Situation in Case of Strong Electrolytes. The X-ray analysis of crystals of ionic solids, such as NaF, NaCl, KCl, Na_2SO_4 and NaOH, which are strong electrolytes, have revealed that the crystal lattice in the case of *these substances consists exclusively of ions. There are no molecules.* Hence, *the question of equilibrium between unionised molecules and their ions, assumed in Arrhenius theory, does not arise at all in such cases.*

As is now well recognised, the formation of ions takes place right at the moment of formation of these compounds by the transference of electrons from one atom to another. Compounds formed in this manner are called *electrovalent compounds.* For example, in the formation of sodium fluoride, there is transference of one electron from a sodium atom to a fluorine atom. As a result, the sodium atom acquires positive charge and fluorine atom acquires negative charge. This explains the formation of ions. *The crystal of sodium fluoride, therefore, consists entirely of sodium ions and fluoride ions.* The ions are held in position by electrostatic forces and are not free to move. When the crystals are melted, the ions acquire freedom of motion and are able to conduct electricity. This explains conductivity of fused salts.

According to Coulomb's law, the electrostatic forces vary inversely as the dielectric constant of the medium. Therefore, when crystals are dissolved in water, the dielectric constant of which is about 80 times greater than that of air, the electrostatic forces of attraction between the ions are considerably weakened. As a result of this, the ions begin to move more freely and conduct electricity more strongly.

Debye-Huckel Theory of Strong Electrolytes

Debye and Huckel, in 1923, put forward their well-known theory of strong electrolytes. A number of other workers also made useful contributions but only a very brief discussion will be possible in the present volume.

Broadly speaking, according to this theory, strong electrolytes which exist as ions even in the solid state *must be completely ionised in solution at all concentrations.* If the solvent has a high dielectric constant (*e.g.,* water), the electrostatic forces, as already mentioned, will be small. Further, if the solution is very dilute, the distance between the ions will be large. Therefore, the electrostatic forces which vary inversely as the square of the distance between the ions, will be weakened all the more. Under these conditions, the forces of attraction between the oppositely charged ions, *i.e.,* **interionic forces,** will become very small and, therefore, the ions will lie far apart from one another. If, on the other hand, the solvent has a low dielectric constant (*e.g.,* ethanol) or if the solution is of a high concentration even when water is used as the solvent, the interionic forces will be appreciable. Under these conditions, some of the ions will not separate out completely from one another and will remain in pairs, such as A^+B^-, known as **ionic doublets.** This state of affairs is expressed by the statement that *the electrolyte is completely ionised but not completely dissociated.*

As the solution is diluted, equivalent conductance increases. Arrhenius attributed this increase to increase in the degree of ionisation and used it as a method of calculating degree of ionisation of an electrolyte by the equation :

$$\alpha = \frac{\Lambda_c}{\Lambda_o} \qquad\qquad ...(cf. eq. 1)$$

But, according to the modern theory of strong electrolytes, *the degree of ionization of strong electrolytes is unity even at moderate concentrations.* Therefore, the above relationship is not correct in the case of strong electrolytes. Debye and Huckel suggested that increase in equivalent conductance with dilution in the case of strong electrolytes is *due to increase in the mobilities of the ions* due to weaker interionic attraction rather than to increase in the degree of ionisation which remains unity all along. Similarly, decrease in equivalent conductance with increase in concentration is not due to fall in the degree of ionization but to fall in mobilities of the ions due to greater inter-ionic effect.

To understand the interionic effect, consider a very dilute solution of sodium chloride. The ions will be so far apart in this case that the forces of attraction between Na^+ and Cl^- ions will be almost negligible. The ions would act independently of each other. Their mobility or conductance will be maximum and they will make full contribution, towards conductance as well as towards colligative properties. Now suppose the concentration is increased. The ions now come closer to one another, comparatively speaking, and the interionic forces of attraction are no longer negligible. In other words, the ionic mobility falls due to mutual attraction of oppositely charged ions. Their contribution towards electrical conductance decreases correspondingly.

As the concentration is increased further, the oppositely charged ions come closer all the more. The interionic forces, therefore, become still more appreciable and the ionic mobility falls further.

