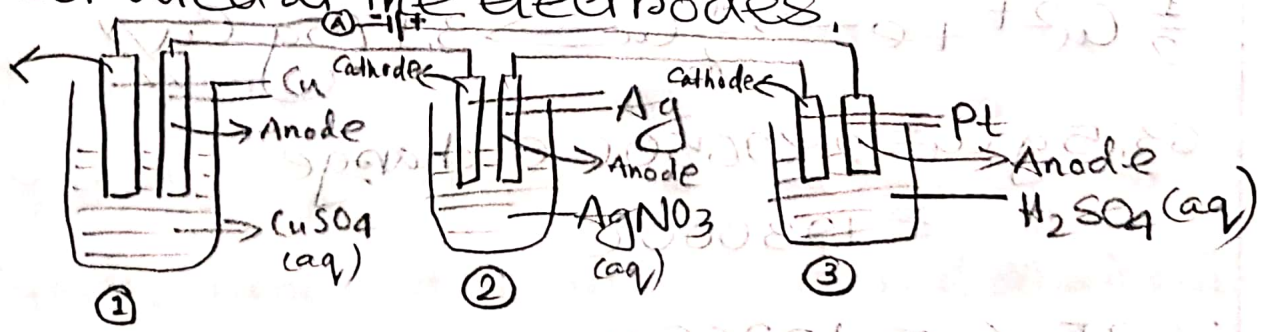
1st law: The amount of substance liberated or dissolved at the electrode is proportional to the charge of electricity.

$Q(C) = \text{charge} \propto i(A) \times t(sec)$

$\Rightarrow \boxed{Q = zit}$ where z is the electrochemical equivalence (~~the charge passed for 1A ele~~

Electrochemical Equivalence (Z) is the amount of substance liberated (or dissolved) when 1A of current is flown for 1 second.

2nd law: When same amount of charge of electricity is passed through different substances, equivalent amount of substance will be dissolved or liberated at the electrodes.



Cathode ①: $Cu^{2+} + 2e^- \rightarrow Cu$

Anode ①: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode ②: $Ag^+ + e^- \rightarrow Ag$

Anode ②: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Cathode ③: $2H^+ + 2e^- \rightarrow H_2$

Anode ③: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

After 30 minutes of electrolysis, 6.35g Cu is deposited at cathode-①. How much O_2 will be liberated at anode-③?

— We must apply the 2nd law of Faraday here using the substances' equivalent masses. Then the no. of electrons exchanged must be kept equal for the substances' reactions.

// $Cu^{2+} + 2e \rightarrow Cu \Rightarrow 6.35g\ Cu$

$\frac{1}{2}Cu^{2+} + e \rightarrow \frac{1}{2}Cu \Rightarrow 3.175g\ Cu$ //

$63.5g\ Cu \equiv 2 \times 96500\ C$ charge

$\equiv 193000\ C$

$\therefore 6.35g\ Cu \equiv 19300\ C$

$4 \times 96500\ C \equiv 1\ mol\ O_2$

$\Rightarrow 19300\ C \equiv \frac{19300}{4 \times 96500}\ mol\ O_2 = \frac{1}{20}\ mol\ O_2$

$= 0.05\ mol\ O_2$

* Conductance is ~~acc~~ the reciprocal quantity of resistance. From Ohm's law, we get —

$E = I \times R$

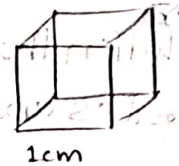
$= I \rho \frac{l}{a}$ → Specific Resistance

K (Kappa) = Specific Conductance

$= \frac{1}{\rho}$ (unit: $mho\ cm^{-1}$)

* Unit of conductance is $mho = ohm^{-1} = S$ (siemens)

*



$V = 1\ cm^3$ The conductance of this structure for any substance is its specific conductance.

* Specific Conductance of a substance is the conductance of 1 cm^3 solution of that substance when the opposite faces of that cube are considered

as cells.

* $\boxed{C = K \times \frac{a}{l}} \Rightarrow \boxed{K = C\frac{l}{a}}$

K → specific ~~constant~~ conductance

C → observed conductance

$\frac{l}{a}$ → cell constant

$\frac{l}{a}$ is constant for a particular cell (specially the commercially available ones).

* Specific conductance deals with the volume of the solution. Molar conductance is related with 1 mol of the substance.

