Chem 4241

Mofazzal Sir

29/03/24 4

Equilibrium and reversible Reactions

$$CuSO_4 \cdot 5H_2 \xrightarrow{heat} CuSO_4 + 5H_2O$$

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$$

} Complete, Not reversible

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

, Not complete, reversible

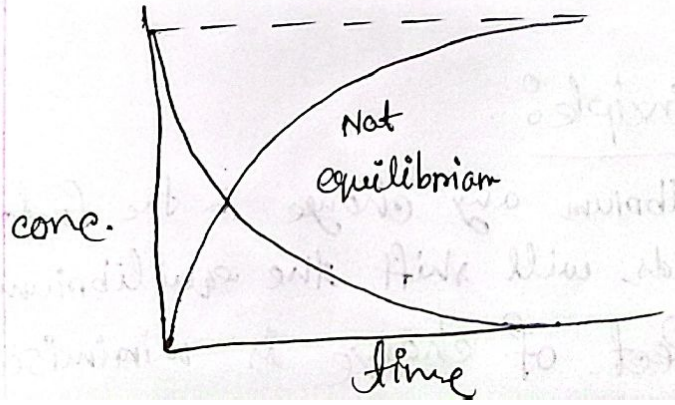
Characteristics

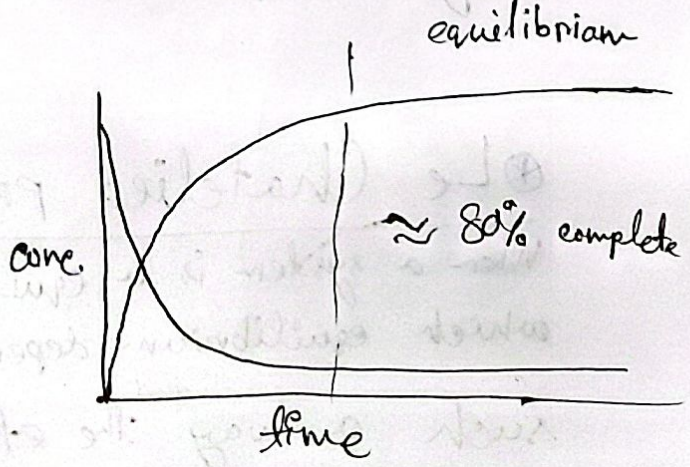
① It is dynamic

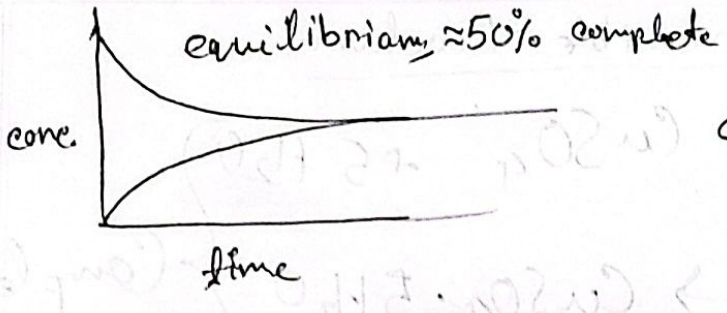
② Rate of the forward reaction = = rate of backward system

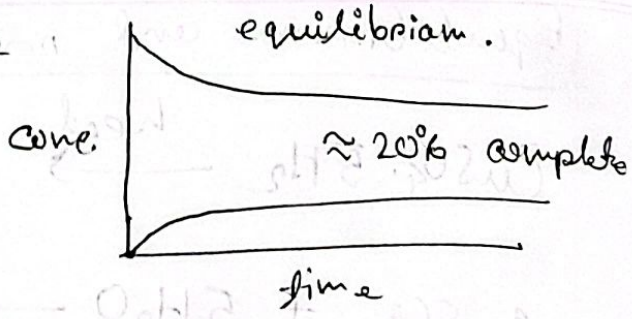
③ Concentration of reactants and products ~~are~~ is const.

④ It is a closed system.









Equilibrium const. (K_c & K_p, both represented by capital K)

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

$$P = \left(\frac{n}{V}\right) RT \quad (\frac{n}{V} = C)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad , \quad K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} \quad , \quad K_p = K_c (RT)^{\Delta n}$$

$$\Delta n = (Pro) - (Rea)$$

Factors affecting equilibrium and equilibrium const. (K)

1. Concentrations of the Rea, Pro
2. Pressure of the gaseous " "
3. ~~Themp~~ Temperature

— These three affect / change the equilibrium const.

Only temperature can affect the value of K.

⊛ Le Chatelier principle:

When a system is a equilibrium any change in the factors on which equilibrium depends will shift the equilibrium in such a way that the effect of change is minimised.

More pressure will ~~let~~ be too costly.

450°C ~~because of~~ to increase rate of the reaction, the activation energy of this reaction is very high.

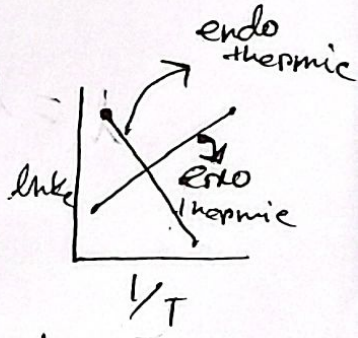
Though the equilibrium will shift a bit to the left but still more efficient. (Cause, say at room temp. after hundreds of year, we'll get more NH_3 than what we get by 450°C in several hours.)

