

Electrochemistry Phy

Que - 1 Debye - Huckel theory of strong electrolyte.

⇒ This theory was given by Peter Debye and E. Huckel in 1923.

→ Acc. to this theory, strong electrolytes which exist as ions even in the solid state must be completely ionised in solution at all conc.ⁿ.

→ Debye Huckel theory is based on four postulates.

(1) Every strong electrolyte, it is completely ionised at all dilution or ionization 100%.

(2) There are two forces acting on the mobile ions.

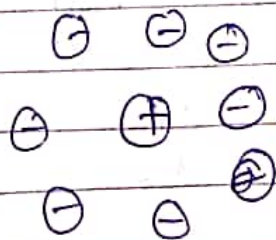
(i) is electrical force (2) is resistance of the medium. So,

Resultant force = Electrical force - resistance ^{or} μ (C/D)

(3) Force that is acting betⁿ the ions are governed by Coulomb law

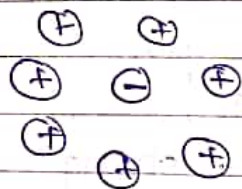
$$F \propto \frac{q_1 q_2}{r^2}$$

(4) Each ion is surrounded by no. of oppositely charged ions such as in spherical manner.



This spherical haze of opposite charge is

is called ionic atmosphere



Ionic atmosphere

(4) Decrease in equivalent conductance with increase in con^n of electrolyte is due to fall in mobility of ions due to greater interionic effect.

(5) Two forces act on the mobile ions

- (1) Electrical force
- (2) Viscosity Drag

Resultant force = Electrical force - viscosity drag

(6) In spite of almost complete ionization α is much less than α_{∞} .

$$\alpha = \frac{dv}{d\infty}$$

here $dv < d\infty$

So, $\alpha \neq 1$

(7) The ratio of Δv does not give degree of dissociation (α) for strong electrolyte.

→ The low value of Δv is due to two factors

(i) Relaxation effect :-

→ Consider an anion is surrounded by cation. In the absence of applied field this ionic atmosphere is symmetrically situated.

→ When electric field is applied then ~~the~~ negatively charged ion (anion) moves towards anode & leaving behind ionic atmosphere of cation.

→ As anion moves, a new ionic atmosphere is under formation.

→ "But new ionic atmosphere is not formed at the same rate as the old ionic atmosphere decay.

→ A definite time required for new ionic atmosphere to build up while old ionic atmosphere's decaying. This

lag of time is known as relaxation time or asymmetric effect

(ii) Electrophoretic effect :-

The solvent molecule attached to moving ion (anion) moves opposite to moving ion (cation) due to which mobility of moving ions also decreases this is known as Electrophoretic effect.

Debye Huckel Onsager eqⁿ

$$d_v = d_{\infty} - \left[\frac{82.4}{\sqrt{\epsilon_r \eta}} + \frac{8.20 \times 10^5}{\sqrt{(\epsilon_r T)^{3/2}}} d_{\infty} \right] \sqrt{c}$$

$$d_v = d_{\infty} - [A + B d_{\infty}] \sqrt{c}$$

② Debye Huckel Oswager equation

→ Debye huckel oswager eqⁿ was derived in 1926.

$$\Lambda = \Lambda^{\circ} - \left[\frac{82.4}{\sqrt{DT} \cdot \eta} + \frac{8.20 \times 10^5}{\sqrt[3]{DT}} \Lambda^{\circ} \right] \sqrt{c}$$

Λ = Equivalent conductance at any consⁿ

Λ° = Equivalent conductance at infinite dilution.

D = Dielectric constant of medium

η = Viscosity of the medium

T = Temperature of solution

c = Conc. of solution.

D, T and η are constant, so,

$$\frac{82.4}{(DT)^{1/2} \eta} = A \quad \text{--- (2)}$$

$$\frac{8.20 \times 10^5}{(DT)^{3/2}} = B \quad \text{--- (3)}$$

56 + 20
17056 - 50

So, eqⁿ (1) can be written as

$$\Lambda = \Lambda^0 - (A + B \Lambda^0) \sqrt{c} \quad (4)$$

$$\Lambda = (A + B \Lambda^0) \sqrt{c} + \Lambda^0$$

$$\Lambda = \Lambda^0 (-A \sqrt{c} - B \sqrt{c} \Lambda^0)$$

$$\Lambda^0 - \Lambda = (A \sqrt{c} - B \sqrt{c} \Lambda^0) \quad (5)$$

When solution is infinitely dilute,
then $c=0$ and

$$\Lambda = \Lambda^0 \quad (6)$$

Greater the value of A and B, lesser
the value of Λ and Λ^0 .

