Arrhenius theory of electrolytic dissociation :

Main postulates of Arrhenius theory of electrolytic dissociation are —

① When an electrolyte is dissolved in water, it breaks up into two types of charged particles called ions. The ions having +ve charge are called cations while those having -ve charge are called anions.

$$AB \longrightarrow A^+ + B^-.$$

e.g. $NaCl \longrightarrow Na^+ + Cl^-$

② The total charge present on the cations in the solution is equal but opposite to that on the anions. Thus, solution as a whole is electrically neutral.

③ The ions are free to move and under the influence of electrical field are directed towards oppositely charged electrodes. i.e. Cations move towards cathode and anions move towards anode.

④ The ions obtained by dissociation of the electrolyte are constantly reunite to form undissociated molecules and a ~~state~~ state of equilibrium exist between the ionised and unionised molecules, which is called the ionic equilibrium.

$$AB \rightleftharpoons A^+ + B^-.$$

⑤ The electrolyte at a given concentration (or dilution) may not be completely ionised and the fraction of the total no. of molecules of the electrolyte that dissociates into ions is called as degree of ionization or dissociation. It is usually denoted by α.

$$\text{Degree of dissociation}(\alpha) = \frac{\text{No. of molecules dissociated into ions}}{\text{Total no. of molecules taken initially}}$$

⑥ The properties of electrolytic solutions are the properties of the ions produced.

⑦ The degree of ionisation depends upon the following factors

ⓐ **Nature of electrolyte:**
Some electrolytes are highly ionised (strong electrolytes) like HCl, NaCl, etc. while the others (NH_4OH, CH_3COOH, etc.) are poorly ionised (weak electrolytes).

ⓑ **Dilution** : degree of ionisation increases ~~with~~ with increase in dilution.

ⓒ **Temperature**: As temp^r increases, more of the molecules split into ions. degree of ionisation increases with increase of temperature.

ⓓ **Presence of common ions:**
The degree of dissociation of an electrolyte decreases when another electrolyte is present which furnishes a common ion. This effect is called common ion effect.
e.g. Dissociation of NH_4OH decreases in the presence of NH_4Cl.

Limitations of Arrhenius theory:

Some of the important limitations of this theory are —

① Arrhenius suggested that ionization of the electrolyte takes place when dissolved in water. However, X ray studies have shown that many such electrolytes are already in the ionised state (e.g. Na^+, Cl^-). It means it is not necessary to dissolve them in water for ionisation.

② Ostwald's dilution law which is based upon Arrhenius theory fails in the case of strong electrolytes. For example dissociation constant K for HCl does not have constant value at different dilutions.

③ As strong electrolytes (KCl, NaCl, etc.) conduct electricity in molten state also, it means ionisation takes place even in the absence of water.

④ Arrhenius simply assumes the existence of ions in solution. It could not explain how and why ions are produced in the solution.

⑤ Arrhenius theory assumes the existence of ions but does not consider interionic forces which may be neglected for weak electrolytes. but are very important for strong electrolytes.

⑥ The degree of dissociation (α) for strong electrolytes calculated from conductance measurements $\left(\alpha = \frac{\Lambda_c}{\Lambda_0}\right)$ was found to be different from that calculated from colligative properties.

⑦ Arrhenius theory could not explain the variation of transport no. with concentration.

Conductivity (C):

The power of the electrolyte to conduct electricity is known as conductance or conductivity. It is the inverse of resistance or resistivity (R). i.e. $C = \frac{1}{R}$. Its S.I. unit is $S\,cm^{-1}$ (Siemen cm^{-1}) or ohm^{-1} or mho.

we know, $R \propto l$, where l is the length and a is ~~specific~~ area of cross section of the wire.

$R \propto \frac{1}{a}$

$\therefore R \propto \frac{l}{a}$

$\Rightarrow R = \rho \frac{l}{a}$, where ρ is Specific Resistance.

$\therefore C \propto \frac{a}{l}$

$\Rightarrow C = \kappa \frac{a}{l}$

$\Rightarrow \frac{1}{R} = \kappa \cdot \frac{a}{l}$

$\Rightarrow \kappa = \frac{l}{a \cdot R}$, where κ (Kappa) is called Specific conductance.

OR:

Resistance power of a material having a volume of 1 cm^3 is called specific resistance.