So, 450°C equilibrium and rate both are considerably favourable.

$$\ln K_{c/p} = -\frac{\Delta H}{RT} + \text{const.}$$

if, $\Delta H < 0$, $\ln K_c = -\frac{\Delta H}{RT} + \text{const.}$

if, $\Delta H > 0$, $\ln K_c = -\frac{\Delta H}{RT} + \text{const.}$



Conclusion,

~~if $\Delta H < 0$, $K_{c/p}$ decreases~~

if $\Delta H < 0$, $T \uparrow$, $K \downarrow$ (exo)

if $\Delta H > 0$, $T \uparrow$, $K \uparrow$ (endo)

NH_3 synthesis is carried out at 450°C and 200 atm, why?

29/03/24

$$2\overset{x}{SO_2}(g) + \overset{y}{O_2}(g) \rightleftharpoons 2\overset{x}{SO_3}(g)$$

① $C_{SO_2} \uparrow$ and $C_{SO_3} \uparrow$ equally

② $C_{O_2} \uparrow$ " $C_{SO_3} \uparrow$ "

③ What happend to the equilibrium?

Ans

① $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = \dfrac{x^2}{x^2y}$ (initially) $= \dfrac{1}{y}$

~~(initially)~~

$= \dfrac{4x^2}{4x^2y}$ (middle) $= \dfrac{1}{y}$

Therefore, equilibrium doesn't change.

② $K_c = \dfrac{x^2}{x^2y} = \dfrac{4x^2}{x^2 2y} = \dfrac{2x^2}{x^2y}$

So, left shift.

Chem 4241

Mofaggal Sir 19/04/24

~~Equilibriam + Ionic equilibriam~~

Ionic Equilibriam

→ in aquous system

→ for weak acid and weak alkali

$$CH_3COOH \xrightleftharpoons{H_2O} CH_3COO^-(aq) + H^+(aq)$$

$$NH_4OH \xrightleftharpoons{H_2O} NH_4^+(aq) + OH^-(aq)$$

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$ [endothermic process]

~~$[H^+][OH^-] = K$~~

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

Solvent and is large access

$$\Rightarrow [H^+][OH^-] = K_c[H_2O] = K_w$$

= ionic product of water

$= 10^{-14}$ at $25°C$

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

$$[H^+] = 10^{-7} \text{ mol } L^{-1}$$

$$pH = 7, \quad pOH = 7$$

At higher temperature, let's assume, $K_w = 10^{-13}$

Temp ↑ Endothermic process. ⇒ K_c ↑ K_w ↑ $[H^+]$ ↑

pH ↓

Calculation of pH

1. Strong acid
2. Strog alkali
3. Weak acid
4. Weak alkali
5. buffer sol^n

Calculate pH of 0.01 mol L^{-1} HCl

0.01 " H_2SO_4

0.01 " CH_3COOH, $K_a = 1.7 \times 10^{-5}$

0.01 " NaOH

0.01 " NH_4OH; $K_b = 1.8 \times 10^{-3}$

$[OH^-]$ for weak alkali	$[H^+]$ for weak acid
$[OH^-] = \sqrt{K_b [alkali]}$	$[H^+] = \sqrt{K_a [acid]}$

$$[OH^-] = \sqrt{1.8 \times 10^{-5} \times 0.01} = 4.24 \times 10^{-4} \, mol\,L^{-1}$$

$$\therefore pH = 14 + \log(4.24 \times 10^{-4}) = 10.627$$

Buffer Solⁿ Defⁿ

Buffer solution is a solution that resists the pH change after addition of small amount of acid or alkali.

① Weak acid and its conjugate base

$CH_3COOH + CH_3COONa$

② weak alkali and its conjugate acid

$NH_4OH + NH_4Cl$

$\left(\underset{\text{weak acid}}{\underline{NH_4^+}} + \underset{\text{conjugate base}}{\underline{NH_3}}\right)$ buffer

$\left(\underset{\text{Weak acid}}{\underline{H_2PO_4^-}} + \underset{\text{conj. base}}{\underline{HPO_4^{2-}}}\right)$ buffer

Mechanism

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

Calculation of pH of buffer:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

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

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

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

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

Henderso-Hasselbalch's eqn.

Self by

Calculate pH of a mixture:

40mL 1×10^{-2} M CH_3COOH

+

20mL 1.5×10^{-2} M CH_3COONa

Ans: pH = 4.6

Self hydrolysis

$NaCl + H_2O \longrightarrow Na^+(aq) + Cl^-(aq)$

No reaction

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

$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$, basic sol^n

self hydrolysis

$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$ acidic Sol^n

$$A^- + H_2O \longrightarrow AH + OH^-$$

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

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

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

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

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

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

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

Chem

Sehion

22/04/24

Calculation of K_c and K_p

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

Initial: 0.4 mol 0.4 mol 0.2 mol 0.2 mol

If the value of value of K_c is 0.64 at 1000 K, calculate no. of moles of each component.