③ Stern Model

→ This model which attempts a synthesis of the Helmholtz perkin and the Gouy Chapman models, eliminates the point charge approximation of the diffuse layer theory.

→ The stern theory divides the solⁿ charge into two contributions. part of q_s on the solution is immobilized close to the electrode in the OHP. (The Helmholtz perkin charge). The remainder is diffusely spread out in the solution. (The Gouy Chapman charge, q_d)

$$q_s = q_H + q_d$$

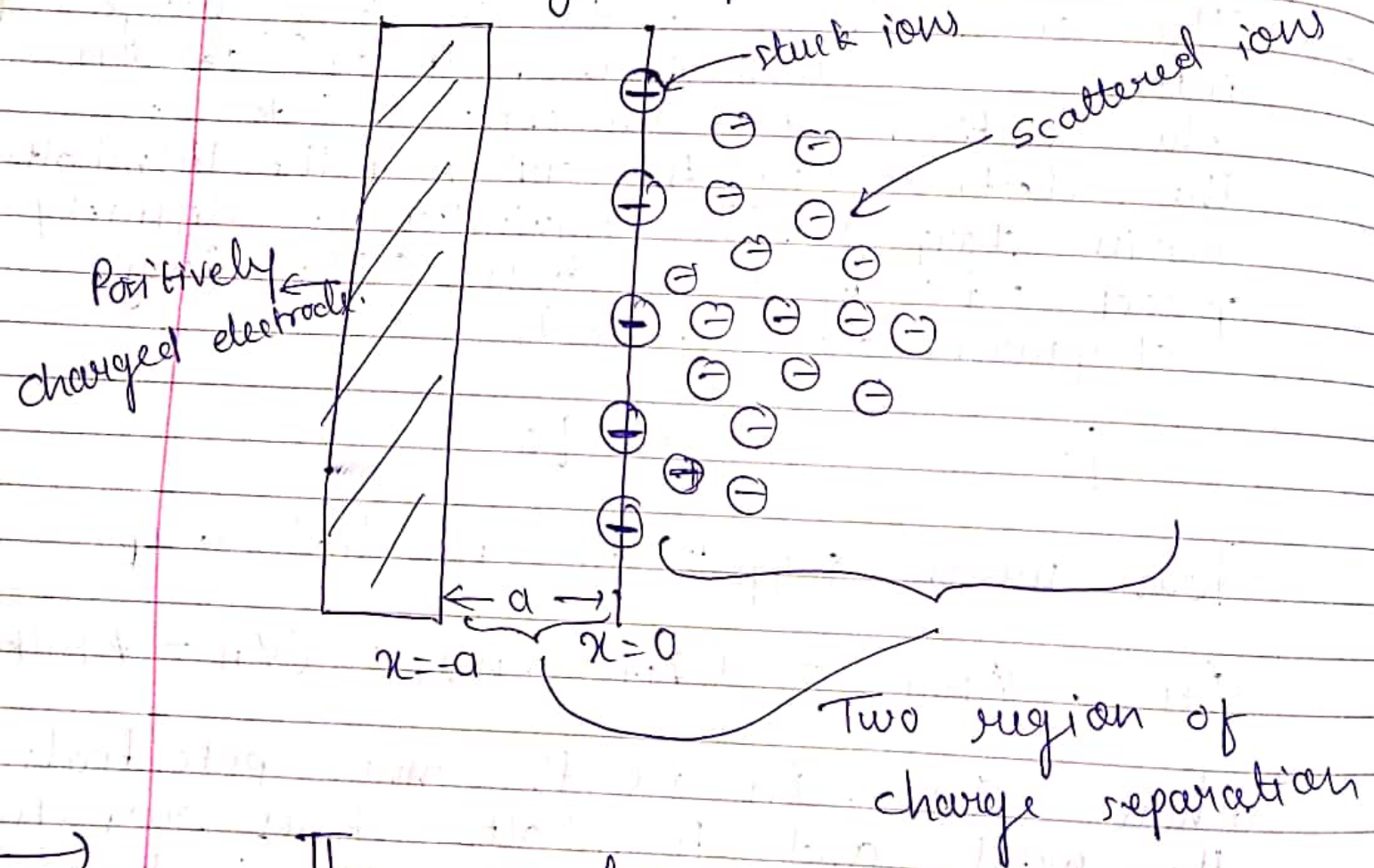
Stern model suggest two potential drops

$$\phi_M - \phi_{\text{bulk}} = (\phi_M - \phi_H) + (\phi_H - \phi_{\text{bulk}})$$