Thus, according to this theory, in the case of strong electrolytes, *Interionic attraction and not partial dissociation is the cause of decrease of conductance with rise in concentration.*

Debye and Huckel derived an equation which enabled them to calculate the magnitude of the interionic effects. The fundamental idea underlying the calculations is that as a result of electrical attraction existing between ions carrying opposite charges, each ion in a solution of finite concentration is surrounded by an atmosphere of oppositely charged ions. For example, in Fig. 27.2 (a), the central ion is positively charged and is surrounded by an atmosphere of negatively charged ions. When an electric field is applied, the ions are set in motion. The central ion moves in one direction and the atmosphere in the opposite direction. Thus, a central positive ion tends to move towards the cathode on the right while its negative ionic atmosphere tends to move towards the anode on the left, as represented in Fig. 27.2 (b). The symmetry of the atmosphere about the ion is thus destroyed and the atmosphere becomes distorted. In other words, whereas the

force of attraction exerted by the atmosphere on the central ion, therefore the passage of electricity, is uniform in all directions and therefore cancels out, it becomes greater behind the ion than in front, on the
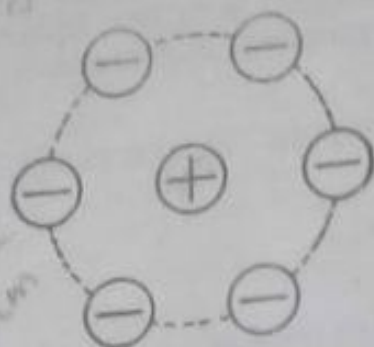
symmetrical
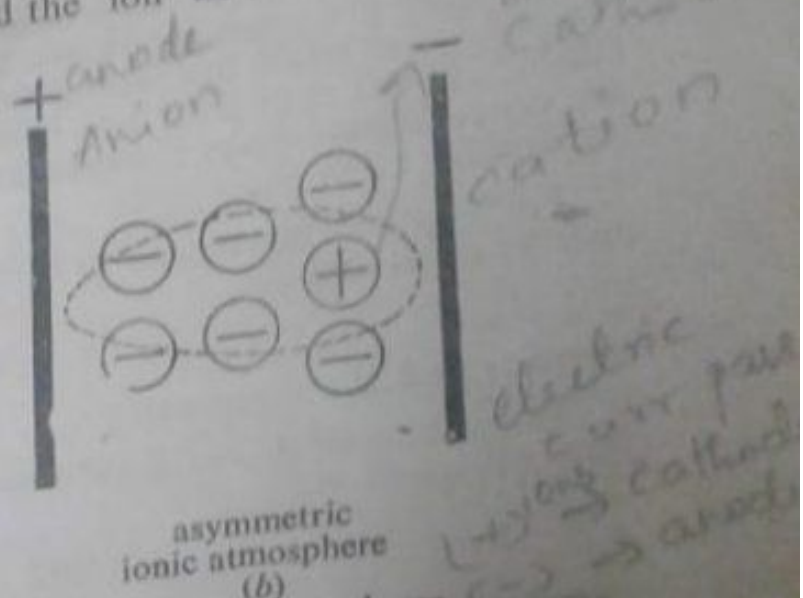ionic atmosphere
(a)

asymmetric
ionic atmosphere
(b)

Fig. 27.2. Symmetrical and asymmetric ionic atmospheres.

passage of electricity, as shown in Fig. 27.2 (b). Consequently, the ion experiences a retarding force, a force which tends to drag it backward. The movement of the ion, therefore, is slowed down. The drag on the central ion is known as the **asymmetry effect** because it arises from a lack of symmetry in the atmosphere of a moving ion. Similarly, we conceive of a negative central ion being surrounded by an atmosphere of positively charged electricity.

Another factor that slows down the motion of the ions at higher concentrations arises from the tendency of the ionic atmosphere associated with molecules of water of hydration to move in a direction opposite to that in which the central ion is moving. Thus, a positive ion, for example, which migrates towards the cathode has to make its way through the medium (water) which, itself, is moving with the negative ionic atmosphere towards the positive electrode. Similarly, a negative ion has to move towards the anode through the medium (water) associated with positive ionic atmosphere which is moving towards the negative electrode. These counter currents slow down the ions in the same way as counter currents in a stream slow down a swimmer. This effect is known as **electrophoretic effect**.