Q

At equilibrium,

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

Equilibrium: $0.4-\alpha$ $0.4-\alpha$ $0.2+\alpha$ $0.2+\alpha$

$$\therefore K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$\Rightarrow K_c = \frac{\frac{0.2+\alpha}{V} \times \frac{0.2+\alpha}{V}}{\frac{0.4-\alpha}{V} \times \frac{0.4-\alpha}{V}}$$

$$\Rightarrow 0.64 = \frac{(0.2+\alpha)^2}{(0.4-\alpha)^2}$$

$$\Rightarrow 0.2+\alpha = 0.8 \times (0.4-\alpha)$$

$$\Rightarrow 1.8\alpha = 0.32 - 0.20$$

$$\therefore \alpha = \frac{0.12}{1.8} = 0.067$$

$\therefore$ $n_{CO_2} = 0.4 - 0.067 = 0.333$ mol

$n_{H_2O} = 0.4 - 0.067 = 0.333$ mol

$n_{CO_2} = 0.2 + 0.067 = 0.267$ mol

$n_{H_2} = 0.2 + 0.067 = 0.267$ mol

Now,

$$2P \rightleftharpoons 2Q + R$$

Initially:	0.2 mol	0	0
Equilibrium:	$0.2-2x$	$2x$	x

$x \Rightarrow$ বিয়োজন ধ্রুবক

$\Rightarrow$ Dissociation constant

Next Quiz

Equilibrium Chapter

Next next friday 3rd may.

Properties of Dilute Solutions

Calligative properties

Defn

The properties which depend on the number of particles present in the Solⁿ, but not on the nature of the ~~Sot~~ substance.

Four properties:

① Lowering of vapour of pressure

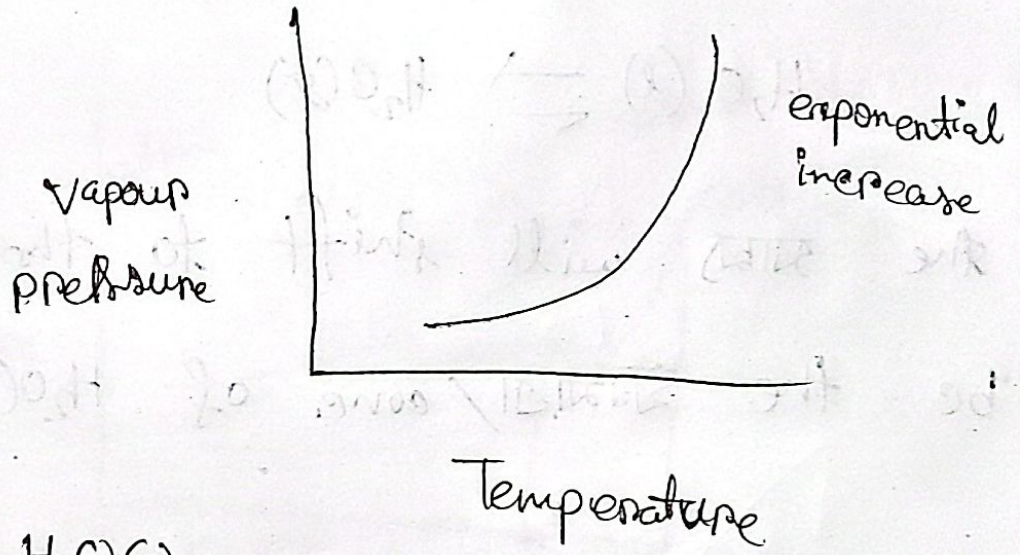
② Elevation of boiling point

③ depression of freezing ~~poing~~ point

④ Osmotic pressure

Vapour pressure:

Vapour pressure is the pressure, ~~that be~~ exerted by the vapour that remains equilibrium ~~to~~ with the liquid.



$H_2O(l) \rightleftharpoons H_2O(g)$, $\Delta H = (+)$

↳ This reaction is endothermic, So ~~temp ↑~~

temp ↑ — V. pressure ↑

also, Kinetic energy of vapours increase.

That's why it rises exponentially.