Specific conductance is the conducting power of all the ions present in a volume of 1 cm^3 of the electrolyte solⁿ.

Molar conductivity (Λm):

It is the conducting power of all the ions present in an electrolyte ~~solving~~ solution having 1 molar strength. It is the conducting power of an electrolyte solⁿ which is made by dissolving 1 mol of the electrolyte in 1 litre of the solvent.

Equivalent conductivity:

It is the conducting power of all the ions present in an electrolyte solution having 1 Normal strength. It is the conducting power of an electrolyte solution which is made by dissolving 1 g equivalent of the electrolyte in 1 litre of the solvent.

If v cm^3 of the electrolyte is placed between two electrodes 1 cm apart, then equivalent conductance.

$$\lambda = K \cdot V$$

If c is the concentration of the electrolyte in g equi L^{-1},

$$V = \frac{1000}{c}$$

$$\Rightarrow \lambda = K \cdot \frac{1000}{c}$$

For, $\Lambda m = \frac{1000 K}{C}$.

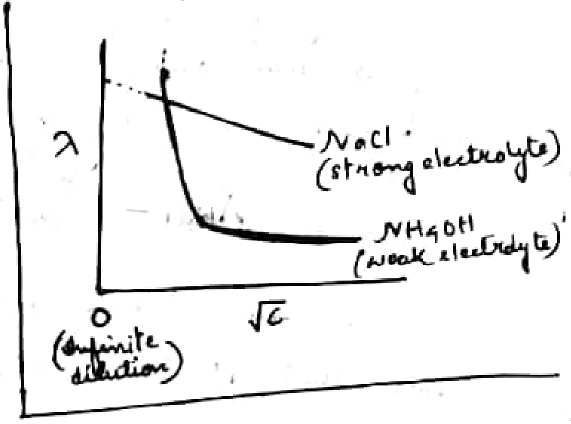
$$c = g\,mol\,L^{-1}.$$

Variation of molar and specific conductance with dilution :

The molar conductance of an electrolyte changes with electrolyte concⁿ for two reasons —

① The ionic concentration may not be proportional to the electrolyte stoichiometric concentration.

② The ionic molar conductivities changes with concentration.



For a weak electrolyte, λ_m increases sharply as Conc. tends to zero. This is mainly because of the rapid increase of degree of dissociation of the electrolyte as conc. goes to zero. This rapid increase in λ_m makes extrapolation to $C = 0$ very different for weak electrolytes.

For strong electrolytes, other than 1:1 electrolyte part of the decrease in λ_m with increase in conc. is due to the formation of ion pairs which reduces ionic concentration, while for most part, the decrease is due to the inter ionic forces. For strong electrolytes, ~~if~~ plot of λ_m vs $\sqrt{c}$ is linear at high dilution and allows extrapolation to $c = 0$. However, increase in no. of ions on dilution is much less in comparison to the total increase in volume of the solution. So, no. of ions per unit volume decreases. Hence, specific conductance decreases with dilution.

Molar Conductivity at infinite dilution :

When concentration is zero or at infinite dilution, the molar conductivity is called molar conductivity at infinite dilution. It is denoted by λ_m^0.

Kohlrausch law of independent migration of ions :

According to Kohlrausch law of independent migration of ions, limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

e.g. If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivity of sodium and chloride ions respectively. Then the limiting molar conductivity for NaCl is given by.

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

In an extensive series of measurements, Kohlrausch see that, at low conc^n, the molar conductivity of strong electrolytes is given by,

$$\boxed{\Lambda_m = \Lambda_m^{\alpha} - K\sqrt{C}.}$$

This is called Kohlrausch law.

where, Λ_m^{α} is the limiting molar conductance,

K is a co-efficient which depends on the nature of electrolyte.

Independent migration of ions:

Kohlrausch surveyed the values of limiting molar conductance for a no. of electrolytes having an ion in common.