Debye and Huckel worked out mathematically the magnitudes of asymmetry and electrophoretic effects in terms of such factors as valency of the ion, ionic concentration, and dielectric constant and viscosity of the medium. For uni-univalent electrolytes, such as KCl, which furnish two univalent ions, the following equation was derived :

$$\Lambda_c = \Lambda_0 - \left[\frac{82\cdot4}{(DT)^{\frac{1}{2}}\eta} + \frac{8\cdot20 \times 10^5}{(DT)^{\frac{3}{2}}} \Lambda_0 \right] \sqrt{c} \qquad ...(8)$$

where D and η are the dielectric constant and coefficient of viscosity of the medium, respectively, at the absolute temperature T, and c is the concentration of the solution in moles per litre.

Significance of the equation. Debye-Huckel equation accounts for the difference between Λ_c and Λ_0. As is evident, Λ_c is less than Λ_0. This is partly due to *electrophoretic effect* and partly due to *asymmetry effect.* The first term in the bracket gives a measure of the electrophoretic effect while the second term gives a measure of the asymmetry effect. The sum of these two effects multiplied with the square root of the concentration gives the decrease of equivalent conductance Λ_c from its limiting value Λ_0.

For a given solvent and at a given temperature, the above equation may be expressed as :

$$\Lambda_c = \Lambda_0 - (A + B\Lambda_0)\sqrt{c} \qquad \ldots(9)$$

where A and B are constants.

The values of A and B for water at $25°$ come out to be $60\cdot2$ and $0\cdot229$, respectively.

$$\therefore \qquad \Lambda_c = \Lambda_0 - (60\cdot2 + 0\cdot229\ \Lambda_0)\sqrt{c} \qquad \ldots(10)$$

If the equation is correct, then by plotting equivalent conductances (Λ_c) against the square roots of the concentrations ($\sqrt{c}$), a straight line of slope equal to $60\cdot2+0\cdot229\ \Lambda_0$, should be obtained. This has been checked in the case of a number of uni-univalent electrolytes and found to be true up to concentrations of the order of $0\cdot02N$, as shown in Fig. 27.3. At higher concentrations, slight deviations are noticed which increase with further increase in concentration. These are attributed to certain approximations assumed in the derivation of the equation which are not valid when concentration is high.

If a solution is at infinite dilution, *i.e.*, if c is almost zero, then the second term on the right hand side of the equation becomes negligible and Λ_c approaches Λ_0, as expected.

Fig. 27.3. Verification of Debye-Huckel equation.

Debye Falkenhagen Effect. Conductance Under High A.C. Frequencies. Debye and Falkenhagen examined the conductance behaviour of a solution of a strong electrolyte by applying alternating current of different frequencies. They predicted that *if the frequency of alternating current is high so that the time of oscillation is small in comparison to the relaxation time of the ionic atmosphere*, the asymmetric effect will be virtually absent. In other words, the ionic atmosphere around the central ion will *remain symmetrical*. 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, also known as **dispersion of conductance**, has been verified experimentally. The conductance remains independent of the frequency of alternating current upto 10^6 cycles per second. But with further increase in frequency, the conductance starts increasing towards a certain limiting value indicating complete absence of asymmetric effect.

Wien Effect. Conductance Under High Potential Gradients. 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 Wien much before the development of the theory of strong electrolytes and is known as the Wien effect.

ACTIVITY COEFFICIENTS OF ELECTROLYTES

Activity Coefficient. Consider, the equilibrium in the case of a uni-univalent electrolyte represented as :

$$MA \rightleftharpoons M^+ + A^-$$
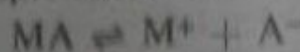
Applying the law of chemical equilibrium, we have :

$$K = \frac{a_{M^+} \times a_{A^-}}{a_{MA}} \qquad \qquad ..(11)$$

The activity is related to concentration by the expression :

$$a = fc \qquad \qquad ...(12)$$

where f is called activity coefficient. Thus

$$K = \frac{f_{M^+} c_{M^+} \times f_{A^-} c_{A^-}}{f_{MA} c_{MA}} \qquad \qquad ...(13)$$

$$= \frac{c_{M^+} \times c_{A^-}}{c_{MA}} \times \boxed{\frac{f_{M^+} \times f_{A^-}}{f_{MA}}} \qquad \qquad ...(14)$$

and, therefore, the solutions behave almost ideally. In such cases, a approaches c and hence activity coefficients are close to *unity*. In case of weak electrolytes, therefore, the second term in equation (14) disappears.