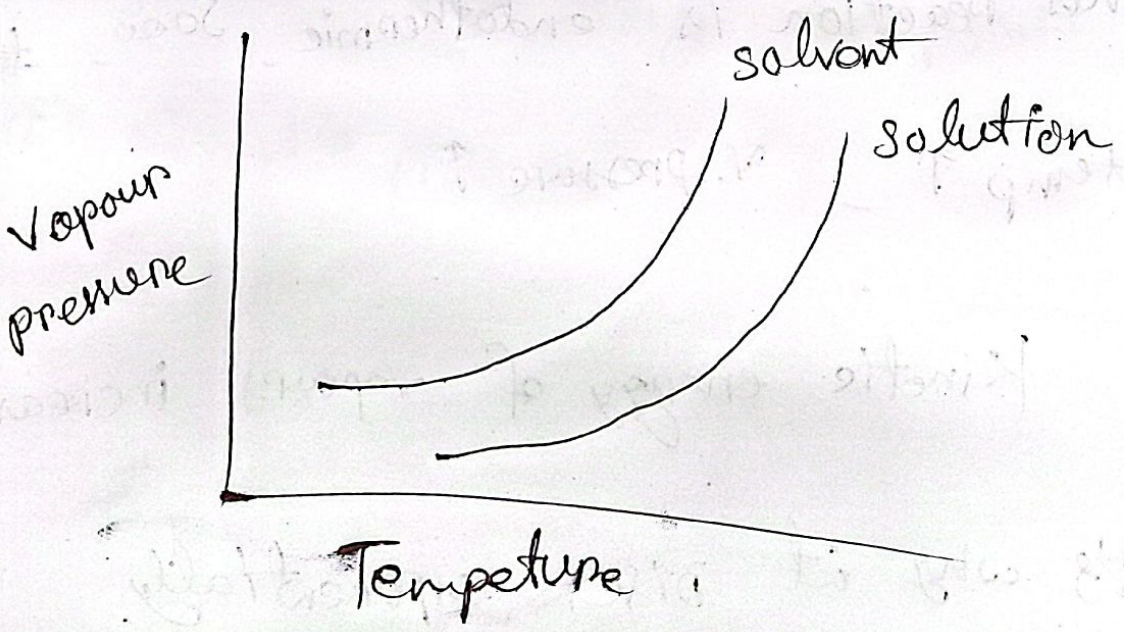
In a solution

the solute will capture some of free H_2O molecules. So,

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

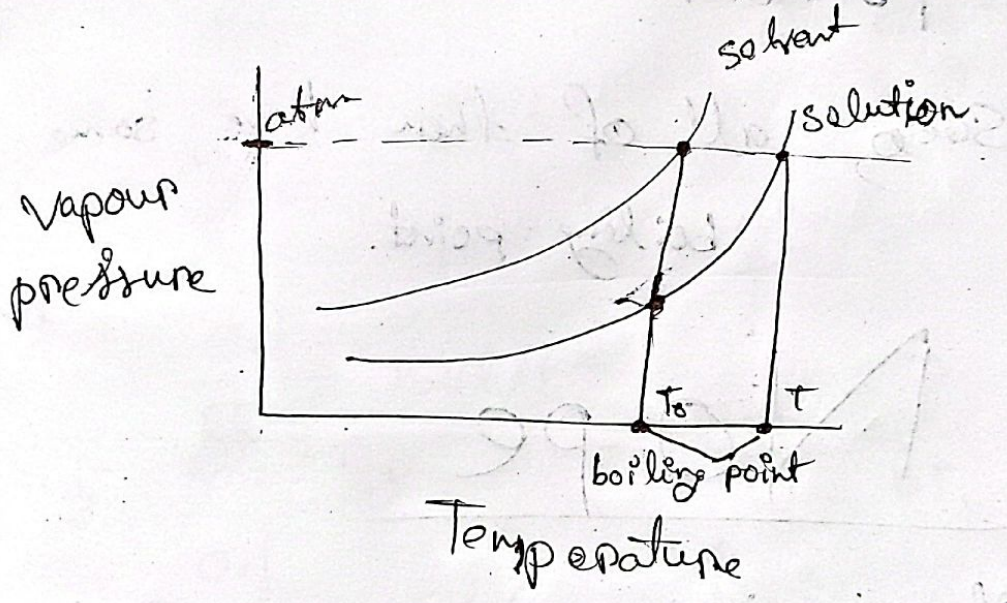
the সাম্য will shift to the left, bc the ঘনমাত্রা / conc of $H_2O(l)$ lowers.

So, vapour pressure lowers.



Boiling Point

def^n: Boiling point is the temperature of a liquid at which vapour pressure is equal to atmospheric pressure.



$T > T_0$, why?

Ans: 1. Solution has lower V.Pressure

2. Boiling point is the temp at which 1atm = V.P.

3. V.P increases with temperature.

so. ~~That~~ Thus

0.01 M	NaCl Sol^n
0.01 M	CH_3OH & CH_3CH_2OH
0.01 M	CH_3COOH

These have same number of particles

So, all of them have same boiling point.

Nope

NaCl is ionic

it will become: $NaCl \Rightarrow Na^+ + Cl^-$

So, NaCl এর particle বেশি তাই এর boiling point higher.

CH_3COOH partially dissociates, so, it will be in the middle.

0.1 g/L NaCl

0.1 g/L KCl

Boiling point high?

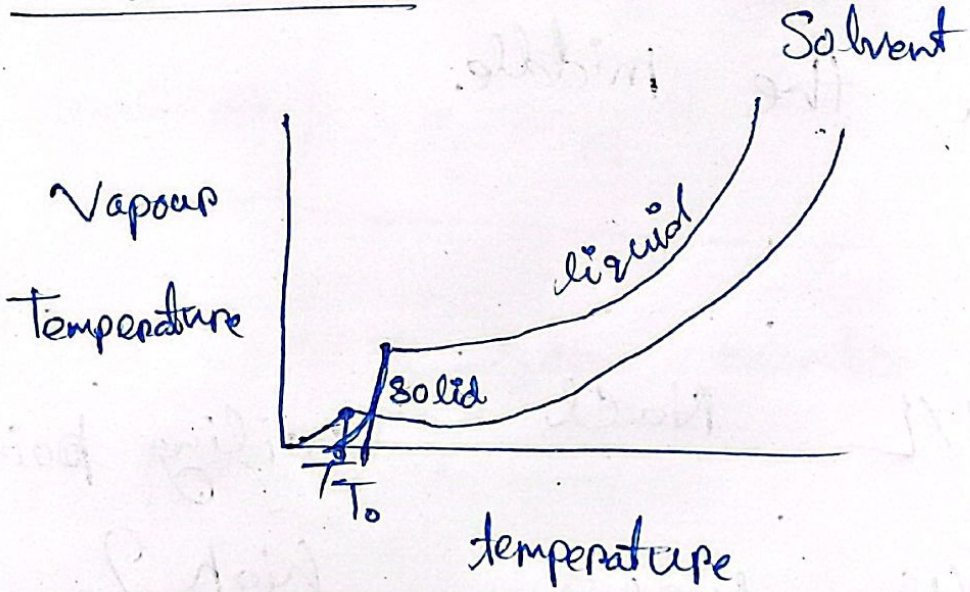
$\frac{0.1}{58.5}$ mol/L

$\frac{0.1}{74.5}$ mol/L

So

$bp_{KCl} > bp_{NaCl}$

Freezing Temp.