Electrolyte	Λ_m^{α}	Electrolyte	Λ_m^{α}	Difference
KCl	130	NaCl	108.9	21.1
KNO_3	126.3	$NaNO_3$	105.2	21.1
difference = 3.7		difference = 3.7		
K_2SO_4	= 133	Na_2SO_4	= 111.9	21.1
difference = 6.7		difference = 6.7		

He obtained that the replacement of K^+ ion by Na^+ ion in any of the electrolytes ~~changes~~ always produces the same difference ie. 21.1 in molar limiting conductance irrespective of the nature of the anion. Similarly replacement of Cl^- by NO_3^- or NO_3^- by SO_4^{2-} produces the same difference. He explained it by saying that at infinite dilution, when dissociation is completed, every ion makes a definite contribution towards the conductance of the electrolyte irrespective of the nature of the other ion with which it is associated in solution.

Thus, if λ_+^α represents the molar conductance of the cation and λ_-^α represents the molar conductance of the anion, then according to Kohlrausch law of independent migration of ions,

$$\Lambda_m^\alpha = \nu_+\lambda_+^\alpha + \nu_-\lambda_-^\alpha$$

where, ν_+ and ν_- are the no. of cations and anions per formula of the electrolyte.

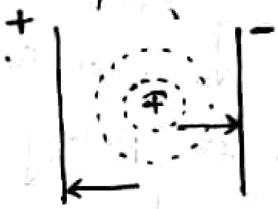
Debye-Huckel Onsager eqn:

This theory is based upon two effects.

① Asymmetric effect: each ion is surrounded in solution by an atmosphere of oppositely charged ions.

Let us consider, a central positive ion, surrounded by (-)ve ions. When the electric field is turned on, the central positive ions, tends to move out of its atmosphere.

absence of electric field



presence of electric field.

The atmosphere is continuously reforming. But since it takes a finite time an asymmetric distribution of ions is produced. The electrical attraction between the asymmetrical atmosphere and the ion reduces the speed of the ion.

As, concentration increases, the density of ions in the atmosphere increases and due to this asymmetric effect, the ionic mobility and hence conductance is further reduced.

② **electrophoretic effect**: Viscous force opposing an ion motion is proportional to the ions speed relative to the solvent. The ions in the atmosphere are moving in the direction opposite of the central ion and are carrying with them the molecules of solvation. Thus the solvent in the immediate vicinity of the central ion has a net motion in the direction opposite to the ions motion. Hence, the ion speed relative to the solvent is greater than the speed relative to the electron. This electrophoretic effect retards the motion of the ion.

The asymmetric effect decreases the electric force on an ion and the electrophoretic effect increases the viscosity. Both these effects decreases the drift speed and mobility. Hence, conductance decreases as conc^n increases.

Debye-Huckel and Onsager applied the theory of ionic interaction to calculate the electric mobility of ions in very dilute solution. The resulting limiting law allows the applications of asymmetric and electrophoretic effect. For a strong electrolyte with no ion pairing,

$$z_1 = |z|.$$

$\Lambda_m = \lambda_m^{\infty} - (A + B\lambda_m^{\infty})\sqrt{c}$, where A and B are constants which depends on the nature of the electrolyte.

Wein Effect: Conductance under high potential gradient.

Speed of an ion in an electric field varies with the applied potential gradient. Thus, under a potential gradient of about 20,000 volt per cm, an ion may have a speed of about 100 cm per sec. The ion, therefore, should pass several times through the thickness of the ionic atmosphere during the time of relaxation The moving ion, therefore, will be almost free from the effect of the oppositely charged ionic atmosphere. The ion will be moving so fast that there will be no time for the ionic atmosphere to be built up. The asymmetry and electrophoretic effects, under these circumstances, may be negligibly small or even absent. Thus, the conductance of a strong electrolyte in aqueous solution increases to a certain limiting value with increase in potential gradient applied. This observation had been verified experimentally by Wein much before the development of the theory of strong electrolytes and is called Wein effect.

Debye - Falkenhagen effect:

Conductance under high alternating currents frequencies.

Debye and Falkenhagen examined the conductance behaviour of a solution of a strong electrolyte by applying alternating currents of different frequencies. They predicted that if the frequency of alternating current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere, the asymmetry effect will be virtually absent. In other words, the ionic atmosphere around the central ion will remain symmetric. The retarding effect due to asymmetry may, therefore, be entirely absent and the conductance may be higher. The conductance of a solution, therefore should vary with the frequency of the alternating current used. The higher the frequency, the higher the conductance, evidently. This effect is also known as dispersion of conductance. The conductance remains independent of the frequency of AC upto 10 cycles per second. But with further increase in frequency, the conductance starts increasing towards a certain limiting value indicating complete absence of asymmetry effect.