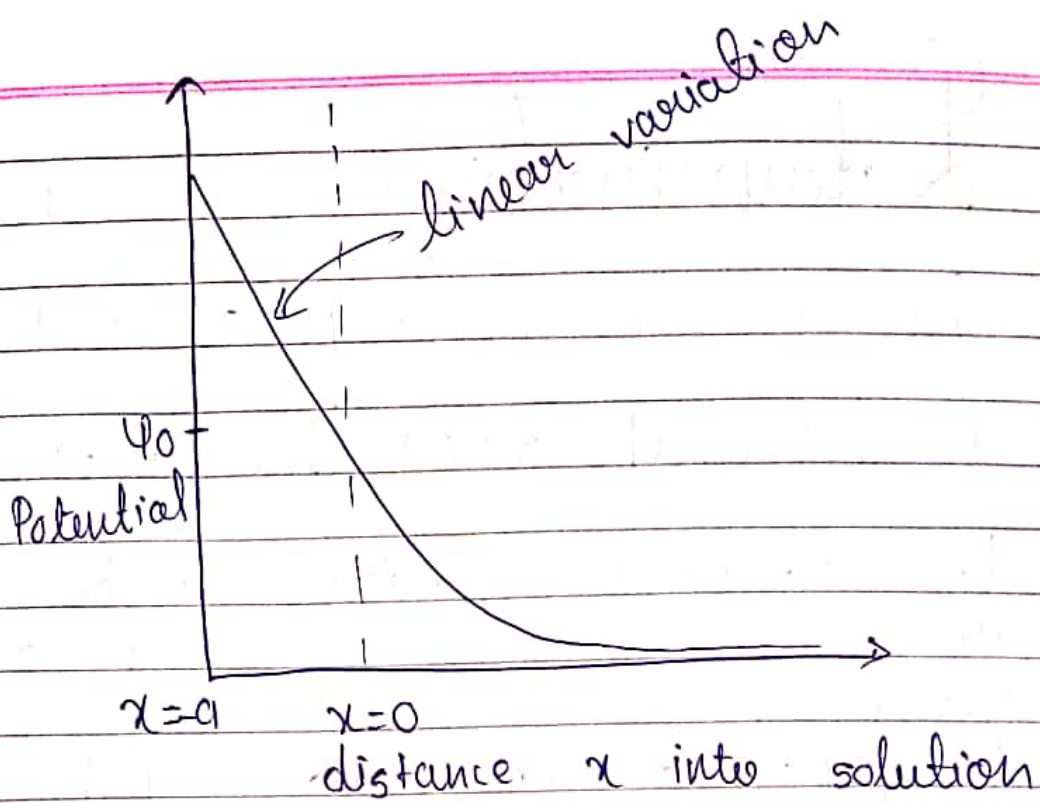
where ϕ_M , ϕ_H are the inner potentials of the metal and Helmholtz planes respectively ϕ_{bulk} is the potential in the bulk of the solution.

→ The stern synthesis of the two models implies a synthesis of the potential distance relation characteristic of these two models

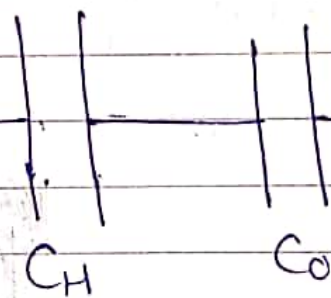
→ A linear variation in the region from $x=0$ to the position of OHP acc. to the Helmholtz perin model, and an exponential potential drop in the region from OHP to the bulk of the soln. acc. to the Gouy Chapman model.



→ The separation of charges and potential regions produces a separation of differential capacities. Differentiating the potential difference across the interface with respect to the charge on the metal q_m



\Rightarrow The corresponding total differential capacity C is given by the Helmholtz and Gouy capacities in series.