T_0 = freezing point of solvent

$T < T_0$

<u>defn</u>: Freezing point is the temp. at which solid solvent remains in equilibrium with the liquid solvent of solution.

[online class] Chem Senior

28/04/24

Quiz ⊙ ⊙ Kc, Kp, Salt hydrolysis, basically last chapter এর উপর হবে।

Colligative properties

lowering vapour pressure

v.p of solvent = p°

v.p of solution = p

lowering of vapour pressure = $p^\circ - p$

Relative " " " " = $\frac{p^\circ - p}{p^\circ}$

Raoult's Law

$$\frac{p^\circ - p}{p^\circ} = \frac{n}{N+n} = x_2$$

n = mole of solute
N = " " solvent
x_2 = mole fraction of the solute

$$\Rightarrow 1 - \frac{P^0 - P}{P^0} = 1 - x_2$$

$$\Rightarrow \frac{P}{P^0} = x_1$$

$$\Rightarrow \boxed{P = P^0 \cdot x_1}$$

[x_1 = mole fraction of the solvent]

Explain Raoult's Law

P, P^0, n, N, x_1, x_2 এগুলো কী এটা লিখতে হবে exam -এ

Ideal Sol^n

Sol^n which obey ~~ideal~~ the Raoult's law, under all temp. and all composition

Determination of molecular mass from relative lowering of vapour pressure.

$$\frac{p^0 - p}{p^0} = \frac{n}{N+n}$$

For dilute sol^n n is very small compared to N,

$$\therefore \frac{p^0 - p}{p^0} = \frac{n}{N} = \frac{w_2/M_2}{w_1/M_1}$$

w_2 = mass of a solute of molecular mass M_2

w_1 = " " " solvent " " " M_1

Elevation of Boiling point

Raoult's Law

ΔT_b = elevation of boiling point

~~$T = \Delta T_b$~~

$T - T_0 = \Delta T_b$

T_0 → boiling point of solvent

$\Delta T_b \propto m \Rightarrow$ molal concentration

$\Delta T_b = K_b m$

K_b → ebullioscopic const.

Thermodynamic derivation of boiling point elevation

pdf -1 vul WTC2

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

↳ Clapeyron-Clausius eqn.

for elevation of boiling point

$$\ln \frac{P}{P^0} = -\frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

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

$$\approx -\frac{\Delta H}{R} \times \frac{\Delta T_b}{T_0^2}$$

$$\Rightarrow \ln x_1 = -\frac{\Delta H}{R} \times \frac{\Delta T_b}{T_0^2}$$

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

$\Rightarrow$

when x_2 is small [dilute sol^n]

$$\ln(1-x_2) \approx -x_2$$

$$\therefore \quad x_2 = \frac{\Delta H}{R} \times \frac{\Delta T_b}{T_0^2}$$

$$\Rightarrow \quad \Delta T_b = \frac{R T_0^2}{\Delta H} \cdot x_2$$

$$= \frac{R T_0^2}{\Delta H} \times \frac{n}{N+n}$$

$$= \frac{R T_0^2}{\Delta H} \times \frac{n}{N}$$

$$= \frac{R T_0^2}{\Delta H} \times \frac{w_2 / M_2}{w_1 / M_1}$$

$$= \frac{R T_0^2 M_1}{\Delta H \times 1000} \times \frac{w_2}{M_2 \cdot w_1} \times 1000$$

$$\therefore \Delta T_b = K_b m$$

Raoult's law for depression of freezing point

① $\boxed{\Delta T_f = K_f m}$ of the solution

K_f → cryoscopic const.

② equimolecular

Osmotic pressure and Osmosis.

Van't Hoff's Law

There are 3 laws

osmotic pressure = Π ~~(capital pie)~~

① $\Pi \propto c$ when T = const.

[This is similar to Boil's law]

② $\pi \propto T$ [c = const]

③ ~~$\pi = K'cT$~~ Equimolecular.

Now,

$$\pi = \frac{nRT}{V}$$

$$\Rightarrow \pi = CRT$$

↳ concentration

Final — 1 এই sir 3টা ques করবে.