Walden's Rule:

Let us consider a single ion immersed in a liquid and subjected to an electric field, E. As the ion moves through the liquid, its motion is retarded by the viscosity of the liquid. The frictional force, f, acting on a spherical ion of radius r, moving with a velocity v, is given by Stoke's law.

$$f = 6\pi\eta v r$$

where, η is the coefficient of viscosity of the liquid. This force is balanced by, the electrical force acting on the ion.

$$\therefore \quad 6\pi\eta v r = zeE$$

where, z is the charge no. of the ion and e is the electronic charge.

Hence the mobility, $u_\pm$ of the ion is given by,

$$u_\pm = v/E = \frac{ze}{6\pi\eta r}$$

We know,

$$\lambda^\circ_\pm = z u^\circ_\pm F .$$

where $\lambda^\circ_\pm$ is the limiting ionic mobility and $\lambda^\circ_\pm$ is the molar ionic conductance at infinite dilution.

$$\therefore \lambda^\circ_\pm = \frac{z^2 e F}{6\pi\eta_0 r} \longrightarrow ①$$

where η_0 is the viscosity of the pure solvent.

In eqn ①, only η_0 is dependent on the medium.

$$\therefore \lambda^\circ_\pm \eta_0 = \text{constant}.$$

This is called Walden's rule.

The larger the viscosity ~~the~~ of the medium, the lesser would be the mobility and hence the lesser would be the conductance of the ion. Walden's rule holds only for large ions such as $(CH_3)_4N^+$ ion and picrate ion $C_6H_{12}(NO_2)_3O^-$.

Q. why larger ions satisfy Walden's rule more accurately than do the smaller ions?

or Q. why smaller ions do not satisfactorily obey Walden's rule?

Ans:- The reason why smaller ions do not satisfactorily obey Walden's rule is that they are solvated. A solvated ion also carries ~~[illegible]~~ along the solvent molecules as it moves, with the result that the effective radius of the ion is larger than the crystallographic radius, and is different in each solvent.

In case of larger ions, since the electric field due to the ion itself is small, the amount of the solvent held to the ion is small. i.e. larger ions are less solvated than the smaller ions so that for larger ions the effective radius is nearly the same in different solvents. This is why larger ions satisfy Walden's rule more accurately than the smaller ions.

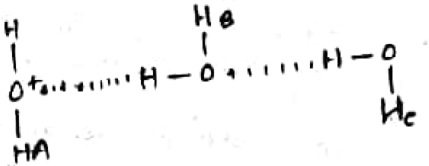
Mobility of Ions (Ionic mobility):

Mobility of an ion is defined as the speed with which the ion moves under a potential gradient of 1 cm. Mobility of an ion decrease with increase in solvent viscosity and increase in ion size.

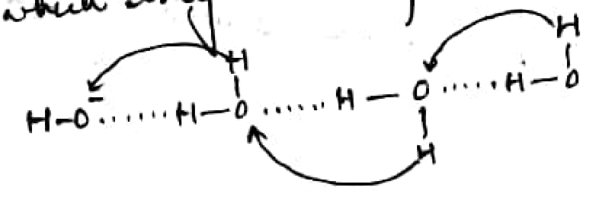
Q. The molar conductivities of alkali metals increases as we go from lithium to sodium. why?

Ans:- Smaller ions give rise to stronger electric field than the bigger ions. Hence, they are more extensively solvated than the bigger ions. Thus an ion of small ionic radii has a larger hydrodynamic radii and thus a low mobility. So, smaller ions have lower molar conductance than the bigger ion of same charge.

Abnormal mobility of H^+ and OH^- ions:



The proton is very small in size and extensively hydrated but it still have an abnormally high value of conductance. This is because, it conducts by Grotthus mechanism that does not involve in the actual motion of the ion to the sol^n. Instead, there is an effective motion of a proton, which involves rearrangement of bonds through a long chain of water molecules. The conductivity of is governed by the rate at which water molecules can rotate into orientation into which they can accept or donate protons.



The abnormal high mobility of OH^- is also administrated by Grotthus law.

Determination of Ionic Mobility :

Ionic mobility can be measured directly by a technique based on the movement of a visible boundary between two electrolytic solutions.