In the case of strong electrolytes, however, the activity coefficient is not unity unless the solution is at extreme dilution. In such cases it is necessary to know the activity coefficients at different concentrations.

In electrochemical work, the concentrations are often expressed on the basis of *molality*, *i.e.*, in terms of *moles per 1000 gm. of the solvent*. The activity coefficient is then represented by γ. The relationship between activity, a, and molality, m, is expressed as :

$$a = m\gamma \qquad \qquad \text{...(15)}$$

The equation (11) is then written as :

$$K = \frac{m_{M^+} \times m_{A^-}}{m_{MA}} \times \frac{\gamma_{M^+}\,\gamma_{A^-}}{\gamma_{MA}} \qquad \text{...(16)}$$

It is evident from equations (12) and (15) that activity (a) is given by : $a = cf = m\gamma$. If concentration is expressed as moles per litre, the activity coefficient is denoted by f and if the concentration is expressed as moles per 1000 gm. of solvent, the activity coefficient is denoted by γ. *In very dilute solutions, the values of γ and f are nearly the same.*

Example 1. *The density of a 0·1 M solution of KI in ethanol at 20°C is 0·8014. Calculate the ratio of the activity coefficients γ and f. ($K=39$; $I=127$).*

The activity (a) is related to f and γ by the expression :

$$a = cf = m\gamma$$

where c is molar concentration and m is molality of the solution.

In the present case :

Concentration, $c = 0\cdot1$ mole per litre

Density of solution $= 0\cdot8014$ gm. ml^{-1}

∴ Weight of 1 litre of solution $= 0\cdot8014 \times 1000 = 801\cdot4$ gm.

Weight of solute $= 0\cdot1 \times 166 = 16\cdot6$ gm.

∴ Weight of solvent $= 801\cdot4 - 16\cdot6 = 784\cdot8$ gm.

∴ Molality of solution $= \dfrac{0\cdot1 \times 1000}{784\cdot8} = 0\cdot1274$

∴ The ratio $\dfrac{\gamma}{f} = \dfrac{c}{m} = \dfrac{0\cdot10}{0\cdot1274} = \mathbf{0\cdot7849}$

Mean Activity Coefficient. It is not possible to have only one kind of ions in a solution. If there are anions, there have to be cations as well such that the total positive charge is equal to the total negative charge in a solution which is, evidently, neutral. The question of determining activities or activity coefficients of individual ions, as provided in equation (14), therefore, does not arise. New terms such as **mean activity** and **mean activity coefficient** need to be introduced.

THEORIES OF IONIZATION   CHAPTER

TABLE 27 4

Mean Activity Coefficients ($\gamma_\pm$) of Electrolytes in Aqueous Solution at 25°C

| Molality	HCl	KCl	NaCl	CaCl₂	ZnCl₂	H₂SO₄	ZnSO₄	KOH
0·001	0·966	0·966	0·966	0·888	0·831	—	0·734	0·989
0·005	0·930	0·927	0·928	0·789	0·767	0·643	0·477	0·954
0·01	0·906	0·902	0·903	0·732	0·708	0·545	0·387	0·920
0·05	0·833	0·816	0·821	0·584	0·556	0·341	0·202	0·822
0·10	0·798	0·770	0·778	0·524	0·502	0·266	0·148	0·789
0·50	0·769	0·652	0·679	0·510	0·376	0·155	0·063	0·750
1·00	0·811	0·607	0·656	0·752	0·325	0·131	0·044	0·760
2·00	1·010	0·577	0·655	1·554	—	0·125	0·035	—
3·00	1·310	0·572	0·719	3·384	—	0·142	0·041	1·062
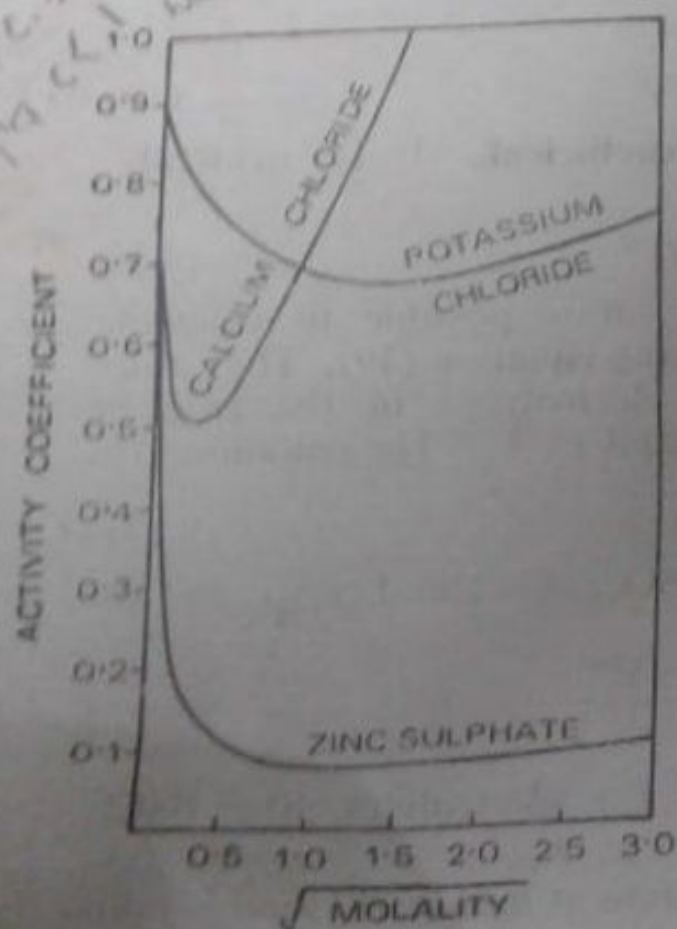
Fig. 27.4. Variation of activity coefficients with concentration.