~~mid থাকবে~~, but mid এর পরের গুলা ~~বেশি না~~ mid এর আগে পরে সব থাকবে। আগের মতো def^n, explanation and Maths থাকবে।

Chem 4241 — 3/02/24

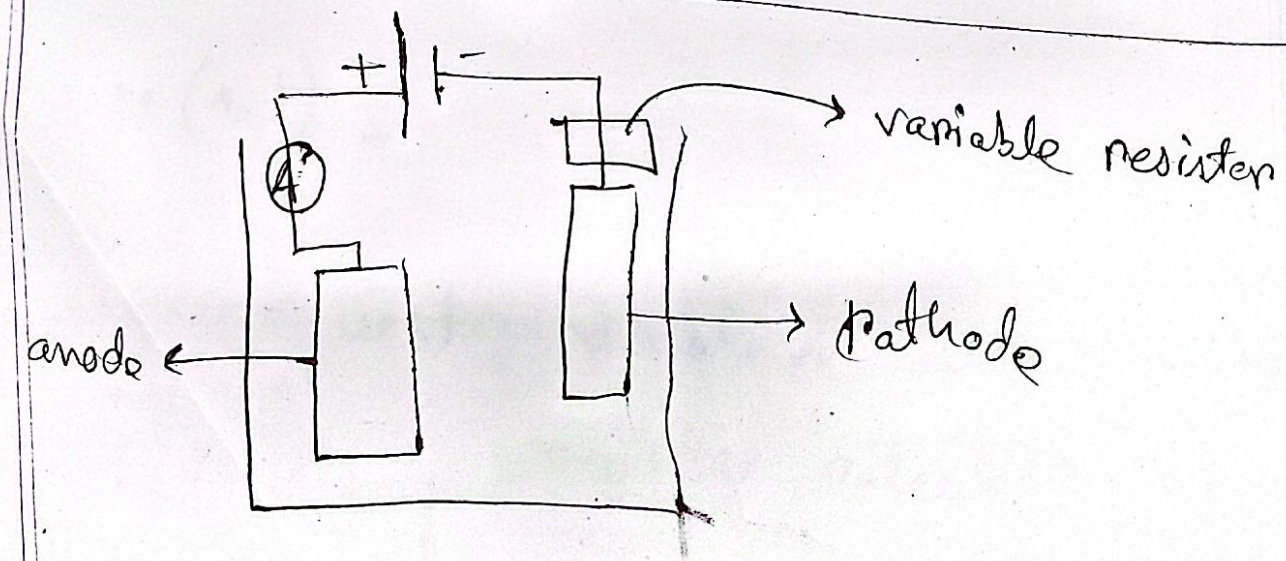
Senior

Last chapter

Electrochemistry

Electrochemical cell

- eleptolytic cell: electricity → chemical energy
- Galvanic cell (Syllabus): Chem → Electric energy.



electrolytic cell

Two different types of electrode

- reactive → Zn, Fe, Cu (u know)
- inert → graphite, Pt, Au (mostly) — doesn't take part in reactions

two different types of electrolytes

- molten salt
- aqueous solution of salts

Electrolyte: $PbBr_2$ (molten)

Electrode: Graphite

Anode:

$$2Br^- \rightarrow Br_2 + 2e^-$$

Cathode:

$$Pb^{2+} + 2e^- \rightarrow Pb$$

Now, Again

Electrolyte: Aqueous NaCl

Electrode: Graphite.

Anode:

$$2H^+ + 2e^- \rightarrow H_2$$

ions present

H^+ Na^+ ✗

OH^- Cl^-

have similar reduction potential so it depends on the concentration

~~Cathode~~ Anode:

so, dilute: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

conc.: $2Cl^- \rightarrow Cl_2 + 2e^-$

Series

K

Na

Ca

Mg

Al

Zn → -0.76

Fe → -0.44

H → 0

Cu → +0.34

Ag Pt

Electrolyte: A $CuSO_4$ (aq)

Electrode: Cu

Anode

$Cu \longrightarrow Cu^{2+} + 2e^-$, Not the reduction of OH^-

Cathode:

$Cu^{2+} + 2e^- \longrightarrow Cu$

Chem

Senior

8/5/24

Electrolysis

Faraday's Law of electrolysis

① First Law:

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

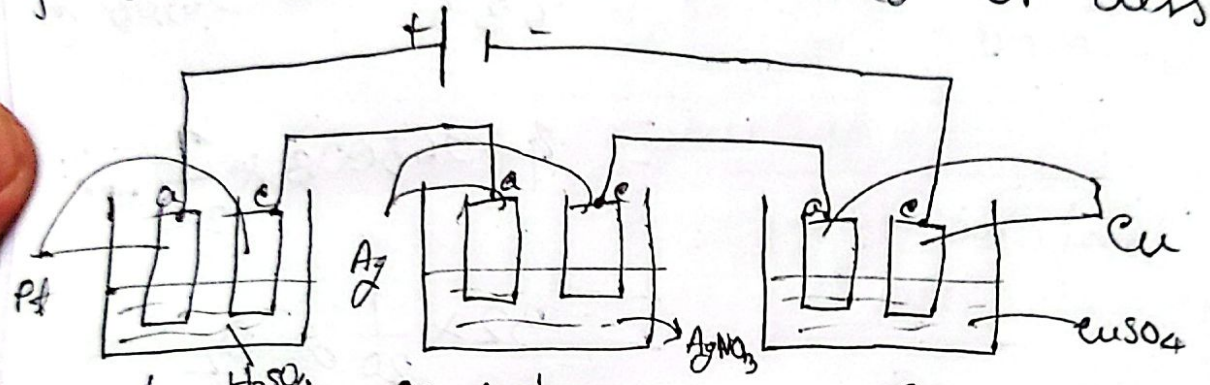
$$Q \propto i\,(amp) \times t\,(s)$$

$$Q = Zit$$

electrochemical equivalence

② 2nd Law:

When same amount of current is passed through different electrolyte cell, the equivalent amount of substance will be liberated or dissolved.