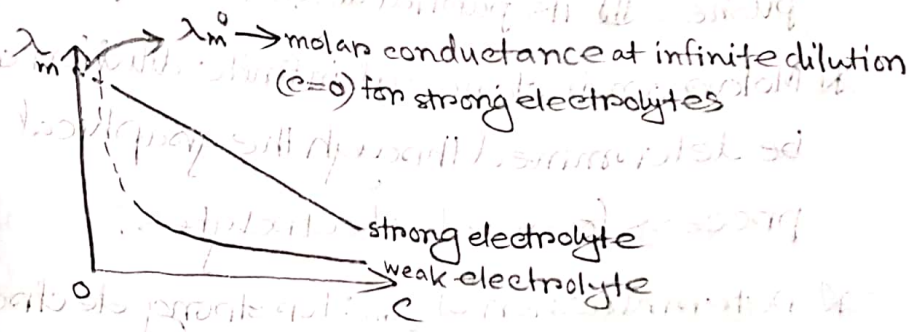
* Molar Conductance is the conductance of 1 mol ~~solution~~ substance (solute) in solution that is present in a cell where electrodes are kept 1 cm apart. It's denoted by the symbol λ_m. The volume of the solution is not specified in this regard.
  λ → lamda.

* $\boxed{\lambda_m = K \times V_{mL}}$

If the concentration is C mol/L, that means C mol substance of the ~~solute~~ is present in 1000 mL solution.

∴ 1 mol substance is present in $\frac{1000}{C}$ mL solⁿ.

∴ $\boxed{\lambda_m = \frac{1000K}{C}}$

* 

Using $\sqrt{c}$ in this graph, it'll compress the horizontal scale to give a better visual impression of the plot.

* Conductance depends on (at constant temperature):
  1. No. of ions.
  2. Mobility of ions.

* Mobility of ions increases during dilation (~~dum~~ due to increase of more ~~blank~~ spaces in the solution).

* No. of ions don't change during dilation for strong electrolytes (because their dissociation is complete). It increases rapidly for weak electrolytes (as dilation pushes its partial dissociation process).

* Molar conductance at infinite dilution can't be determined through the graphical process for weak electrolytes.

* <u>Determination of λ_m°</u>: For strong electrolytes,

<u>Step-1</u>: Calculate λ_m at different C's to plot the graph.

<u>Step-2</u>: If it's a straight line, it can be extended back to $C=0$ to get λ_m°.

Observed Conductance $\rightarrow$ Specific Conductance $\rightarrow$ Molar Conductance $\rightarrow \lambda_m^\circ$

For weak electrolytes, the graphical approach fails as extrapolation of any curve isn't acceptable. We use here the Kohlrausch's law:

$$\boxed{\lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ}$$

Molar conductance at infinite dilution for any (weak) electrolyte is the sum of molar conductances of the cations and the anions at infinite dilution.

This law is applicable for all types of electrolytes.

For $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$, we get—

$$\lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

To fetch these values, we must select 3 strong electrolytes: CH_3COONa, HCl and NaCl. For these, we can write—

$$\lambda^\circ_{CH_3COONa} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}$$

$$(+)\ \lambda^\circ_{HCl} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$$

$$(-)\ \lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

$$\underbrace{\lambda^\circ_{CH_3COONa} + \lambda^\circ_{HCl} - \lambda^\circ_{NaCl}}_{\text{can be calculated from the graph}} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} = \lambda^\circ_{CH_3COOH}$$

For NH_4OH, we could've picked NH_4Cl, NaOH and NaCl. Na could be replaced by any metals as per our choice.

* **Transport Number**: Fraction of current carried by each ionic species is called (its) Transport Number. It can be represented as t_+ and/or t_-.

$$\boxed{t_+ = \frac{u_+}{u_+ + u_-}} \quad \boxed{t_- = \frac{u_-}{u_+ + u_-}} \quad \boxed{t_+ + t_- = 1}$$ as they're fractions

where u_+ and u_- denote the mobility of the ions (cations and anions, respectively).

Mobility is the velocity of the ions under unit potential gradient. (Unit: cm/sV)

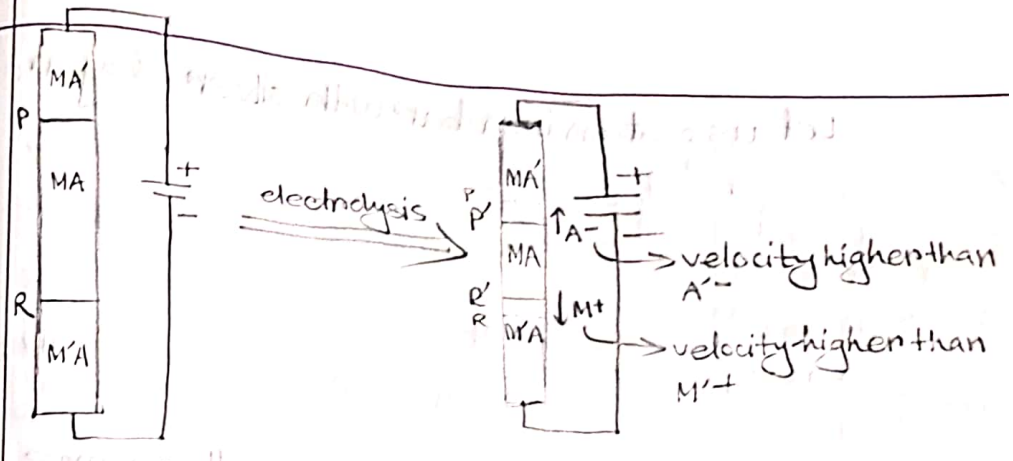
* **Determination of Transport Number:**