It is seen that at lower concentrations, the activity coefficient is close to unity, *i.e.*, the departure from ideal behaviour is small. But as concentration increases, the activity coefficient falls much below unity and approaches a certain minimum value indicating much larger departures from the ideal behaviour. As concentration rises further, the activity coefficient starts increasing and in some cases even exceeds unity, *i.e.*, activity becomes greater than concentration (molality). This behaviour is shown more clearly in Fig. 27.4 in which activity coefficients of some of the electrolytes have been plotted against square roots of molalities.

Reference to Table 27.4 also shows that the electrolytes of the same valency (*e.g.*, NaCl and KCl) have almost equal values at the same concentration particularly when the concentration is not too high

Ionic Strength. The ionic strength (μ) of a solution is *a measure of the electrical intensity due to the presence of ions in the solution. It is given by half of the sum of all the terms obtained by multiplying the*

DEBYE- HUCKEL THEORY OF STRONG ELECTROLYTE:

According to this theory,

1. The strong electrolytes are completely ionised in solution at all concentrations.

2. If the solution is very dilute, the distance between the ions is large and hence the electrostatic force is very less

3. If the solution is of high concentration, the inter ionic force will be more and the electrolyte will remain in pairs such as A^+B^- known as **ionic doublet** and hence conductance decreases

4. Each ion is surrounded by ions of opposite charge giving rise to an **ionic atmosphere**
   Thus a cation is surrounded by a group of anions as represented below.

5. When an electric field is applied, the ions are set into motion . The driving force due to the applied electric field is given by

$$F = \epsilon Z V \text{-----------------------------} 1$$

where ϵ is electric field, z- charge and V – potential.

6. The movement of ion is slow down by three factors namely **viscous force, Asymmetric effect** and **Electrophoretic effect.**

1. Viscous effect(frictional force):

It arises from the viscous drag of the solvent on the movement of ions. The frictional force of solvent is given by
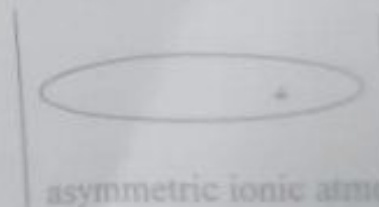
$$F_1 = Ki\ u \qquad \text{where} \quad K \text{ - coefficient of friction of solvent.}$$

2.Asymmetric effect (relaxation effect):

On passing current, the central ion moves in one direction and the ionic atmosphere in the opposite direction. The symmetry of the atmosphere about the ion is destroyed.

symmetric ionic atmosphere
(attraction is uniform in all direction)

asymmetric ionic atmosphere

Before passing current the forcing of attraction is uniform in all direction. But now the force of attraction on the central ion , becomes greater, behind the ion than in front. Consequently ,the ion experiences a retarding force which drags it backward. The movement

more strongly.