Let us suppose, the mobility of K^+ ions is to be determined. Then KCl is considered as the principal electrolyte and the another electrolyte called the indicator electrolyte should have the same anion with lower mobility of its cation than K^+ ion. Let, $CdCl_2$ be the indicator electrolyte.

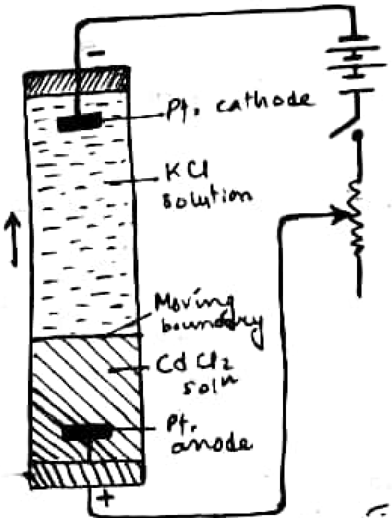


Fig. Direct determination of Ionic Mobility.

The system contains a decimolar solution of KCl held over a solution of similar concn of $CdCl_2$ in a tube of uniform bore. The anode is placed at the lower end and the cathode at the upper end of the tube, as shown in the figure. Both the electrodes are made of platinum. When a small current flows through the cell, the K^+ ions followed closely by Cd^{2+} ions, move upward. As there will be no gap in ~~between~~, the boundary will continue to remain sharp. The rate of movement of the boundary will be determined by the velocity of K^+ ions.

Suppose, the boundary moves through a distance of x m in t seconds when the fall of potential in the electric field is z volts per metre (say). Then;

$$\text{Mobility of } K^+ \text{ ions} = \frac{\text{Speed of ion}}{\text{Potential gradient}} = \frac{(x/t)\, m\, s^{-1}}{z\, V m^{-1}}$$

$$= (x/tz)\, m^2 s^{-1} V^{-1}.$$

Transference numbers:

The transference or transport no.s is defined as the fraction of total current carried by an ion of a particular type. In case of a solution of two kinds of ions, the cation transport no is,

$$t_+ = \frac{I_+}{I}.$$

And the anion transport no. is,

$$t_- = \frac{I_-}{I}.$$

$$\therefore I = I_+ + I_-.$$

$$\therefore t_+ + t_- = \frac{I_+}{I} + \frac{I_-}{I}.$$

$$= \frac{I_+ + I_-}{I}$$

$$= \frac{I}{I}$$

$$\Rightarrow \boxed{t_+ + t_- = 1}$$

Relation between transport no and mobility:

The quantity of current carried through certain volume of an electrolytic solution by ions of the ith current $\propto$ to conc^n c_i in mol L^{-1}, to the charge z_i carried by its ion and the mobility μ_i of its ion.

$$\therefore I = K c_i z_i \mu_i$$

where, K is a proportionality constant.

In the simple case of an electrolyte yielding two ions the transport no. is.

$$t_+ = \frac{I_+}{I}.$$

$$\Rightarrow t_+ = \frac{K c_+ z_+ \mu_+}{K(c_+ z_+ \mu_+ + c_- z_- \mu_-)} \quad \left\{\because I = I^+ + I^-\right\}$$

while,

$$t_- = \frac{I_-}{I}.$$

$$\Rightarrow t_- = \frac{K C_- Z_- \mu_-}{K(C_- Z_- \mu_- + C_+ Z_+ \mu_+)}.$$

∵ The soln is neutral.

$$\therefore C_+ Z_+ = C_- Z_-.$$

$$\therefore t_+ = \frac{K C_+ Z_+ \mu_+}{K(C_+ Z_+ \mu_+ + C_+ Z_+ \mu_-)}.$$

$$\Rightarrow t_+ = \frac{K C_+ Z_+ \mu_+}{K C_+ Z_+ (\mu_+ + \mu_-)}.$$

$$\Rightarrow t_+ = \frac{\mu_+}{\mu_+ + \mu_-}.$$

Similarly, $t_- = \frac{\mu_-}{\mu_+ + \mu_-}$.

$$\therefore t = t_+ + t_-$$

$$= \frac{\mu_+}{\mu_+ + \mu_-} + \frac{\mu_-}{\mu_+ + \mu_-}.$$

$$\Rightarrow \boxed{t = \frac{\mu_+ + \mu_-}{\mu_+ + \mu_-}}$$

$$\Rightarrow \boxed{t = 1.}$$

Determination of transference no.s using ① Hittorf Method:

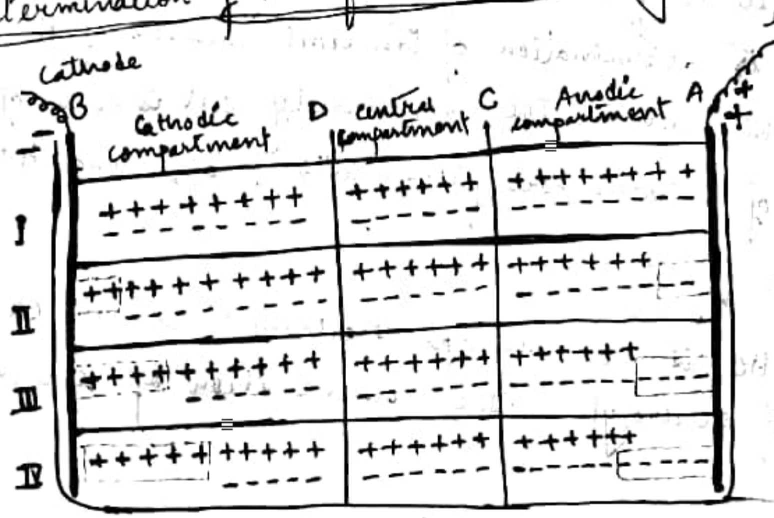


Fig. Hittorf's theoretical device

In this method, an electrolytic cell is divided into ~~two~~ three compartments, and an amount It of electricity is passed. An amount, $\frac{It}{z_+F}$ is discharged at the cathode while an amount $t_+\left(\frac{It}{z_+F}\right)$ of cations migrate into the cathodic compartment.

∴ change in amount of cations in the cathodic compartment $= t_+\left(\frac{It}{z_+F}\right) - \frac{It}{z_+F}$.

$$= \frac{It}{z_+F}\left(t_+ - 1\right).$$

$$= \frac{It}{z_+F}\left(t_-\right) \qquad [\because t_+ + t_- = 1).$$

$$= t_-\left(\frac{It}{z_+F}\right).$$

∴ By measuring the change in composition in the cathodic compartment, the anion transport no. t_- can be deduced. Similarly, change in amount of anions in the anodic compartment is $t_+\left(\frac{It}{z_+F}\right)$ from which t_+ is obtained.

(ii) Moving Boundary Method:

This method is based on the direct observation of migration of ions in an electric field. The principle may be explained with reference to determination of transport numbers of H^+ ions in HCl. In this method the conductivity cell consists of a vertical tube of uniform bore filled with $CdCl_2$ and HCl as shown in the figure.

Here, HCl is the principal electrolyte while $CdCl_2$ is the indicator electrolyte. The concentration of the solutions are adjusted in such a way that HCl solⁿ is lighter than the $CdCl_2$ solⁿ and thus floats over the $CdCl_2$ solⁿ. A clear sharp boundary appears between the two solutions. The mobility of Cd^{2+} ion is less than that of H^+ ion and it has a common anion with HCl.

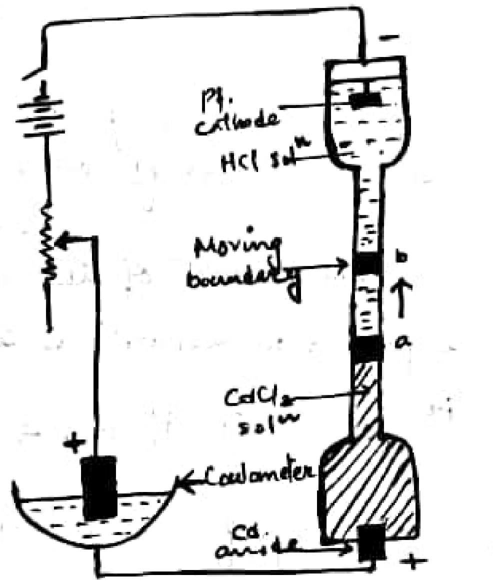


Fig: The moving boundary method

The anode at the bottom is of cadmium metal while the cathode at the top is a Pt. foil. When a small current is passed through the conductivity cell, the Cl^- ions move towards the anode while H^+ ions followed by Cd^{2+} ions move towards the cathode.

