1. The molar refraction is given by

$$\frac{n^2-1}{n^2+2} \times \frac{m}{d}$$ Ans:- b

(ii) Total vapour pressure is $P = P_A + P_B$ Ans:- a

(iii) Half-life value is independent of initial concentration for a first order reaction. Ans:- a

(iv) All of these :- Ans:- d

(v) $\alpha = \dfrac{\lambda_v}{\lambda_\infty}$; i.e; Ans:- b

(vi) The flow of a liquid can be expressed in term of fluidity ϕ

$\phi = \dfrac{1}{\eta}$ fluidity is reciprocal of viscosity

(vii)   Ex: $H_2O - HNO_3$
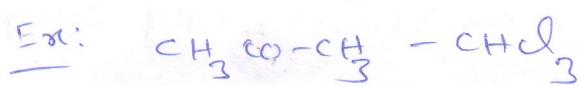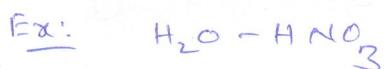
Ex: $CH_3CO-CH_3 - CHCl_3$ } Negative deveation from Raoult's law.

(viii)   Second order

(ix) Effect of pH on Enzyme catalysis:-

$$
\begin{array}{l}
\text{Rate of reaction} \uparrow \\
\end{array}
$$

→ optimum pH

→ pH
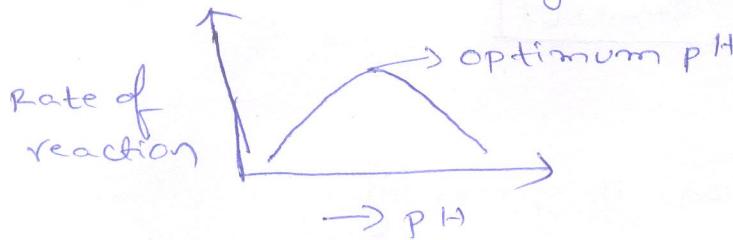
(x) Transport number:-

The fraction of total current carried out by a given ion in an electrolyte

$$
\text{transport number} = \frac{\text{Current carried out by +ve or -ve ion}}{\text{Total current produced by electrolyte}}
$$

Section-B:

Parachor

The surface Tension of liquid was related to the densities ρ_L and ρ_v of liquid & vapour respectively through the equation,   'r' is surface tension

$$\frac{\gamma^{1/4}}{\rho_L - \rho_v} = c \quad \text{where 'c' is constant}$$

If the above equation is multiplied by 'm'

$$\frac{m\gamma^{1/4}}{\rho_L - \rho_v} = cm = \text{constant} = [P] \text{ is parachor}$$

If the liquid is not very near to its critical temp, ρ_L is greater than ρ_v and above expression becomes

$$\left[\frac{m}{\rho_L}\right]\gamma^{1/4} = [P] \quad (or) \quad V_m \gamma^{1/4} = [P]$$

If S.T is equal to unity, $V_m = [P]$

parachor is an additive property. with the help of parachor values, one can caluclate parachor values of different isomers.

3.

we know from ostwald viscosity.

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

<u>Given</u> that viscosity of pure water $\eta_1 = 1.002 \times 10^{-3}$ $Nm^{-2}s$

Time requires to flow through $= 102.2$ Sec
(t_1) (for H_2O) viscometer

Time requires for toulene to flow through $= 68.9$ Sec viscometer (t_2)

Density of toulene $= 0.886 \, gm/cm^3$ (ρ_2)

Density of water $= 0.998 \, gm/cm^3$ (ρ_1)

Viscosity of Toluene $= \eta_2 = \frac{\rho_2 t_2}{\rho_1 t_1} \times \eta_1$

$$= \frac{0.886 \times 68.9}{0.998 \times 102.2} \times 1.002 \times 10^{-3}$$

$$= 0.598 \times 10^{-3} \, Nm^{-2} sec$$

$$= 5.9 \times 10^{-4} \, Nm^{-2} sec$$

(4) The liquids, which are not completely miscible with each other under normal conditions. → Partially miscible. <u>Solubility of partially miscible liquids</u>

Phenol-H_2O system is the ⊕shows solubility of partially miscible liquids.

Phenol-H_2O system form partially miscible liquids at low temp. Upon increasing the temperature, two layers become single layer; they are miscible only over a certain range of temp.

Approximately above 68°C, both phenol-H_2O system forms one layer as shown in diagram below.