Debye–Hückel Theory of Strong Electrolytes

Peter Debye and E. Hückel, in 1923, put forward their well known theory of strong electrolytes. Broadly speaking, according to this theory, strong electrolytes which exist as ions even in the solid state must be completely ionised in solution at all concentrations. If the solvent has a high dielectric constant (e.g., water), the electrostatic forces, as already mentioned, will be small. Further, if the solution is very dilute, the distance between the ions will be large. Therefore, the electrostatic forces which vary inversely as the square of the distance between the ions, will be weakened all the more. Under these conditions, the forces of attraction between the oppositely charged ions, i.e., interionic forces, will become very small and, therefore, the ions will lie far apart from one another. If, on the other hand, the solvent has a low dielectric constant (e.g., ethanol) or if the solution is of a high concentration even when water is used as the solvent, the interionic forces will be appreciable. Under these conditions, some of the ions will not separate out completely from one another and will remain in pairs, such as A^+B^-, known as **ionic doublets.** This state of affairs is expressed by the statement that *the electrolyte is completely ionised but not completely dissociated.*

As the solution is diluted, its molar conductance increases. Arrhenius attributed this increase to increase in the degree of ionisation and used it as a method of calculating the degree of ionisation of an electrolyte by the equation

$$\alpha = \Lambda_m / \Lambda_m^\circ$$

(Eq. 4)

But, according to the modern theory of strong electrolytes, the degree of ionization of strong electrolytes is unity even at moderate concentrations. Therefore, the above relationship is not correct in the case of strong electrolytes. Debye and Hückel suggested that increase in molar conductance with dilution in the case of strong electrolytes is due to increase in the mobilities of ions due to weaker interionic attraction rather than to increase in the degree of ionisation which remains unity all along. Similarly, decrease in molar conductance with increase in concentration is not due to fall in the degree of ionization but to fall in the mobilities of ions due to greater **interionic effect.**

To understand the interionic effect, consider a very dilute solution of sodium chloride. The ions will be so far apart in this case that the forces of attraction between Na^+ and Cl^- ions will be almost negligible. The ions would act independently of each other. Their mobility or conductance will be maximum and they will make full contribution towards conductance as well as towards colligative properties. Now suppose the concentration is increased. The ions now come closer to one another, comparatively speaking, and the interionic forces of attraction are no longer negligible. In other words, the ionic mobility falls due to mutual attraction of oppositely charged ions. Their contribution towards electrical conductance decreases correspondingly.
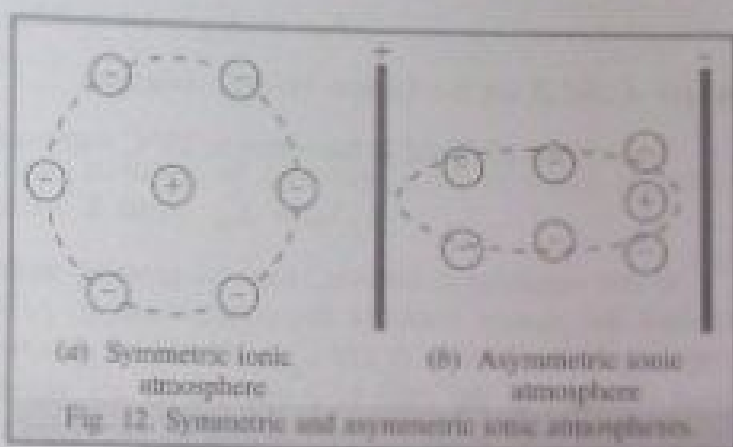
As the concentration is increased further, the oppositely charged ions come closer all the more. The interionic forces, therefore, become still more appreciable and the ionic mobility falls further.

Thus, according to this theory, *in the case of strong electrolytes, interionic attraction and not partial dissociation is the cause of decrease of conductance with increase in concentration.*

Debye and Hückel derived an equation which enabled them to calculate the magnitude of the interionic effects. The fundamental idea underlying the calculations is that each ion is surrounded by ions of opposite charge giving rise to an **ionic atmosphere**. The formation of the ionic atmosphere is explained as follows : Two opposing factors control the state of affairs in solutions of electrolytes : (1) the coulombic interaction which tends to arrange the ions in an ordered and organised structure and (2) the thermal collisions between the ions and solvent molecules which tend to prevent the existence of an organised structure in solution. At higher temperature, the structure is still less organised because of increased thermal collisions. As a result of the above two opposing factors, a situation arises when the negative ions end up as the nearest neighbours of a given central positive ion and vice versa. Thus, a cation is surrounded by more anions than cations. This gives rise to the ionic atmosphere where the central ion is surrounded by a group of ions of opposite charge.