∴ Let, the boundary moves through a distance l cm (say from a to b). Then the volume of the liquid has moved up lA cm^3, where A is the cross-sectional area of the tube in cm^2; Let the concentration of the acid be c gram equivalents per litre.

∴ The no. of gram equivalents of H^+ ions carried towards the cathode $= \frac{lAc}{1000}$.

∵ Each gram equivalent carries one faraday of electricity.

∴ Electricity carried by H^+ ions $= \frac{lAc}{1000} F$.

Let, Q faradays be the total quantity of electricity.

∴ Transport no. of H^+ ions $= \frac{lAc}{1000Q}$.

Application of conductance measurement:

① Degree of dissociation of weak electrolytes:

The degree of dissociation of a weak electrolyte at any dilution can be calculated by the relationship.

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}.$$

② Determination of ionic product of water (K_w): dissociation of water is as follows,

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

The product of the concentration of H^+ and OH^- ions expressed in mol dm^{-3} is known as ionic product of water (K_w)

i.e. $[H^+][OH^-] = K_w$. , K_w is constant at a given temp^r.

The specific conductance of purest water at 25°C is

$$= 5.54 \times 10^{-6}\ S\ m^{-1}.$$

∴ The conductance of one cubic meter of water $= 5.54 \times 10^{-6}\ S\ m^{-1} \times 1\ m^3$

$$= 5.54 \times 10^{-6}\ S\ m^2.$$

~~The molar conductance of water if it is completely ionised to give one mole of H⁺ ions and one mole of OH⁻ ions, is obtained by adding up~~ Molar ionic conductances of H^+ and OH^- ions ~~which~~ are $349.8 \times 10^{-4}\ S m^2 mol^{-1}$ and $198.5 \times 10^{-4}\ S m^2 mol^{-1}$ respectively.

∴ The molar conductance of water $= (349.8 + 198.5) \times 10^{-4}\ S m^2 mol^{-1}$

$$= 548.3 \times 10^{-4}\ S m^2 mol^{-1}.$$

Thus, if the molar conductance of 1 m^3 of water is $5.54 \times 10^{-6}\ S m^2$, the amount of H^+ ions per m^3 is,

$$\frac{5.54 \times 10^{-6}\ S m^2}{548.3 \times 10^{-4}\ S m^2 mol^{-1}} = 1.01 \times 10^{-4}\ mol^{-1}.$$

The no. of moles of OH^- ions will also be the same.

$\therefore [H^+] = [OH^-] = 1.01 \times 10^{-4}$ mol m^{-3} = 1.01×10^{-7} mol dm^{-3}

$\therefore K_w = [H^+][OH^-] = 1.01 \times 10^{-7}$ moldm^{-3} × 1.01×10^{-7} moldm^{-3}

$= 1.02 \times 10^{-14}$ mol^2 dm^{-6}.

$\simeq 10^{-14}$ mol^{2}dm^{-6} at 25°C.

③ Determination of solubilities and solubility products of sparingly soluble salts :

The ~~salt~~ solubilities of some sparingly soluble salts ~~as~~ such as silver chloride, barium sulphate, lead sulphate, etc. which can't be determined by any chemical method, can be determined by conductance measurements.

Let us consider that the solubility of silver chloride in water is to be determined at 25°C. AgCl is repeatedly washed with conductivity water to remove any soluble impurities. It is then suspended in conductivity water, warmed and cooled at 25°C. A very minute quantity of salt will pass in solution and the rest will settle down. The conductivity cell is placed in a thermostat at 25°C. The conductance of water used in the preparation of the soln is also determined.

Let, the specific conductance (κ) of the soln be z S m^{-1}. The solubility of AgCl is x mole m^{-3}.

$\therefore$ Concentration of AgCl in the aqueous solution, $c = x$

$\therefore$ Molar conductance of the soln, $\Lambda_m = \frac{\kappa}{c}$

$= \frac{z\,S\,m^{-1}}{x}$

$\because$ Solubility of AgCl is extremely low.

$\therefore$ At 25°C, $\Lambda^\circ_{m\,AgCl} = \lambda^\circ_{Ag^+} + \lambda^\circ_{Cl^-}$

$= (61.92 + 76.34) \times 10^{-4}$ S m^{2}mol^{-1}.