As shown in the diagram, sample consists of two Phases in equilibrium with each other (P=2), the more abundant consists of Phenol saturated with water and minor one is water saturated with phenol. The entire phase diagram is could be constructured by repeating the observations at different temp.

$$68°C \quad \uparrow T$$
Temp

P=1

P=2

→ % of composition
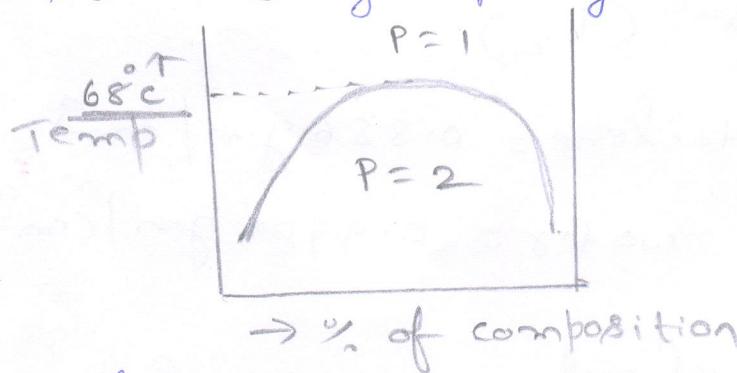
<u>Upper critical solution temp</u>:- T_{uc} is the highest temp at which phase separation occurs. Above T_{uc}, two components are fully miscible. This temp exists because greater thermal motion overcomes any Potential Energy.

<u>Ex</u>: Nitrobenzene - Hexane

<u>Low critical solution temp</u>:- T_{Lc} is the below which they mix in all proportions and above which they form two phases.

<u>Ex</u>: $H_2O - Et_3N$

⑤ Derive the equation $k = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$ for first order reaction and find out expression for $t_{1/2}$

For a reaction, $A \longrightarrow P$, a first order rate law takes from

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

where $[A]$ represents the concentration of reactant at any time 't' and k is the rate constant,

Rearranging above equation, $\dfrac{-d[A]}{[A]} = k\,dt$

Integrating the above equation,

$$\int \frac{d[A]}{[A]} = -k \int dt$$

$$\ln[A] = -kt + I, \quad \text{where } I \text{ is the integration constant.}$$

The value of I can be determined from initial conditions

At time, $t = 0$, $[A] = [A]_0$

$$\ln[A]_0 = -k \times 0 + I$$

$$\therefore I = \ln[A]_0$$

Substituting 'I' value in $\ln[A] = -kt + I$

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln[A] - \ln[A]_0 = -kt$$

$$\therefore \ln\frac{[A]}{[A]_0} = -kt \qquad \therefore \ln\frac{[A]_0}{[A]} = kt$$

$$2.303 \log\frac{[A]_0}{[A]} = +kt \quad \Rightarrow \quad k = \frac{2.303}{t} \log\frac{[A]_0}{[A]}$$

Suppose initial concentration of 'A' is represented as 'a' moles/lit at $t=0$. After time 't', suppose 'x' moles/lit of it is decomposed.

$\therefore$ concentration of 'A' after time $t = a-x$ moles/lit

$$\therefore k = \frac{2.303}{t} \log\frac{a}{a-x}$$

when half of the reaction is completed;

$$x = \frac{a}{2} \text{ at } t_{1/2}$$

$$t_{1/2} = \frac{2.303}{K} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{K} \log 2 = \frac{0.693}{K}$$

$$\therefore t_{1/2} = \frac{0.693}{K}$$

---

6. Expression for degree of dissociation (α) of weak electrolyte using ostwald dilution law.

Consider the ionization of weak Electrolyte

i.e : CH_3COOH
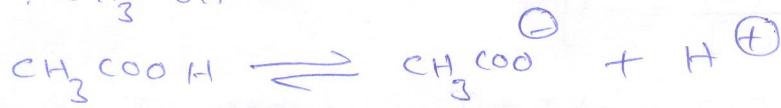
$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$

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

if "α" is the degree of dissociation and "c" is the initial conc. of weak electrolyte, then $[H+] = [CH_3COO^-] = c\alpha$

$$[CH_3COOH] = c(1-\alpha)$$

$$\therefore K = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c \times \alpha^2}{1-\alpha}$$

Since $\alpha \ll 1$, $\quad K = c\alpha^2 \quad \therefore \alpha = \sqrt{K/c}$

According to ostwald dilution law, dissociation increases as "c" decreases. As α is increased, the conc. of $[H+]$ & $[CH_3COO^-]$ are also increased. Thus, the increase of conductance for a weak electrolyte is primarily due to increase in n.o of ions.

$$\therefore \alpha = \frac{\lambda c}{\lambda_\infty}$$

The mechanism of enzyme catalysed reactions was proposed by michalies and menten.