For example, in Fig. 12(a), the central ion is positively charged and is surrounded by an atmosphere of negatively charged ions. When an electric field is applied, the ions are set in motion. The central ion moves in one direction and the atmosphere in the opposite direction. Thus, a central positive ion tends to move towards the cathode on the right while its negative ionic atmosphere tends to move towards the anode on the left, as represented in Fig. 12(b). The symmetry of the atmosphere about the ion is thus destroyed and the atmosphere becomes distorted. In other words, whereas the force of attraction exerted by the atmosphere on the central ion, before the passage of electricity, is uniform in all directions and, therefore, cancels out, it

(a) Symmetric ionic atmosphere (b) Asymmetric ionic atmosphere

Fig. 12. Symmetric and asymmetric ionic atmospheres.

becomes greater behind the ion than in front, on the passage of electricity, as shown in Fig. 12(b). Consequently, the ion experiences a retarding force, a force which tends to drag it backward. The movement of the ion, therefore, is slowed down. The drag on the central ion is known as the **asymmetry effect** because it arises from a lack of symmetry in the atmosphere of a moving ion. Similarly, we conceive of a negative central ion being surrounded by an atmosphere of positively charged ions.

Another factor that slows down the motion of the ions at higher concentrations arises from the tendency of the ionic atmosphere associated with molecules of water of hydration to move in a direction opposite to that in which the central ion is moving. Thus, a positive ion, for example, which migrates towards the cathode has to make its way through the medium (water) which, itself, is moving with the negative ionic atmosphere towards the positive electrode. Similarly, a negative ion has to move towards the anode through the medium (water) associated with positive ionic atmosphere which is moving towards the negative electrode. These counter currents slow down the ions in the same way as counter currents in a stream slow down a swimmer. This effect is known as **electrophoretic effect.**

The third factor which affects the mobility of ions is the **viscous effect**. It arises from the viscous drag of the solvent on the movement of ions. The ion tends to move in the direction of the applied electric field. This electrical force is opposed by the frictional viscous drag exerted by the solvent. For an ion with a given charge, size and shape, the greater the viscosity of the solvent, the greater is the viscous drag and hence the smaller is the ionic mobility and the conductance.

In 1926, Debye, Hückel and Onsager worked out mathematically the magnitudes of asymmetry and electrophoretic effects in terms of such factors as valency of the ion, ionic concentration and dielectric constant and viscosity of the medium. For uni–univalent electrolytes, such as KCl, which

of ion is therefore slow down. This is known as **asymmetric effect or relaxation** effect. The magnitude of relaxation force is given by, **Onsager** which is

$$\text{Relaxation force } F_2 = \frac{e^2 z k w V}{60 KT}$$

ϵ - constant, z - charge per unit volume, k - Reciprocal of thickness, $w = 2 - \sqrt{2}$, V - Applied potential, D - Dielectric constant, K - Frictional coefficient, T - Temperature

3.Electrophoretic effect: Debye Huckel Onsager eqn.

The ionic atmosphere associated with water of hydration, moves in a direction opposite to that in which the central ion is moving. Thus a negative ion moves towards the positive electrode while the medium , moves towards the negative electrode. This counter current slows down the ions. This effect is known as **electrophoretic effect.**

Debye and Huckle derived an expression for electrophoretic effect using Stoke's law

$$\text{Electrophoretic force } F_3 = \frac{\epsilon z k}{6\pi\eta} K_i V$$

where K_i - coefficient of frictional resistance

The driving force due to the applied electric field is balanced by the three forces

$$\therefore \epsilon Z V = F_1 + F_2 + F_3$$

Substituting the values of F_1, F_2 and F_3

$$\epsilon Z V = K_i u + \frac{e^2 z k w V}{6 DKT} + \frac{\epsilon z k}{6\pi\eta} K_i V \quad\text{---------2}$$

Rearranging,

$$\therefore K_i u = \epsilon Z V - \frac{e^2 z k w V}{6 DKT} - \frac{\epsilon z k}{6\pi\eta} K_i V$$