C: $Ag^+ + e^- \rightarrow Ag$

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

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

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

C: $2H^+ + 2e^- \rightarrow H_2$

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

If current is passed for 30 mins, 6.35 g Cu diposited.

[equivalence ≡ number of e^-]

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

↓ Coulomb

$4 \times 96500\ C \equiv 32g\ O_2$

Now,

$$6.35g\ Cu \equiv \frac{6.35}{63.5} \times 2 \times 96500\ C$$

$$\equiv 4 \times 96500\ C \times \frac{1}{20}\ C$$

$$\equiv 32 \times \frac{1}{20}\ g\ O_2$$

$$\equiv 1.6\ g\ O_2$$

Now, H_2SO_4 ki conc increases or decreases? (in the first beaker)

<u>Ans:</u> It increases. Bc Only the ions/molecules of H_2O takes part in the electrolysis, not H_2SO_4. As a result, volume of H_2O decreases and H_2SO_4 ki conc increases.

Conductance

$$\text{Conductance} = \frac{1}{\text{Resistance}} \quad (\text{ohm})^{-1} \text{ or mho}$$

$$\text{Specific conductance}, \; K = \frac{1}{\rho} = \text{ohm}^{-1}\,\text{cm}^{-1}$$

$$= \frac{1}{\text{specific resistance}}$$

$$R = \rho\left(\frac{l}{a}\right)$$

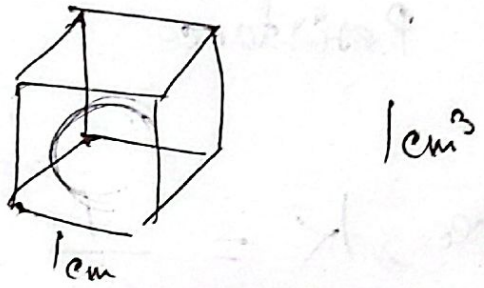
$$\frac{1}{R} = \frac{1}{\rho} \times \frac{a}{l}$$

$\Rightarrow$ Conductance = specific conductance $\times \frac{a}{l}$

$\Rightarrow$ Specific conductance = conductance $\times \frac{l}{a}$

= conductance $\times$ cell const.

Df^n of specific conductance



~~the~~ Conductance of $1cm^3$ solution is specific conductance.

Molar conductance:

Conductance of 1 mol substance in solution ~~the two electrode seperated by 1cm~~ / that is placed between two electrodes 1cm apart.

molar conductance at different conc.

$\lambda_m = K \times V$ (mL)

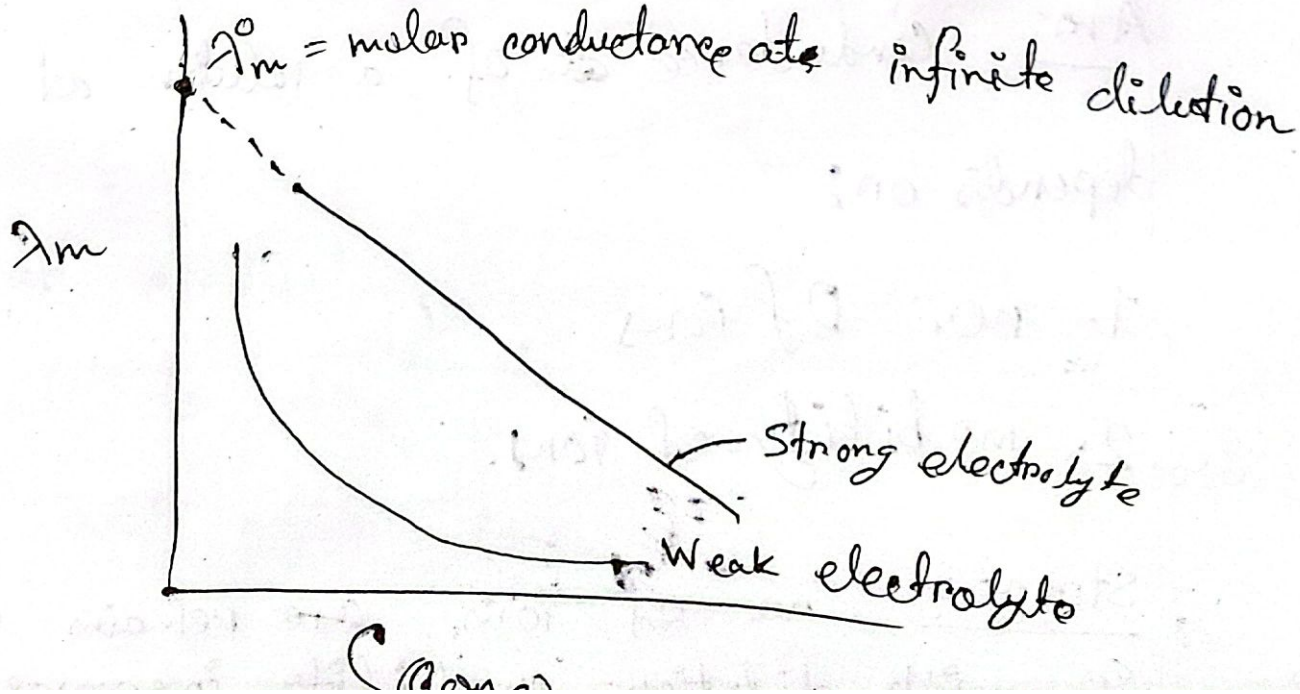
[C = conc. of a solution (mol L⁻¹)]