$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_0}$$

C = total capacity of the interface

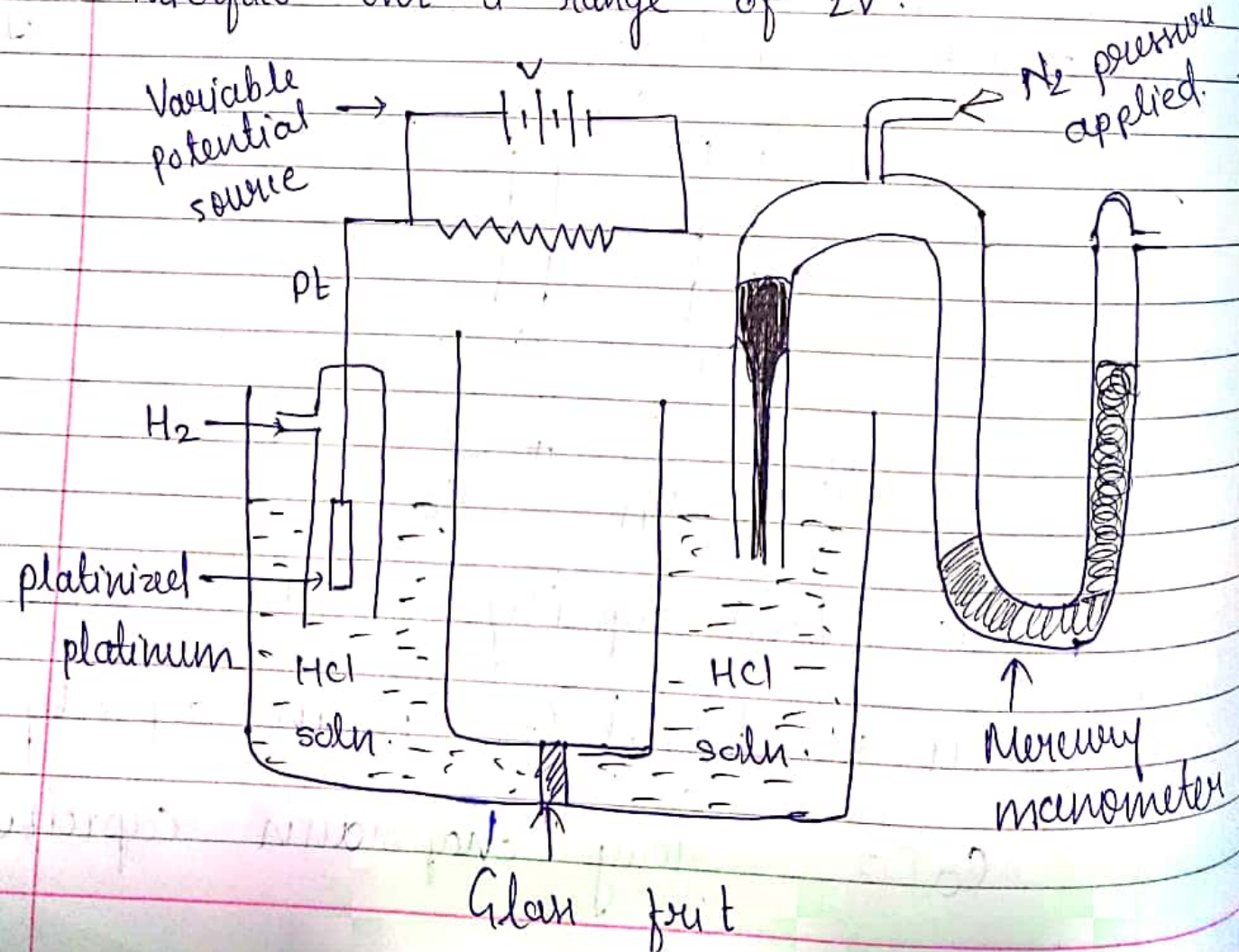
C_H = Helmholtz per unit capacity

C_0 = Gouy chapmann capacity

④ Determination of interfacial tension of mercury as a function of potential across the interfaces.

→ The interfacial tension can be related to the surface excess of various species in solution.

→ A great advantage of metal mercury interface is that the mercury solution interface approaches closest to the ideal polarizable interface over a range of 2V.



- Its essential parts are
- (1) A mercury soln.
 - (2) A polarizable interface
 - (3) A non polarizable interface
 - (4) An external source of variable potential difference $e \quad v$
 - (5) An arrangement to measure the surface tension of the mercury in contact with the soln.