Dividing by K_i

$$\therefore u = \frac{\epsilon Z V}{K_i} - \frac{e^2 z k w V}{6 DKT K_i} - \frac{\epsilon z k V}{6\pi\eta}]$$

If the potential gradient is one volt/ cm then $V = \frac{1}{300}$

$$u = \frac{1}{300}\frac{\epsilon Z}{K_i} - \frac{1}{300}\frac{e^2 z k w}{6 DKT K_i} - \frac{1}{300}\frac{\epsilon z k}{6\pi\eta} \quad\text{---------3}$$

At infinite dilution,the thickness of ionic atmosphere is zero and hence

$K_i = 0$ and $u = U^0$ substituting in the above we get

$$U^0 = \frac{1}{300}\frac{\epsilon Z}{K_i} \quad(\text{or}) \quad 300 U^0 = \epsilon Z \quad\text{---------4}$$

Therefore equation 2 becomes

$$u = U^0 - \frac{1}{300}\frac{e^2 z k w}{6 DKT K_i} - \frac{1}{300}\frac{\epsilon z k}{6\pi\eta}$$

Lipmann potential

If the charge density is plotted against potential, it is seen that the charge on the electrode passes through a zero- charge value. The potential difference across the cell, at which the charge on the electrode is zero, is called **Lipmann potential or potential of zero charge (E_{pzc}).**
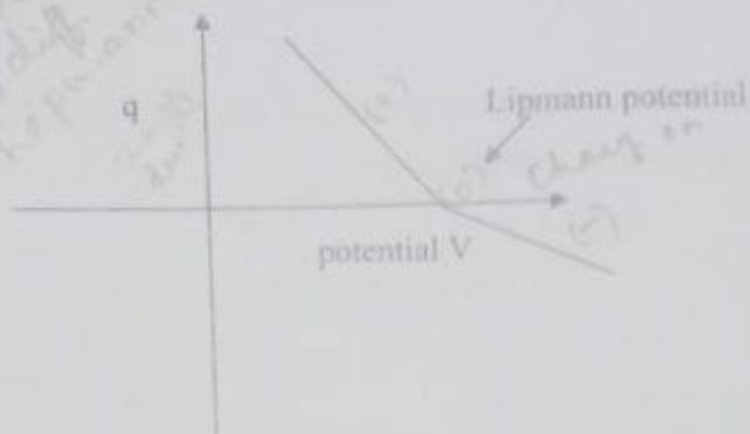
Lipmann capillary electrometer:

The relation between surface tension and potential is studied by lipmann capillary electrometer.

The apparatus consists of 1. A polarisable mercury surface 2. A non polarisable electrode calomel electrode) 3. An external source for varying potential 4. An arrangement to measure the surface tension of mercury in contact with the solution.

Diagram:

A tube narrowing to a capillary at its end is immersed in the electrolyte. The lower meniscus in the capillary is shifted by raising and lowering the mercury bulb. The height of the mercury column is measured. The surface tension is obtained by the following relation

$$\gamma = \frac{hr\rho g}{2}$$

where h – height of the mercury

Correction proposed by Shedlovsky

The above equation can be written as

$$\lambda = \lambda^0 - (A + B\lambda^0)\sqrt{C}$$
$$= \lambda^0 - A\sqrt{C} - B\lambda^0 \sqrt{C}$$
$$= \lambda^0 (1 - B\sqrt{C}) - A\sqrt{C}$$

$$\lambda + A\sqrt{C} = \lambda^0 (1 - B\sqrt{C})$$

$$\therefore \lambda^0 = \frac{\lambda + A\sqrt{C}}{(1 - B\sqrt{C})}$$

an emprical correction proposed by Shedlovsky is $\lambda^0 = \frac{\lambda + A\sqrt{C}}{(1 - B\sqrt{C})}$

$$\Lambda = \Lambda_0 - \left(\Lambda + B\Lambda_0\right)\sqrt{C}$$

$$\Lambda = \Lambda_0 - A\sqrt{C} - B\Lambda_0\sqrt{C}$$

$$\Lambda = \Lambda_0\left[1 - B\sqrt{C}\right] - A\sqrt{C}$$

$$\Lambda + A\sqrt{C} = \Lambda_0\left[1 - B\sqrt{C}\right]$$

$$\frac{\Lambda + A\sqrt{C}}{1 - B\sqrt{C}} = \Lambda_0$$