Method-1: Moving Boundary Method

Let us consider the electrolyte $MA(M^+ + A^-)$.

To determine t_{M^+} and t_{A^-}, we take a column with the electrolyte in it.

Now, we need to choose two more electrolytes of the forms: MA′ and M′A. A′ must have lower velocity than A and M′ must have lower velocity than M.



Velocity of M^+ and A^- are proportional to PP′ and RR′, respectively.

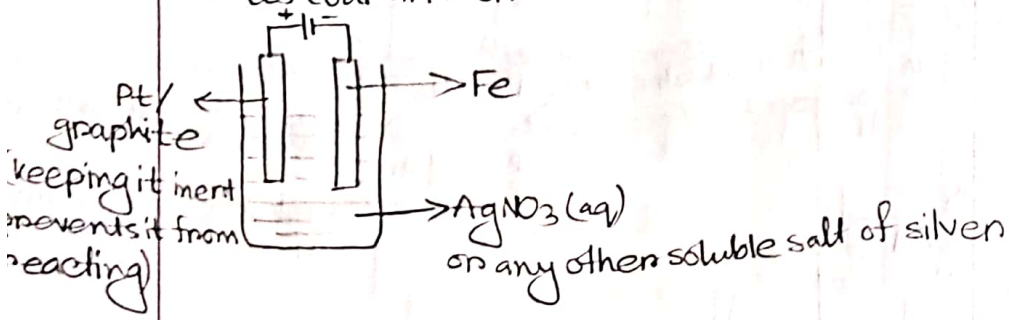
$$\therefore t_{M^+} = \frac{PP'}{PP' + RR'} \text{ and } t_{A^-} = \frac{RR'}{PP' + RR'}$$

* As mobility of ions can't be determined directly, we must consider characteristics related or proportional to mobility to experimentally calculate an ion's transport number.

~~Eleno~~ **Electroplating**

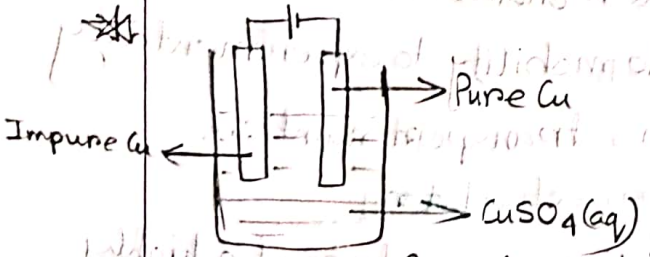
It's an electrolytic process to coat a highly reactive element/substance with a layer of less reactive elements/substances.

Let us coat an iron bar with silver's layer:



* Galvanization, although serves the same purpose, is slightly different from electroplating in the sense that galvanization uses molten salt of Zn. Since Zn's melting point is easy to reach, it's often melted to be put ~~the metal rod ins~~ all over the metal bar or rod or instrument.

*



If the impure Cu is contaminated by Zn, mass lost > mass gained. Because between Cu and Zn, Zn will dissolve as it's more reactive. Then the reactions will be:

$\underset{65g}{Zn} \rightarrow Zn^{2+} + 2e^-$ $\quad Cu^{2+} + 2e^- \rightarrow \underset{63,5g}{Cu}$

Cu will partially dissolve as well.

If the contamination came ~~as~~ in the form of Ag, then mass lost > mass gained. As Ag is less reactive, it'll ~~precipitat~~ create anodic ~~slush~~ sludge as it drops and piles up below the anode in metallic form. Cu will dissolve from the anode and ~~Cu fro will~~ will go to be added on to the cathode. The additional loss of silver will cause the inequality between mass gained and lost.

* Galvanization's coating is made of a relatively reactive metal Zn whereas electroplating creates a layer of less reactive metals. While electroplating involves the process of electrolysis, simply dipping the metal into molten zinc accomplishes galvanization.