→ The surface tension is measured by using a fine capillary and adjusting the height of mercury column so that the mercury surface tension f is stationary. The surface tension f is obtained from the expression.

$$f = \frac{1}{2} h \rho g r$$

r = radius of the capillary

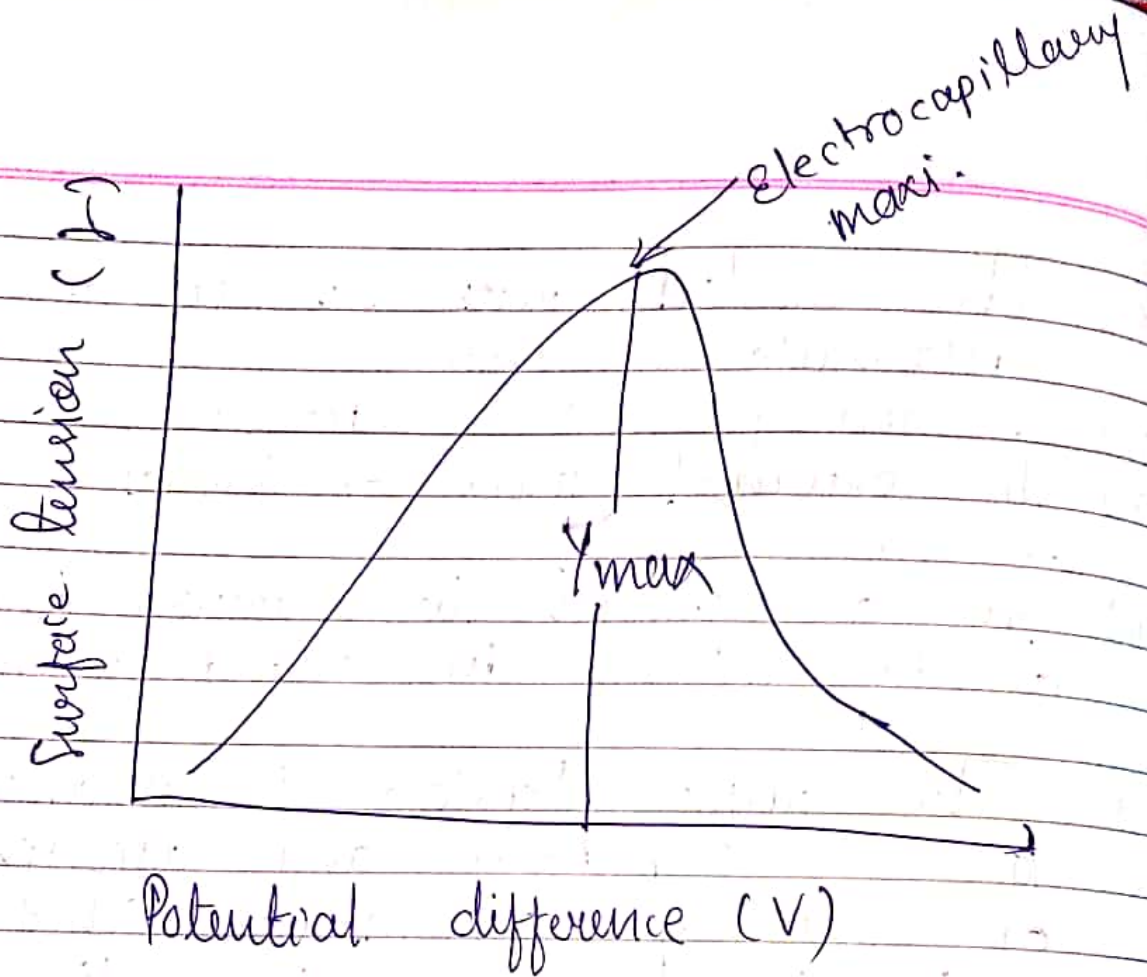
ρ = density of mercury

g = acceleration due to gravity

h = height to which mercury rises or falls in capillary.

→ The interfacial tension depends on the forces arising from the particles present in the interface region.

→ The f versus v curves, obtained is the graph of



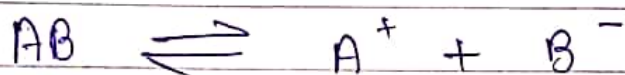
→ The potential at which the surface tension is a maximum is known as the potential of the electrocapillary maximum.

The measurement also shows that the surface tension varies with the composition of the electrolyte.