Let us consider, the substrate [S] forms a complex [E], enzyme

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [ES]$$ where k_1 & k_2 are equilibrium constants

$$[ES] \xrightarrow{k_3} P + E$$ The complex [ES] decomposes to give product 'p' and 'E'
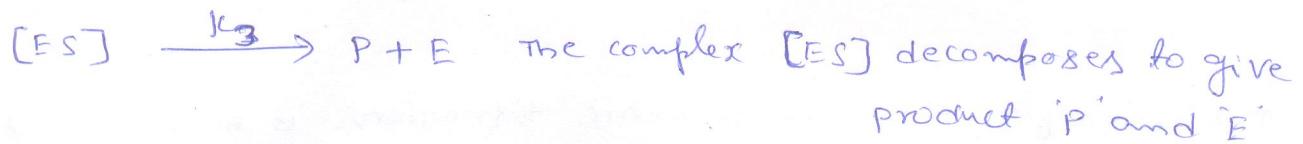
Applying steady state approximation, rate of formation of intermediate is zero

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_2[ES] - k_3[ES] = 0$$

$$k_1[E][S] = k_2[ES] + k_3[ES]$$

$$\therefore [ES] = \frac{k_1[E][S]}{k_2 + k_3}$$

Rate of formation of product is given by $\frac{-d[P]}{dt} = k_3[ES]$

Total Enzyme concentration $[E_0]$ is a measurable quantity and is related to [E] & [ES] as $[E]_0 = [E] + [ES]$

$$\therefore [E] = [E_0] - [ES]$$

$$\therefore [ES] = \frac{k_1\{[E_0] - [ES]\}[S]}{k_2 + k_3}$$

$$[ES] = \frac{k_1[E_0][S]}{k_1[S] + k_2 + k_3} \qquad \therefore [ES] = \frac{[E_0][S]}{[S] + \left(\frac{k_2 + k_3}{k_1}\right)}$$

$$\therefore [ES] = \frac{[E_0][S]}{[S] + k_m}$$ where $k_m = \frac{k_2 + k_3}{k_1}$ is known as michalies-mententen constant

$$\therefore \text{Rate of reaction} = k_3[ES] = \frac{k_3[E_0][S]}{[S] + k_m}$$

if substrate conc, [S] is large, $[S] + k_m \approx [S]$

$$\therefore \frac{k_3[E_0][S]}{[S]} = k_3[E_0] - \text{independent of conc ie zero order}$$

Enzymes are proteins, which possesses catalytic functions and are large biological molecules responsible for sustaining life.

(8) The principle of conductometric titrations is based on the fact that during the titration, one of the ion is replaced by other and invariably these two ions differ in the ionic conductivity with the result, the conductivity of the solution varies during the course of reaction.

Let us take acetic acid being titrated with NaOH. Before the addition of alkali, soln shows poor conductance due to acetic acid. Initially addition of alkali causes conductance of soln decreases in begining. But very soon the conductance starts increasing as addition of NaOH neutralizes the undissociated HAc. The increase in conductance continues right up to the equivalence point. Beyond this point, conductance increases more rapidly due to highly conducting OH^- ions.

volume of NaOH →
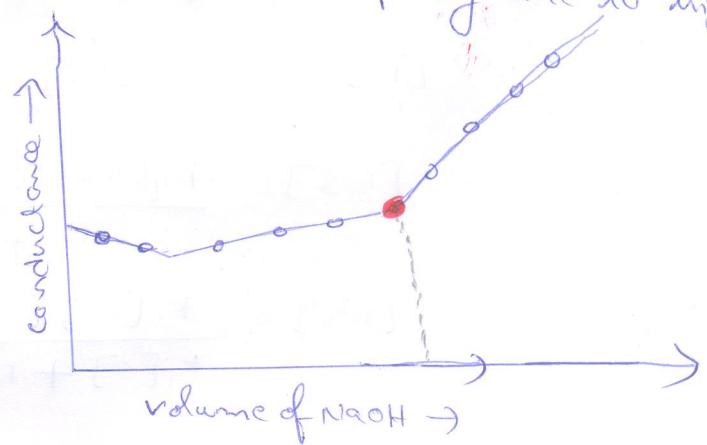
AgNO₃ vs KCl :

It belongs to precipitation titrations.

→ vol of precipitant