If conc. of a solution is C mol/L

C mol present in 1000 mL

1 " " " $\frac{1000}{C}$ mL

$\therefore \lambda_m = K \times \frac{1000}{C} = \frac{1000\,K}{C}$



Q: principal for determination of λ_m° (Strong electrolyte)

Ans: Steps 1: conductance বের করা

2: ~~spec~~ K বের করা

3: λ_m বের করা

4: graph এঁকে বর্ধিত করা / extrapolation of graph.

Q: Why the curves differ [λ_m vs C / $\sqrt{C}$] for strong and weak electrolyte?

Ans: Conductance ~~at~~ of a solution at temp. T depends on:

1. no. of ions
2. mobility of ions.

Strong: no. of ions ~~are~~ remains const
So, with dilution, mobility increases.

and so λ_m increases.

<u>Weak:</u> With dilution, no. of ions increases very rapidly. So,

λ_m increases rapidly.

Determination of molar conductance at infinite dilution (λ_m°) for weak electrolyte:

Kohlrausch's Law:

$$\lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$$

Molar conductance at infinite dilution is equal to the sum of molar conductance of positive ions and negative ions.

Example: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

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

CH_3COONa ; $\lambda^\circ_{m(CH_3COONa)} = \lambda^\circ_{(CH_3COO^-)} + \lambda^\circ_{(Na^+)}$ — (i)

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

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

(i) + (ii) − (iii) ⇒

$$\lambda^\circ_{(CH_3COONa)} + \lambda^\circ_{HCl} - \lambda^\circ_{NaCl} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

Principal:

Step 1: Choose 3 strong electrolyte.

2: Get the λ°_m for them

3: From the equation, we'll get the

NH_4OH کا case ←

NH_4Cl

$NaOH$

$NaCl$

Chem

Senior

10/5/24

Transport number

Fraction of current carried by each ionic species is called transport number. It is represented by t_+ or t_-,

$$t_+ = \frac{u_+}{u_+ + u_-}, \quad t_- = \frac{u_-}{u_+ + u}$$

u_+ is the mobility of the cation

u_- " " " " " anion

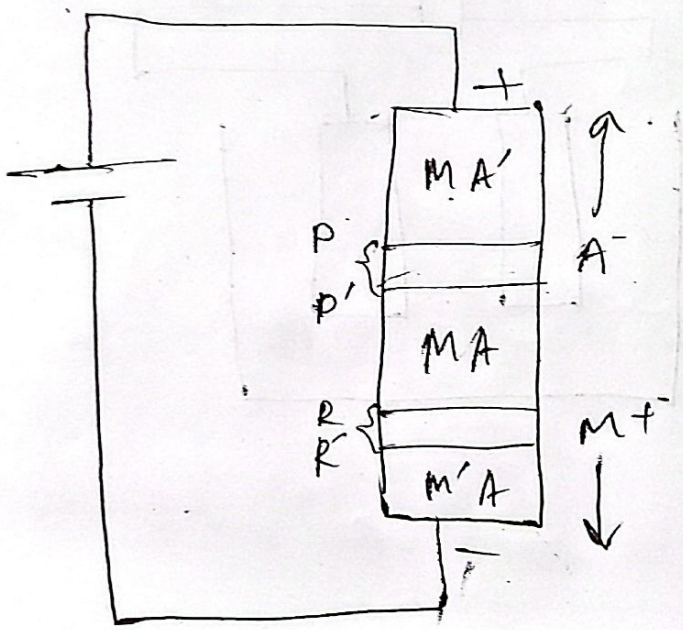
Velocity of the ions per unit potential gradient is called mobility.

Determination of transport numbers

① Moving boundary method

Electrolyte = MA M^+

A^-

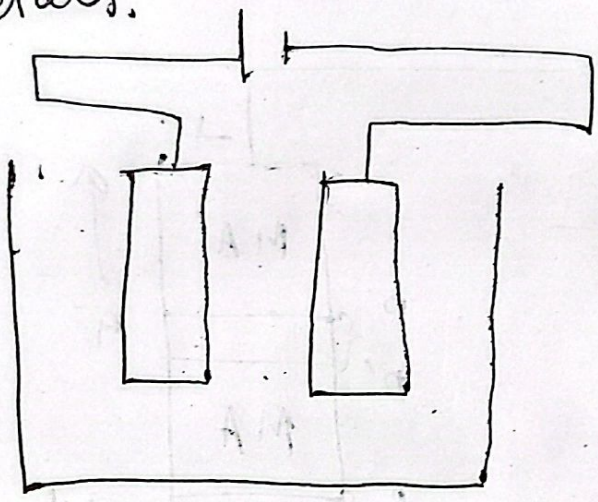


A' has lower velocity than A

M' has lower velocity than M

PP' is proportional to the velocity of = M^+

RR' is proportional to the velocity of = A^-

Electroplating related to electrolysis

Electroplating is the formation of a layer of less ~~elective~~ reactive metals over more reactive metals.