⑤ Determination of dissociation constant of mono basic acid by conductometer

→ ~~Main~~ Apparatus : Mainly operated conductivity bridge, thermostat, beakers, measuring flasks, burette etc.

Theory : The ionisation of a weak electrolyte AB can be represented as.



On applying the law of mass action.

$$K = \frac{[A^+][B^-]}{[AB]} \quad \text{--- (P)}$$

K = dissociation constant of the substance AB

If we start with 1 mole of an electrolyte and if α be its degree of ionisation. V litres is the total volume.

$$[A^+] = \frac{\alpha}{V}$$

$$[B^-] = \frac{\alpha}{V}$$

$$[AB] = \frac{1-\alpha}{V}$$

$$K = \frac{\alpha^2}{(1-\alpha)v}$$

→ α can be neglected.

$$K = \frac{\alpha^2}{v}$$

$$\alpha = \frac{dv}{d\infty}$$

dv = equivalent conductivity at any dilution
 $d\infty$ = " " " " at infinite dilution $v \text{ cm}^3$

$$d\infty = d\alpha + dc$$

Procedure :- 1st cell constant is determined.

→ An approximate $N/2$ solution is 1st prepared by diluting the glacial acetic acid. Then it is titrated against $N/2$ NaOH soln. and exact strength determined. It is then diluted to get exact $N/2$. Clean and dry the conductivity cell. It is then washed with $N/2$ acetic acid soln. and its observed resistance determined.

Then we prepare $N/4$, $N/8$, $N/16$... soln. of acetic acid from the stock $N/2$ soln. by proper dilution by using conductivity water. The cell is then washed with each soln. in turn and observed resistance is measured.

→ Observations : Cell constant $\alpha =$ _____

Calculation :

$$\alpha = \frac{dV}{dC} = \frac{dV}{dC + dC}$$

Q

Dissociation constant of poly basic and mono basic acid by potentiometric

Ans

Apparatus : pH meter, glass electrode, reference electrode, beaker (400 ml), burette, stirrer etc.

Theory : When an alkali is added to an acid solution, the pH of the solution increases slowly. The rate of change of pH of the solution is very rapid. From the sharp break in the curve, we can find the equivalence point from which the strength can be calculated by normality equations.

⇒ Procedure : 1st standardise the pH meter against a buffer of known pH.

Now 1st wash the glass electrode and reference electrode with distilled water and then with the acid soln. Take 5 ml of HCl soln in a 400 ml beaker. Add sufficient ^{water} _{so glass} electrode completely dipped. Note the pH of pure acid soln. Now add 1 ml of 0.1 N NaOH from burette. Stir the contents well. Note the pH of the soln. Now go on adding ^{beⁿ} 4 and 6 ml, the alkali should be added in fractions.

Observation : Volume of acid taken = 5 ml.

Vol. pH	0	1.0	2.0	3	4	5	6	7	8	9	10
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* Calculation.

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{Acid} & & \text{Alkali} \end{array}$$

$$N_1 \times 5 = \frac{N}{10} \times x$$

$$N_1 = \frac{N \times x}{10 \times 5}$$

$$\text{Strength of HCl soln} = \frac{36.5 \times x}{10 \times 5} \text{ g/ltr}$$

poly

Apparatus : Same as in preceding exp.

Theory : Same as in preceding experiment.
Here the stronger acid (HCl) will be neutralised first. while the weaker acid (CH_3COOH) will be neutralised afterwards. The 1st end point will be due to HCl. while the 2nd due to CH_3COOH .

Observation : Same in preceding exp.

★ Obs. Procedure: Same as in preceding exp. It is advisable to take 5 ml of the mix. in the beaker. This is to avoid taking a large no. of reading by the pH meter.

★ Observation: Same as in preceding exp.

★ Calculation:

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{HCl} & & \text{NaOH} \end{array}$$

$$N_1 \times 5 = \frac{N}{10} \times x$$

$$N_1 = \frac{N \times x}{10 \times 5}$$

$$\text{Strength of HCl} = \frac{36.5 \times x}{10 \times 5} \text{ g/litre}$$

$$\begin{array}{ccc} N_3 V_3 & = & N_4 V_4 \\ \text{CH}_3\text{COOH} & & \text{NaOH} \end{array}$$

$$N_3 \times 5 = \frac{N}{10} \times y$$

$$N_3 = \frac{N}{10} \times \frac{y}{5}$$