$= 138.26 \times 10^{-4}$ S m^2 mol^{-1}.

$$\therefore \frac{z\ S\,m^{-1}}{x} = 138.26 \times 10^{-4}\ S\,m^2\,mol^{-1}.$$

$$\Rightarrow x = \frac{z\ S\,m^{-1}}{138.26 \times 10^{-4}\ S\,m^2\,mol^{-1}}$$

$$\Rightarrow x = \frac{z}{138.26 \times 10^{-4}}\ mol\,m^{-3}.$$

i.e. The solubility of AgCl in water at 25°C is $\frac{z}{138.26 \times 10^{-4}}\ mol\,m^{-3}$.

or $\frac{z}{138.26 \times 10^{-7}}\ mol\,dm^{-3}$ or $\frac{z}{138.26 \times 10^{-7}}\ mol\,dm^{-3} \times 143.5\ g\,mol^{-1}$.

$$= \frac{z}{138.26 \times 10^{-7}}\ g\,dm^{-3}.$$

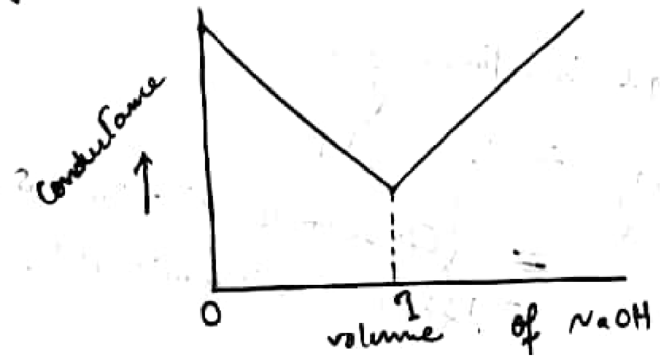
④ Conductometric Titrations:

~~Conductomet~~ Conductance measurements are frequently employed to find the end points of acid-alkali and other titrations. The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

Some typical conductometric titration curves are:

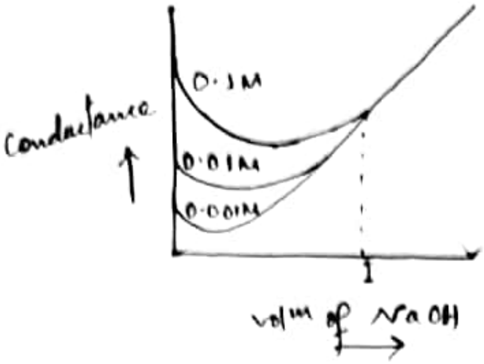
ⓐ Strong acid with a strong base:

eg. HCl with NaOH



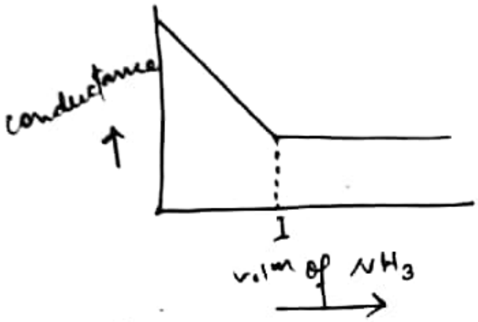
ⓑ Weak acid with a strong base :

e.g. CH_3COOH with NaOH.



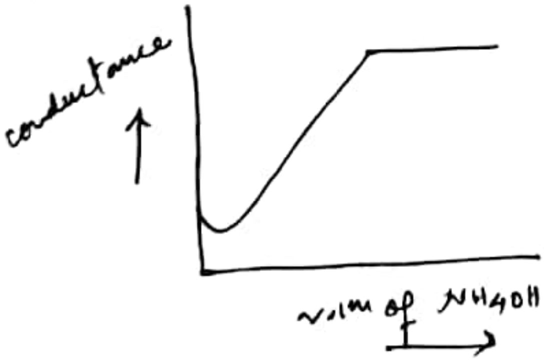
ⓒ Strong acid with a weak base :

e.g. H_2SO_4 with dil. NH_3



ⓓ Weak acid with a weak base :

e.g. CH_3COOH with NH_4OH



ⓔ Mixture of a strong acid and a weak acid vs. a strong base: