Chapter 9

ELECTROCHEMISTRY

9.1 INTRODUCTION

Electrochemistry is a branch of Physical chemistry which deals with the study of all physical and chemical processes which are brought about by electrical energy and the processes which proceed with the generation of electrical energy. It concerns itself with the interrelation of electrical energy (electricity) and chemical phenomena i.e. the conversion of electrical energy into chemical energy and vice versa. Simply one can say that electrochemistry deals with the relationship between the electrical energy and chemical changes.

Much of the Chemistry involves species that have charge. Electrons, cations and anions all are charged particles that interact chemically. Often electrons move from one chemical species to another to form something new. These movements can be spontaneous, or they can be forced. They can involve systems as simple as hydrogen and oxygen atoms, or as complex as million-peptide protein chain. The presence of discrete charges on chemical species introduces a new aspect that we must consider, the fact that like charges repel and opposite charges attract. In considering how charged particles interact, we have to understand the work involved in moving charged particles together and apart, and the energy required to perform that work. Energy, work-these are concepts of thermodynamics. Therefore, our understanding of chemistry of electrically charged particles, *electrochemistry*, is based on thermodynamics.

Electrochemistry is concerned with the appearance and disappearance of electrical energy in the surroundings when the chemical reactions occur in a system, it is necessary that the system must be electrically conducting. Such a communication between the system and surrounding can be achieved by using either a metallic or an electrolyte conductor. It is, in fact, the study of lather, which is generally assumed to fall under the purview of electrochemistry. For the fact that electrolytic solutions need a metallic conductor for developing an electrical contact, the electrochemistry, to be more specific involves the study, or processes at the metal-electrolyte and electrolyte-electrolyte interfaces.

Few people realize the applications of electrochemistry in modern life. All batteries and fuel cells can be understood in terms of electrochemistry. Batteries, which produce, electrical energy by means of chemical reactions, are used to power toys, flash light, electronic calculators, pacemakers, that maintain the rhythm of heart, radios, tape recorders and even some automobiles (hybrid cars). Any oxidation-reduction process can be considered in electrochemical terms. In the laboratory electrical measurements enable us to monitor chemical reactions of all sorts, even there is systems as tiny as living cells. In industry many important chemicals-including liquid bleach (sodium hypochlorite) and lye (sodium hydroxide which is used to manufacture soap) are manufactured by electrochemical reactions. In fact, if its were not for electrochemical reactions, the important structural metals (aluminium and magnesium) would be only laboratory curiosities. Corrosion of metals, non-metals and ceramics is electrochemistry. Besides the practical applications fundamental information about the chemical reactions is available from the electrical measurements, for example, free energy changes, equilibrium constants etc. Many of the virtually important biochemical reactions involve the transfer of charge, which is electrochemistry.

Electromechanical processes non-a-days have found wide applicability. The electrolytic and electrosynthetic methods are frequently employed for the preparation of chemical products. Electrochemical methods of analysis, e.g., electrolysis, conductometry potetniometry polarography, voltametry etc. have been greatly developed in the recent years.

9.2 CONDUCTORS AND INSULATORS

We know that electrical energy or electricity is a stream of electrons. The substances which allow the passage of electricity or electric current through them are called *conductor*. It may, however, be pointed out that not all the conductors conduct electricity to the same current. Depending upon the ease with which they allow the passage of electricity they are named as *good conductors* or *bad conductors*. Although it is not possible to sharply distinguish between the good or bad conductors, but a rough division is possible on the basis of relative ease with which the conductors allow the passage of electric current. The substances which do not conduct electric current are called *insulators* or *non-conductors*, e.g. wood, rubber etc.

Conductors, in general, can be classified into three categories, viz. gaseous metallic and electrolytic.

(i) The gases conduct electric current under high potential differences at low pressure, or when exposed to certain radiation.

(ii) In the metallic or electronic conductors, the charge carries are the electrons, the atomic nuclei remaining stationary, and the passage of electric current is not accompanied by any movement of matter. Such a mode of conduction of electric current is called *metallic* or *electronic conduction*. It is exhibited by pure metals, alloys, carbon and certain solid salts and oxides. Metallic conductors are the best conductors of electric current. This mode of conduction decreases with rise in temperature.

(iii) The electrolytic conductors (also known as ionic conductors) transport electric current through the movement of charged particles of atomic or molecular dimensions called *ions*. Since ions are heavy, the electrolytic conductor are less conducting as compared to metallic conductors. The ionic conduction increases with rise in temperature. Solutions of salts, acids and bases in water or some other solvents are examples of ionic conductors.

The above classification of conductors is a relative one. Certain solids like β-Ag_2S, ZnO, CuO etc. exhibit mixed conductivity. A transition form electrolytic to mixed conductivity is also observed in some salts, e.g. Cu_2Cl_2 when they are heated. A similarly transition to mixed conductivity is observed in solutions of the alkali and alkaline earth metals in liquid ammonia at higher salt concentrations. Conduction of current through metallic and ionic conductors may be briefly distinguished as given below.

Metallic Conduction	Ionic Conduction
(i) It is by virtue of flow of electrons in the conductor.	(i) It is by virtue of the movement of ions in the solution or a fused electrolytes.
(ii) It involves no change in the chemical properties of the conductor.	(ii) It involves chemical reactions which take place at electrodes e.g. oxidation-reduction.
(iii) It does not involve the transfer of matter.	(iii) It involves the transfer of matter in the form of ions.
(iv) It decreases with rise in temperature offered to the moving electrons by the oscillating atoms or ions composing the conductors.	(iv) It increases with rise in temperature due to increase in the mobility of ions and increase in the degree of ionization of electrolytes.

9.3 OHM'S LAW AND ELECTRICAL UNITS

An electrolytic solution contains free ions in addition to other kinetically identifiable species. When an electrical potential is applied across the solution, the macroscopic observations arc; the flow of the current through the solution and the chemical changes generally resulting in the liberation or dissolation of the electrode material at the points where the current enters or leaves the solution. This phenomenon of decomposition of solution by electric current is termed *electrolysis*. The relationship between the applied potential and the current flowing is given by Ohm's law.

According to Ohm's law the strength of an electric current (I) flowing through a conductor is directly proportional to the potential difference applied (V) across the conductor and inversely proportional to the resistance (R) offered by the conductor to the current, i.e.,

$$I = \frac{V}{R} \tag{9.1}$$

By making appropriate choice of units, the constant of proportionality is made unity. According to International System, the units of current, resistance are potential are ampere, ohm and volt respectively.

The international ampere is defined as the invariable current of such strength of that on passing through an aqueous silver nitrate solution will deposit 0.001118 g of silver in one second.

The international ohm is *defined as the resistance at 0°C of a column of uniform cross section, 106.3 cm long and containing 14.4521 of g mercury.*

The international volt is *defined as the potential difference required to send a current of one ampere through a resistance of one ohm.*

The quantity of electricity is *measured in international columns. It is the quantity of electricity passing through a conductor when a current of one ampere flows in one second. Hence the quantity of electricity is given by the relation.*

$$Q = I \times t \quad (9.2)$$

Another unit to measure the quantity of electricity is the *Faraday (F). It is equal to 96,500 coulombs. The main significance of F is that it is the amount of change that produces one equivalent of chemical change.*

The electrical work (W) performed when a current of strength I passes for t second through a resistance across which the potential difference is V, is given by

$$W = VIt = VQ \quad (9.3)$$

where w is expressed in joules. The Joule is the electrical unit of energy and is defined as the amount of work performed by a current of one ampere following or one second under a potential difference of one volt.

$$1J = 1 \times 10^7 \text{ ergs} = 0.2390 \text{ cal}$$

Finally, the rate at which work is being done by an electric current is expressed in watt. A *watt* is worked performed at the rate of 1 Joule per second, and is a unit of electrical power.

9.4 ELECTROLYTIC CONDUCTANCE

Electrolytic or ionic conductors are good conductors of electricity. The electrical conductance of an electrolyte is due to the ions it contains. The greater the concentration of the ions, the higher will be the conductance. The interesting feature off electrolytic solutions is not that they resist the flow of electricity, but that they allow it to flow. Consequently, the important value is electrochemistry is conducting power. The conductance (L) of a system is reciprocal of its resistance (R). Thus conductance is defined as

$$L = \frac{1}{R} \quad (9.4)$$

The SI unit of conductance is Siemen (symbol S). Since resistance (R) is measured in ohms (symbol Ω, omega), its reciprocal, the conductance is defined with the units of reciprocal ohm, ohm^{-1} or mho and denoted as Ω^{-1} (omega inverse). Following the SI system of units, we shall use S to define the conductance.

To compare the conductivity of different solutions, the size of the electrodes and the distance between the electrodes must be standardized. It has been found that the resistance offered by a solution is directly proportional to the distance between the electrode and inversely proportional to the area of the cross section of solution between the electrodes

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

$$R = \rho \frac{l}{A} \qquad (9.5)$$

where l is the difference between the electrodes, A is the area of cross section and ρ(rho) is the constant of proportionality known as the *specific resistance* or *resistivity*. If in the above equation $l = 1\text{m}$, $A = 1\text{m}^2$, then $R = \rho$. Hence the specific resistance is the resistance of a conductor of unit length and of a unit area of cross section. In other words, specific resistance is the resistance of a meter cube of the material. The SI units of the specific resistance is ohm.m or Ω.m.

The *specific conductance* or *conductivity* of any conductor is defined as the reciprocal of the specific resistance. It is represented by LS.

Since $Ls = \frac{1}{\rho}$

Equation (9.5) becomes

$$\rho = R \cdot \frac{A}{l}$$

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A}$$

Hence $Ls = \frac{1}{R} \cdot \frac{l}{A}$ $\qquad \left(\because L = \frac{1}{R}\right)$

$$Ls = L \cdot \frac{l}{A} \qquad (9.6)$$

Now if $l = 1\text{m}$, and $A = 1\text{m}^2$, then

$$Ls = L \qquad (9.7)$$

Hence the specific conductance is the conductance of a material of unit length and unit area of cross section.

Alternatively, specific conductance is the conductance of a one meter cube of the material. For electrolytic solutions, it is the conductance of a meter cube of the solution. Since the specific resistance is measured in ohm × m, the units of the specific conductance will be $\text{ohm}^{-1} \cdot \text{m}^{-1}$ or mho m^{-1} or S m^{-1}.

Conductance (L) and specific conductance (Ls) are additive properties. If a number of electrolytes are present together in a dilute solution, the total conductivity is equal to the sum of Ls values of individual electrolytes.

$$Ls = \sum_i Ls_i + Ls_{H_2O}$$

Likewise $L = \sum_i L_i + L_{H_2O}$

where $\sum_i Le_i$ denotes the sum of the conductivities of all the electrolytes present in the solution and Le_{H_2O} is the conductivity of water. By repeated distillation of water with small amounts of $KMnO_4$ added to it (to oxidize organic impurities) specific conductance of water (Le_{H_2O}) can be reduced to minimum. Water prepared in this manner is called conductivity water ($LeH_2O = 1 \times 10^{-8}$ S m^{-1}). Conductivity water is used for property solutions of electrolytes for conductivity measurements.

9.5 EQUIVALENT AND MOLAR CONDUCTANCE

At any fixed temperature, the conductivity of a solution depends partly on the number of charges per unit volume, which for different solutions may contain different amounts of electrolytic charges. Since the point of interest is to compare the current carrying ability of a given number of electrolytic charges at different concentrations, it is not much rewarding the consider the conductivity/specific conductance as a fundamental quantity. In order to compare the conductance of an electrolyte with another electrolyte, the fundamental weight of an electrolyte must be dissolved in the same volume of the solution. This weight is either the equivalent weight or the molecular weight.

The *equivalent conductance* of an electrolyte is defined as the conductance of a volume of the solution containing one gram equivalent of dissolved substance when placed between two parallel; electrodes 1m apart, and large enough to contain between them all of the solution. It is represented by $\wedge$ (lambda) and never determined directly, but is calculated form the specific conductance. It represents the conductivity power of all the ions produced by dissolving one gram equivalent of the electrolyte at a given dilution and temperature.

$$\wedge = Ls \times V \tag{9.8}$$

If C represents the concentration of a solution in gram equivalent per litre, then the volume containing one equivalent of the electrolyte is $\frac{10^{-3}}{C}$ m^3. If Ls represents the specific conductance S m^{-1}, then the equivalent conductance is given as

$$\wedge = \frac{Ls \cdot 10^{-3}}{C} \tag{9.9}$$

The units of equivalent conductance are S m^2 eq^{-1}, but in common use the last term is generally dropped out. The SI unit is S m^2.

Another quantity which is quite often used is the *molar conductance* (μ). it is defined as the conductance due to ions produced by one mole of the electrolyte at a given dilution and temperature. It may be defined as the conductance of a volume of a solution containing one mole of the electrolyte when placed between two parallel electrodes 1m apart and large enough to contain between them the whole of the solution. It is equal to the product of specific conductance (La) and volume of the solution containing one mole of the electrolyte.

$$\mu = La \times V$$

If C represents the concentration in mole per litre, then

$$\mu = \frac{La \times 10^{-3}}{C} \text{ S m}^2 \text{ mol}^{-1} \qquad (9.10)$$

$\wedge$ is related to the μ through the relation

$$\wedge = \frac{\mu}{\text{Total no. of equivialents of cationic (or anionic)charges per mole of salt}} \qquad (9.11)$$

or $$\wedge = \frac{\mu}{Z} \qquad (9.12)$$

where Z = total positive charge carried by cations or total negative charge carried by anions furnished by a molecule of an electrolyte on dissociation. For example,

$$NaCl \longrightarrow Na^+ + Cl^- \qquad (Z = 1)$$

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^{-1} \qquad (Z = 2)$$

$$Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-} \qquad (Z = 6)$$

9.6 MEASUREMENT OF CONDUCTANCE

The conductance of a solution of an electrolyte can be determine by measuring the resistance offered by the solution contained within the two electrodes of a conductivity cell. By knowing the resistance, one can determine the conductance just by reciprocating the resistance. The measurement of the resistance is most frequently carried out with some form of Whetstone bridge circuit, the principle of which may be explained with the aid of Fig.9.1. Four resistance R_1, R_2, R_3 and R_4 are connected in such a way so as to form a loop/mesh ABCDA. A battery of emf 'E' is connected between point B and D and a galvanometer 'G' is connected between A and C. This circuit is known as whetstone bridge circuit. The bridge is said to be balanced if no current from battery E flows through the galvanometer G. When no current flows through the galvanometer, it means that the potential difference from the one terminal of the galvanometer to the other terminal of the galvanometer is the same. This is known a balancing condition of the bridge. Galvanometer is a device which detects small amount of electric current.

The solution whose conductance is to be found out in terms of resistance, is placed in a special type of cell, called conductivity cell. It is placed in one arm of the bridge and a variable standard resistance (Rs), e.g. a resistance box in the other arm. AC is a uniform slide wire across which moves a contact point D. The resistance Rs is such adjusted that when the contact point D is moved along AC, the galvanometer shows no deflection, i.e. the null point is obtained. One can also use some other

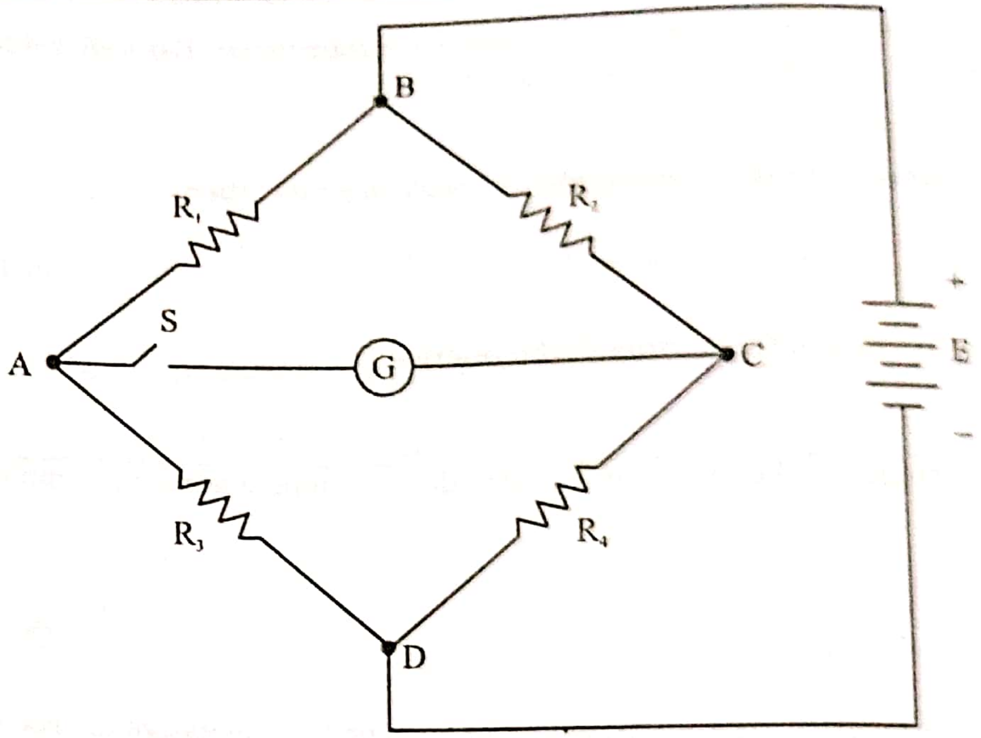


Fig. 9.1 Wheatsonte bridge circuit for resistance measurement

detecting devices like earphone, which gives minimum sound at the null point. When this state of balanced is achieved, the two terminals of the detector arc at the same potential. The potential difference/drop across the different parts of the bride must be such that

$$E_X = Es \quad (9.13)$$

and $$E_a = E_b \quad (9.14)$$

According to Ohm's law ,the difference of potential E, is equal to the current (I) and the resistance (R)

$$E_X = R \times I_X \quad E_S = R_s I_s$$

$$E_a = R_a I_a \text{ and } E_b = R_b I_b$$

According to Equ. (9.13) and (9.14)

$$R_X \times I_X = R_s I_s \quad (9.15)$$

$$R_a I_a = R_b I_b \quad (9.16)$$

Dividing Eq. (9.15) by Eq. (9.16), we get

$$\frac{R_X I_X}{R_a I_a} = \frac{R_s I_s}{R_b I_b} \quad (9.17)$$

Further $I_X = I_a$ and $I_s = I_b$, since the current flowing through two resistance in series must be same in each resistance.

Under the balanced conditions, when no current flows through the detector, then Eq. (9.17) reduces to

$$\frac{R_X}{R_a} = \frac{R_s}{R_b}$$

$$R_X \text{ (unknown)} = \frac{R_a}{R_b} \times R_s \qquad (9.18)$$

The resistance R_a and R_b are proportional to the length of the wire AD and CD respectively. Thus, we have

$$R_X = \frac{\text{Length AD}}{\text{Length CD}} \times R_s \qquad (9.19)$$

Since R_s, length AD and CD are known, the resistance R_X of the solution can be calculated, from which one can determined the conductance, specific conductance and equivalent/molar conductance. As the conductance is affected by the temperature, the conductivity cell is always placed in the thermostat which is maintained at constant temperature. (Fig. 9.2)

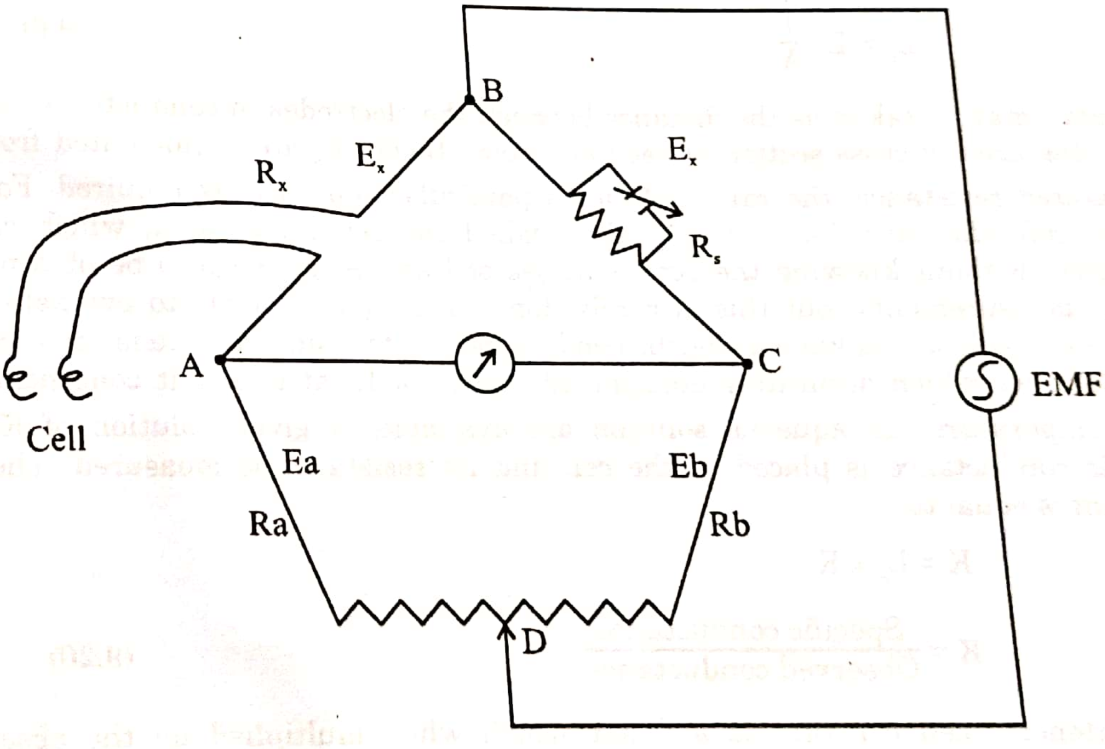


Fig. 9.2 A.C. Whetstone bridge for conductance measurement

Although the principle of the whetstone bridge as given above remains the same several modifications in technique are necessary before resistance of an electrolytic solution can be measured by this method. Direct method cannot be used, as this would cease electrolysis and concentration changes at the electrodes. The gas if liberated increases the resistance at the electrodes. These gases also set up a counter emf of polarization which opposes the passage of the current. To avoid these, an alternatively current is employed, usually a frequency of 500 — 2000 Hz is supplied by either a vibrating tuning fork or a vacuum-tube oscillator. In AC current, the direction of the current is reversed about a thousand times per second with the result that the polarization produced by each pulse of the current is neutralized by the next pulse.

The conductivity cells are constructed of glass with electrodes of either platinum or gold. To overcome imperfections in the current and other effects, so as to decrease the effects of polarization of electrodes, the electrodes are coated with a layer of finely divided platinum black. This is done by electrolysis of 3% solution of chloroplatinic acid containing traces of lead acetate. If the finely divided platinum serves either as a catalyst for decomposition or oxidation of the solution or as an adsorbents for adsorption of ions, the grey platinum surface electrodes may be employed instead. The latter can be obtained by heating the platinized electrode to red heat.

9.7 CELL CONSTANT

The specific conductance of an electrolytic conductor is defined as

$$L_s = \frac{1}{R} \cdot \frac{l}{A}$$

$$L_s = L \cdot \frac{l}{A} \qquad (9.6)$$

where l may be taken as the distance between the electrodes in conductivity cell and A is the area of cross section of each electrode. Before L_s an be calculated from the measured resistance, the ratio (l/A) for a particular cell used, is required. For any given cell, the ratio has a fixed value, called the *cell constant* K, which can be obtained without knowing the actual values of l and A. It can also be obtained by direct measurements, but this is rarely done, since it is possible to evaluate it by means of a solution of known specific conductance. Potassium chloride is the accepted standard for which accurately determined values of L_s at different concentrations and temperatures in aqueous solution are available. A given solution of KCl of specific conductance is placed in the cell and its resistance is measured. The cell constant is equal to

$$K = L_s \times R$$

$$K = \frac{\text{Specific conductance}}{\text{Observed conductance}} \qquad (9.20)$$

Hence, cell constant is a factor which when multiplied by the observed conductance of a solution, gives its specific conductance. KCl is available in pure state. It is 1 : 1 electrolyte and ionic mobilities of K^+ and Cl^- ions are comparable. The ionic radii of both ions are equal. Its values of specific conductance are available in the literature at different concentrations and temperatures. The dimensions of cell constants are

$$K =- \frac{l}{A} = \frac{m}{m^2} = \frac{1}{m} = m^{-1}$$

Table 9.1 shows the specific conductance of 0.01, 0.1 and 1.0 N solutions of KCl at different temperatures.

Table 9.1 Specific Conductance of KCl solutions

Concentration eqiv. dm^{-3}	L ($S\ m^{-1}$)		
	273 K	291 K	298 K
1.0	6.5170	9.7840	11.1900
0.1	0.7140	1.1166	1.2890
0.01	0.0774	0.1221	0.1413

Example 9.1

A conductivity cell was filled with 0.01 M KCl which was known to have a specific conductivity of 0.1413 $S\ m^{-1}$ at 298 K. Its measured resistance at 298 K was 94.3 ohms. When the cell was filled with 0.02 M $AgNO_3$, its resistance was 50.3 ohms Calculate (i) the cell constant, (ii) the specific conductance of $AgNO_3$ solution.

Solution

Here LS = 0.1413 $S\ m^{-1}$

R = 94.3 ohms

(i) Using the relation

$$L_s = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$

$$\left(\frac{l}{A}\right) = \text{cell constant} = L_s \times R$$

$$= (0.1413)\ (94.3)$$

$$= 13.32\ m^{-1}$$

(ii) Now R = 50.3 ohms

$$\frac{l}{A} = 13.32\ m^{-1}$$

$$L_s = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$

$$= \frac{13.32}{50.3}$$

$$= 2.648 \times 10^{-1}\ S\ m^{-1}$$

Example 9.2

The resistance of a conductivity cell was 720 ohms when filled with 0.1 N KCl solution (specific conductance = 0.14807 S m^{-1}) and 6920 ohms when filled with 0.01 N acetic acid solution. Calculate cell constant and equivalent conductance of the acid solution.

Solution

The cell constant is given as

$$\left(\frac{1}{A}\right) = L_s \cdot R$$

$$= (0.14807)\,(702)$$

$$= 103.94\ \text{m}^{-1}$$

The specific conductance of acetic acid is given by

$$L_s = \frac{1}{R} \cdot \left(\frac{1}{A}\right)$$

$$= \frac{103.94}{6920}$$

$$= 1.50 \times 10^{-2}\ \text{S m}^{-1}$$

Now $\quad C = 0.01\ \text{N} = 0.01\ \text{mol dm}^{-3}$

Therefore,

$$\wedge = \frac{LS}{C} \times 10^{-3}$$

$$= \frac{1.50 \times 10^{-2}}{0.01} \times 10^{-3}$$

$$= 1.5 \times 10^{-3}\ \text{S m}^2\ \text{eqiv}^{-1}$$

9.8 VARIATION OF CONDUCTANCE WITH CONCENTRATION

We know that the specific conductance of a solution increases with increasing concentration. For strong electrolytes, the increase in specific conductance with increase of concentration is sharp. However, for weak elect5olytes, the increase in specific conductance is more gradual. In both cases, the increases in conductance with concentration is due to an increase in the number of ions per unit volume of the solution. For strong electrolytes, which are completely ionized, the increase in specific conductance is almost proportional to the concentration. In weak electrolytes, however, the increase in specific conductance is not large due to low ionization of the electrolytes, and consequently the specific conductance does not go up so rapidly as in the case of strong electrolytes.

Table 9.2 shows the variation of equivalent conductance of a number of electrolytes at various concentration at 298 K. It is observed that in contrast to the specific conductance, the equivalent conductance Λ invariably increases with decreasing concentration for both weak and strong electrolytes.

Table 9.2 Equivalent Conductance of Electrolytes in Aqueous Solutions at 298 K ($10^4 \times S\ m^2\ equiv.^{-1}$)

Equivalent Per liter	KCl	NaCl	HCl	$AgNO_3$	CH_3COH	CH_3COONa
1.0	111.9	89.9	332.8	–	–	49.1
0.1	129.0	106.7	391.3	109.1	5.2	72.8
0.05	133.4	111.1	399.1	115.7	7.4	76.9
0.01	141.3	118.5	412.0	124.8	16.3	83.8
0.005	143.5	120.6	415.8	127.2	22.9	85.7
0.001	146.9	123.7	421.4	130.5	49.2	88.5
0.0005	147.8	124.5	422.7	131.4	67.7	89.2

The above results are depicted in Fig.9.3 in which the equivalent conductance, Λ, of electrolytes at a constant temperature is plotted against $\sqrt{C}$. It ma be seen from the figure that two different types of behaviours are exhibited. The electrolytes which show a linear plot (almost straight lines) are classed as strong electrolytes. e.g. salts like NaCl, KCl or acids such a H_2SO_4, HCl etc. The electrolytes which seem to approach the dilute solution limits almost tangentially are classed as weak electrolytes, e.g. ammonia, acetic acid etc. It is however, impossible to draw a sharp line of demarcation between the two categories as many substance are known to exhibit intermediate behavior, e.g., $NiSO_4$. Such electrolytes are sometimes called moderately strong electrolytes.

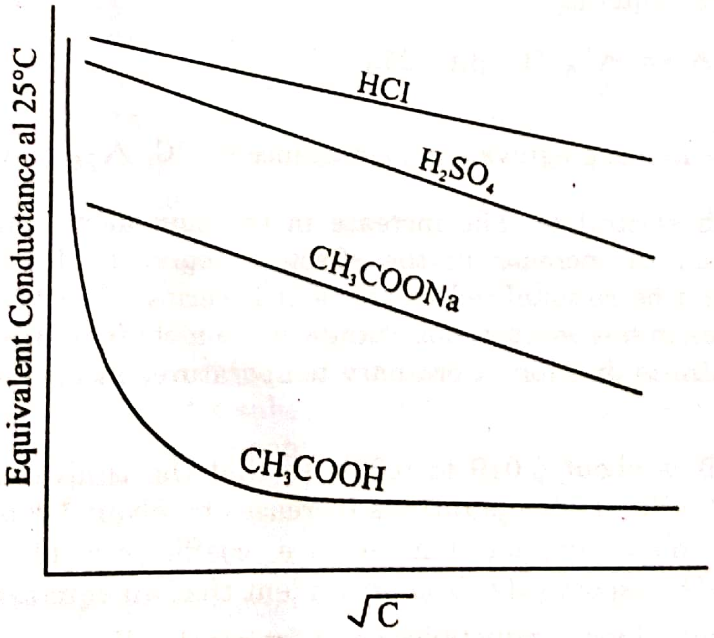


Fig.9.3 Equivalent conductance of strong and weak electrolytes

The conductance of a solution depends on the number of ions and the speed with which the ions move in solution. In case of strong electrolytes, the number of ions is the same at all dilutions (since strong electrolytes are completely ionised) and the variation of equivalent conductance with dilution is therefore due to the change in the speed of the ions with dilution. In a concentrated solution of such electrolytes, the interionic attractions among the oppositely charged ions would be quite appreciable. The ions may also form some ion-pairs of the type A^+B^- which would not contribute to the conductance. These interionic forces considerably lower the speed of ions and hence the conductivity of the solution. As the dilution is increased the interionic attractions decrease with the result that the ions will move more freely and independently of their co-ions and thus increasing the equivalent conductance with dilution.

In case of weak electrolytes, the increase in equivalent conductance with dilution is mainly due to (a) an increase in the number of ions in the solution (degree of ionization increases with dilution), and (b) smaller inter-ionic attractions at higher dilutions.

For weak electrolytes, the increase in the number of ions has been explained on the basis of Arhenius theory of electrolytic dissociation whereas for strong electrolytes has been explained on the basis of Debye-Huckel-Ousager theory. In brief, the increase in the number of ions in case of weak electrolytes is due to the increase in the degree of ionization of the electrolyte on dilution, whereas in the case of strong electrolytes, this increase is due to the weakening of the ion-ion interactions on dilution.

9.9 EFFECT OF TEMPERATURE ON THE CONDUCTANCE

The conductance of all electrolytes increases with temperature. The variation of equivalent conductance at infinite dilution ($\wedge_0$) with temperature can be represented by the equation

$$\wedge_{t^\circ} = \wedge_{25^\circ}\,[1 + \beta(t - 25)] \qquad (9.21)$$

where $\wedge_{t^\circ}$ is the limiting equivalent conductance at t°C, $\wedge_{25^\circ}$ that at 25°C, and β a constant for each electrolyte. The increase in the equivalent conductance may be explained in terms of increase in the effective degree of dissociation at higher temperature or can be rationalized in terms of lowering of restricting potential for migration with rise in temperature (or change in the mobility of the ions). Equivalent conductance at infinite dilution at ordinary temperatures increases by about 2% per degree.

For salts β is about 0.019 to 0.021, so that the equivalent conductance at infinite dilution at ordinary temperatures increases by about 1.9 to 2.2% per degree. Acids and bases have smaller temperature coefficients (β values) they are approximately 0.018 respectively. It is an evident that an equation similar to (9.21) must hold for individual ion conductances and for nearly all ions, except H^+ and OH^-. For H^+ the value of β is 0.0142 and for OH^- it is 0.016. As a rough generalization, it may be said that the higher the ionic conductance, the smaller the temperature coefficient.

The above results apply particularly to infinite dilution, but similar conclusions hold for strong electrolytes at appreciable concentration. Weak electrolytes however, show some abnormalities; the conductance of such solutions is mainly dependent on the degree of ionization. This usually decreases with rise in temperature, the conductance, may increase to maximum and then decrease as the temperature is raised.

The conductance of a solution varies slightly with pressure, the effect being mainly due to the change in the viscosity of the medium, and consequently alternation in the speed, and hence the conductance, of ions. The viscosity of a dilute solution is generally decreased by an increases of pressure; this is accompanied by an increase of the equivalent conductance, provided the pressure is not too high. This effect is more marked with a weak than with a strong electrolyte; increase of pressure favours the ionization in case of weak electrolyte.

9.10 EFFECT OF DIELECTRIC CONSTANT OF THE SOLVENT ON CONDUCTANCE

The conductance behaviour observed in non-aqueous solvents depends much on the dielectric constant of the medium. The dielectric constant of water is high, 78.6 at 25°C, whereas that of most other solvents is considerably lower. The dielectric constants at 25°C for methanol, ethanol and dioxane arc, 31.5, 24.3 and 2.2 respectively. As the dielectric constant of the solvent is lowered, the conductance of the electrolyte in the medium also decreases. Beyond this conductance drop, the conductance behaviour of these substances is not very different in nonaqueous solvents from that in water, provided the dielectric constant is above 25.

For examples, the halides and nitrates of alkaline metals, the thiocyanates of alkali and alkaline earth metals, and the tetraalkyl ammonium salts are strong electrolytes in methyl and ethyl alcohols and behave pretty much as do strong electrolytes in water. In solvents of dielectric constant less than 25, the dependence of equivalent on concentration becomes complex. In these solvents ions exhibit a tendency to associate into complexes such a $A^+ B^-$, $A^+B^-A^+$ and $A^-A^+B^-$ which decreases the number of ions available to carry current, and hence the conductance.

9.11 EFFECT OF VISCOSITY ON CONDUCTANCE

It has been observed that the movement of an ion is not influenced by other ions in an infinitely dilute solution, so the movement may be considered to be identical with the movement of a spherical particle in a medium of viscosity η. That is to say that Stokes's law may be applied to the movement of an ion. It follows that the product of the speed of the ion and the viscosity of the medium should be constant. The equivalent conductance of and ion at infinite dilution depends only on its speed, and so the product of ion conductance an viscosity should be independent of the nature of the solvent. This relationship known as *Walden's* rule was put forward by P. Waldeen (1906) in the form

$$\Lambda_o \eta_o = \text{constant} \tag{9.22}$$

for a given electrolyte, when η_0 is the viscosity of the solvent in which the equivalent conductance at infinite dilution is Λ_0. The Walden's rule may be started in words as, "The product of limiting equivalent conductance of a given solute and viscosity of the pure solvent is constant."

The constant in Equ. (9.22) is independent of temperature and nature of the solvents and the value of $(C_2H_5)_4$ NI in more than 30 solvents at 0°C is 0.70, i.e.,

$$\Lambda_0\eta_0 = 0.70$$

The above rule of Walden does not apply to water and glycol as solvents. For water $\Lambda_0\eta_0 = 1$ and the value of constant was observed to vary with the nature of solute. A particular ion does not have the same effective radius in different solvents. It is probable that the ions are solvated in the solution. Since the extent of solvation as well as the size of solvating molecules, varies with the nature of the solvent, the effective radius will not be constant. The ions have different effective radii in different solvents due to difference in the extent of solvation. As the solvation effects are quite prominent for smaller ions (particular small cations), the deviation from the Walden's rule would be quite severe for smaller cations. Larger cations do not undergo solvation to an appreciable extent, and hence the Walden's product for such ions remains constant even in different types of solvents.

9.12 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the behavior of solutions of electrolytes. Arrhenius (1887) put forward the theory of electrolytic dissociation in aqueous solutions. The main points of this theory in this modern form may be summed up as follows:

(i) The electrolytes in solution are dissociated into electrically charged particles called ions. The positively charged particles are called cations and the negatively charged particles are known as anions. A dynamic equilibrium exists in the solution between the undissociated molecules and the ions which dissociate from the electrolytes, that is

$$MA \rightleftharpoons M^+ + A^-$$

(ii) The ions are free to move independently under the influence of an applied electric field. Cations move towards the negative electrode or cathode and the anions move towards the positive electrodes or anode.

(iii) The number of positively charged cations and negatively charged anions may be different. However, the total charge carried by cations is equal to the total charge carried by anions. The net result is that the solution as a whole is electrically neutral in spite of the presence of charged particles.

(iv) The extent of dissociation is different for different electrolytes and depends on the concentration of electrolyte, temperature and nature of electrolyte.

The amount of electrolyte which dissociates into ions varies with its concentration. It may then be anticipated from the law of chemical equilibrium that the extent of dissociation increases with the decrease in concentration and attains a limiting value at very high dilution. At extreme dilutions, all the electrolytes are completely dissociated into ions. The fraction of the total number of molecules dissociated, is called the degree of dissociation (α). Thus

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Total numbr of molecules}}$$

Calculation of the degree of dissociation for various electrolytes in aqueous solutions show that practically all salts, and strong acids and bass are highly ionized in water. These are known as strong electrolytes. Aqueous solutions of these electrolytes are therefor good conductors of electricity. On the other hand, there are many substances whose aqueous solutions are poor conductor of electricity. These include many organic acids and bases (such as acidic acid, benzoic acid, methyl amine, aniline etc.), inorganic acids and bases (such as carbonic acid, hydrocyanic acid, ammonium hydroxide etc.). These are called weak electrolytes. This division into strong and weak electrolytes is a qualitative one. There are some electrolytes such as $BaCl_2$ etc. which exhibit an intermediate behaviour.

Limitations of the Arrhenius Theory

Arrhenius theory is satisfactory for weak electrolytes. However, when applied to strong electrolytes many anomalies have been observed which seriously question the validity of some of the postulates of theory. Some of the important discrepancies are:

(i) The degree of dissociation obtained from conductivity measurement and form colligative properties are in good agreement for weak electrolytes. But for the strong electrolyte the agreement is very poor.

(ii) The Ostwald's dilution law is obeyed by weak electrolytes but not all by strong electrolytes.

(iii) Arrhenius theory assumes the existence of ions but does not take into account the electrostatic attraction between ions. The effect of interionic attractions is quite small in solutions of weak electrolytes, but in case of strong electrolytes, this effect is quite pronounced.

These points conclude that Arrhenius theory is essentially valid for weak electrolytes but does not describe the behavior of strong electrolytes.

9.13 THE OSTWALD'S DILUTION LAW

Arrhenius theory of electrolytic dissociation assumes a dynamic equilibrium between ions and unionized molecules. The law of mass action can also be applied to equilibrium involving ions in the same manner as was done in chemical equilibrium. The application of the law of mass action to the weak electrolytes was first attempted by Ostwald (1888) and the equation deduced by him is known as Ostwald's dilution law.

Consider a binary electrolyte AB which dissociates into charged ions A^+ an

B^- according to the equation

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

$$\text{and} \quad C = 0.505 \text{ mol dm}^{-3}$$

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{2.211 \times 10^{-4}}{390.71 \times 10^{-4}} = 0.0057$$

Applying Ostwald's dilution law in case of acetic acid dissociating as

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{(0.505)\,(0.0057)^2}{1-0.0057}$$

$$= 1.65 \times 10^{-5}$$

9.14 THEORY OF STRONG ELECTROLYTES

The conductance of solution of given electrolyte depends on two factors, namely, the number of ions and their speeds. If the electrolyte is completely dissociated, it is called *strong electrolyte* and if it dissociates partially, it is called *weak electrolyte*. With regard to the conductances of both weak and strong electrolytes, it was observed that the equivalent/molar conductances decreases with increase in concentration. Why?

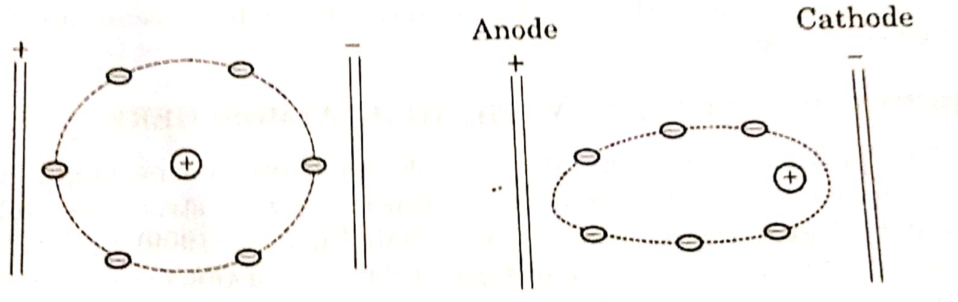
The decrease in equivalent conductance with increase in concentration for weak electrolytes can be explained as due essentially to a decrease in the degree of ionization. Degree of ionization decreases with increase in concentration. With decrease in the degree of ionization, the number of ions per unit volume decreases and this results in the decrease in the equivalent conductance. However, such an explanation cannot apply to strong electrolytes, since these are almost completely dissociated in all dilute solutions. Consequently, to account for the variation of equivalent conductance with concentration in strong electrolytes, some other explanation must be sought, and this is found in the Debye-Hickcl-Onsager Theory of conductance.

In 1923, P. Debye and E. Hickecl put forward a theory of interionic attraction for dilute solutions of strong electrolytes. This theory occupies a dominant place in all consideration involving electrolytes and their kinetic and thermodynamic behaviour. Debye and Huckel suggest that strong electrolytes exist in solutions as ions. They believe that strong electrolytes at least in dilute solutions are completely ionized and the effect observed is due to unequal distribution of ions resulting from interior attraction. Debye and Huckel showed that, because of the electrostatic attraction between charged ions, each positive ion in the solution must be surrounded on an average with more negative ions than ions of like charge; and conversely, each negative ion must be surrounded on an average with more positive than negative ions. In other words, each ion solution is surrounded by *ionic atmosphere whose net charge is opposite to that of the central ion.* They showed, further, that the properties of an electrolyte are determined by the interaction of the central ion with its atmosphere. Since the nature of the atmosphere is determined by the valencies of the ions in the solution, their concentration, the temperature and dielectric constant of the medium, it must follow that these are also the factors controlling the thermodynamics properties of the electrolyte. At any given temperature and in a given solvent, the temperature and dielectric constant are fixed, hence the properties of an electrolyte depend only on the charges of the ions and their concentrational not at all on the nature of each electrolytes. These conclusion are only valid for dilute solutions.

According to Debye-Hickel theory of interionic attraction, each ion in solution is surrounded by an ionic atmosphere of opposite ions whose net charge is on the average opposite to that of the central ion. This ionic atmosphere is spherical and symmetrical in nature in the absence of any disturbing factor such as the application of potential across the two electrodes immersed in the solution during the conductance measurement. However, when potential is applied, the ions start moving towards the respective electrodes and as a result the ionic atmosphere is distorted which results in a decrease in the speed of the ions. Debye and Huckel showed that these affects are due to two factors, namely, (i) Asymmetric or Relaxation effect and (ii) Electrophoretic effect.

(i) Asymmetric or Relaxation Effect

According to Debye-and Huckel theory each ion in the solution of an electrolyte is surrounded by an ionic atmosphere of oppositely charged ions. For example, a positively charged ion is surrounded by atmosphere of negatively charged ions and vice versa. When the ions have no external force applied on them, this atmosphere is spherically and symmetrically distributed about the ion. However, when an external force is imposed, as when a potential is applied across the two electrodes, the ions present in the solution move forward their respective electrodes. The central +ve ion will tend to move towards *cathode*, while its negatively charged ion atmosphere will more towards *anode*. As a result, he symmetry of the ionic atmosphere about central ion is destroyed. As long as the ionic atmosphere is symmetrical: it will exert uniform force of attraction on the central ion from all possible directions and the net effect will be nil. (Fig.9.4(a))



(a) Symmetrical ionic atmosphere (No field)

(b) Asymmetric ionic atmosphere (Electric field)

Fig.9.4 Asymmetric effect showing distribution of ionic atmosphere in the pressure of an applied field

But in case of distorted ionic atmosphere a shown in Fig. 9.4(b), the of force attraction from the rarer becomes prominent on the moving central ion. Therefore, the central moving ion experiences a backward pull or a retarding force. Its mobility is slowed down and hence, the effective conductance of the solution decreases. This backward pull of the central ion is known as *asymmetric effect* as it is the due to the lack of symmetry in the ionic atmosphere. Once the ionic atmosphere is destroyed, a finite time is required for rebuilding another symmetric ion-atmosphere. This time is called relaxation time. This time of relaxation is considered to explain the retardation in the motion of the central moving ion by the ionic atmosphere, therefore asymmetric effect is also known as relaxation effect.

(ii) Electrophoretic Effect

In addition to the asymmetry effect, there is another factor with retards the mobility of ion, the electrophoretic effect. This effect arises from the fact that an ion, in moving through the solution, does not travel through a stationary medium, but through one that moves in a direction opposite to that of the ion. Ions are generally solvated, and when these move, they carry with them solvent. Any +ve ion migrating towards the cathode, has, then, to thread (pass into its way through the medium moving with negative ions towards anode. Similarly –ve ions have to migrate through the molecules of solvent carried by +ve ions in the opposite direction. These counter movements have a retarding influence on the mobility of the central ion. This effect is known as electrophoretic effect. This causes an additional viscous force which further slows down the speed of the ions and hence the conductance.

It is called electrophoretic effect because it is somewhat analogous to that opposing the movement of colloidal particles in the electric field. It shows down the speed of the ions in the same way as swimming against the current in a river would slow down a swimmer. For any dilute solution, the ionic atmosphere is almost non-existent, so asymmetric effect is zero. Similarly at infinite dilution, the electrophoertic effect is also negligible, but both effects have definite values in concentrated solutions. Debye and Huckel showed that both of these retarding effect on an ion produce a decrease in the equivalent conductance. These are the theoretical explanation for the decrease of equivalent conductance in case of solutions of strong electrolytes.

9.15 DEBYE-HUCKEL THEORY: THE IONIC ATMOSPHERE

The possibility that the attractive forces between ions might have some influence on the electrolytic conductance, especially with strong electrolytes, was considered by Noyes (1904), Sutherland (1906) Bijerum (1909) and Miller (1912) among others. But the modern quantitative treatment of this concept is due mainly to the work of Debye and Huckel and its extension chiefly by Onsager and Falkenhagen.

When an electrolyte is dissolved in a polar solvent, it gets dissociated into ions and the solutions may contain a large number of kinetically identifiable species in addition to the solvent molecules which are always in equilibrium with each other. A completely random distribution of ions around each other can not be physically possible. A positive ion will have a negative ion in its immediate vicinity, thereby, resulting in an ordered arrangement, which is offset by thermal motions. Thus the resulting situation is a dynamic compromise between the electrostatic interactions and kinetic collisions. The net result is that in a small volume element of the solution around an ion, on time average, there is slightly greater concentration of the ions carrying opposite charge than those carrying similar charge. Thus, each ion have an ionic atmosphere of oppositely ions, whose net electrical charge is equal and opposite to that of the central ion. This forms an essential postulate of the Debye-Huckel theory for dilute solutions of strong electrolytes.

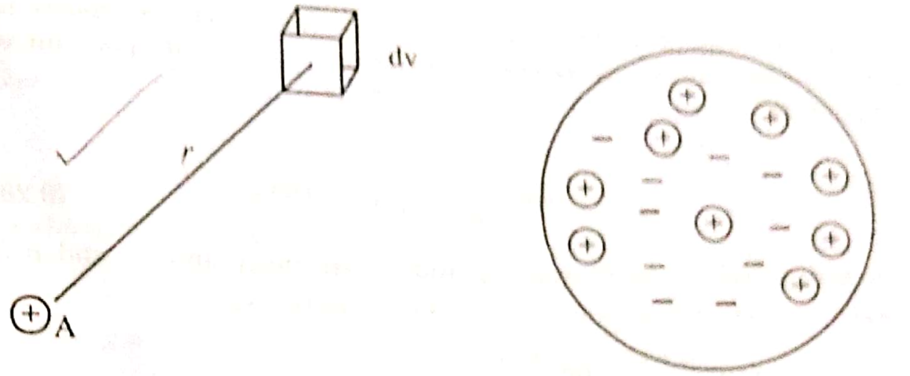


Fig. 9.5 The ionic atmosphere and time average distribution of ions around a reference ion

Let us consider a positive ion situated at A(Fig.9.5). Suppose there is small volume element dv at the end of radius vector r; the distancer is supposed to be of the order of less than about 100 times, as the diameter of the ion. Due to thermal movement of ions sometimes there occurs an excess of positive ions and sometimes an excess of negative ions in the volume dv. If a time average is taken, however, it will be found to have, as a consequence of electrostatic attractions by the positive charge at A, a negative charge density. In this way every ion may be assumed to have an ionic atmosphere of opposite sign. The net charge of the ionic atmosphere is equal in magnitude and opposite in sign to that of the central ion. It is possible to define the effective thickness of the ionic atmosphere.

Debye and Huckel took the interionic attraction into consideration and calculated the ratio of activity to the concentration of an ion in dilute solutions. Suppose the time average of the electrical potential in the center of the volume element dv in Fig.9.5 is Ψ. It is defined as the work done in bringing a unit charge from infinity to a particular point. The work done in bringing a positive ion of valence Z_+ and carrying a charge ϵ to that point is given by $Z_+\epsilon\Psi$. Similarly the work done in bringing a negative ion is $Z_-\epsilon\Psi$. Z_+ and Z_- are numerical values only, and do not include the sign. If the concentrations of the ions at a considerable distance form the given ion, where Ψ may be taken as zero, are n_+^0 and n^0 per unit volume, then by the Boltmann distribution law for particles in a filed of varying potential, the concentration of the positive and negative ions, i.e., n_+ and $n-$, at the point under consideration, are given by

$$n_+ = n_+^0 e^{-(Z_+\epsilon\Psi/kT)} \tag{9.26}$$

and $$n_- = {}^{0}_{-} e^{-(Z_+ \epsilon \Psi/kT)} \tag{9.27}$$

where k is the Boltmann constant. Since Z_+ and Z_- are the numerical values only, it is clear that n_- is greater than n_+, and so there are on the average more negative ions than positive ions in the vicinity of any positive ion, the reverse will be true for negative ion. It is seen, therefore, that every ion is surrounded by an oppositively charged ionic atmosphere.

In the vicitinity of A^+, the density of electricity or electrical charge density (ρ) at any point is equal to the excess positive or negative electricity per unit volume at that point, that is,

$$\rho = n_+ Z_+ \epsilon - n_- Z_- \epsilon$$

$$\rho = \epsilon[n_+ Z_+ e^{-(Z_+ \epsilon \Psi/kT)} - n_- Z_- e^{-(-Z_- \epsilon \Psi/kT)}] \tag{9.28}$$

For uni-univalent electrolyte, Z_+ and Z_- are unity and n_+ and n_- must be equal because of electrical neutrality hence, Eq.(9.28) reduces to

$$\rho = \epsilon(ne^{-\epsilon\Psi/kT} - ne^{\epsilon\Psi/kT})$$

or $$\rho = \epsilon n(e^{-\epsilon\Psi/kT} - e^{\epsilon\Psi/kT}) \tag{9.29}$$

or $$\rho = \epsilon n(e^{-x} - e^{x}) \tag{9.30}$$

where n is the number of either kind of ion in unit volume. Expanding the two exponential series and writing x in plane of $\epsilon\Psi/kT$, one gets,

$$e^{x} = 1 + \frac{X}{1!} + \frac{X^2}{2!} + \frac{X^3}{3!} + \ldots$$

$$e^{-X} = 1 - \frac{X}{1!} + \frac{X^2}{2!} - \frac{X^3}{3!} + \ldots$$

$$-e^{X} = -1 - \frac{X}{1!} - \frac{X^2}{2!} - \frac{X^3}{3!} \ldots$$

$$(e^{-X} - e^{X}) = 1 - \frac{X}{1!} + \frac{X^2}{2!} - \frac{X^3}{3!} \ldots - 1 - \frac{X}{1!} - \frac{X^2}{2!} - \frac{X^3}{3!} \ldots \infty$$

$$(e^{-X} - e^{X}) = -\frac{2X}{1!} - \frac{2X^3}{3!} - \frac{2X^5}{5!} - \ldots \infty$$

$$(e^{-X} - e^{X}) = \frac{-2X}{1!}\left(1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \ldots\right)$$

$$\rho = \epsilon n\left(-\frac{2\epsilon\Psi}{kT}\right)\left[1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \ldots\right]$$

or $$\rho = -\frac{\epsilon^2\Psi}{kT} 2n\left(1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \ldots\right) \tag{9.31}$$

If it is assumed that X is small in comparison with unity, all terms beyond the first in the parenthesis may be neglected

$$\rho = -\frac{\epsilon^2\Psi}{kT}\,2n \tag{9.32}$$

where $2n = Z_+^2 n + Z_-^2 n$

$$2n = n_+Z_+^2 + n_-Z_-^2$$

This is only true for 1 : 1 electrolyte. Here Eq.(9.32) may be written as

$$\rho = -\frac{\epsilon^2\Psi}{kT}\,(n_+Z_+^2 + n_-Z_-^2 \tag{9.33}$$

In the general case where Z+ and Z– are not necessarily unity and if the solution may contain several kinds of the ions, Eq.(9.33) may take the following form.

$$\rho = -\frac{\epsilon^2\Psi}{kT}\,\sum_i n_iZ_i^2 \tag{9.34}$$

Where n_i and Z_i represent the number per unit volume and valence of the ions of ith kind. The summation is taken over all kinds of ions present in the solution and Eq.(9.34) is applicable irrespective of the number of different kinds of ions.

In order to solve for Ψ it is necessary to have another relationship between ρ and Ψ and this may be obtained by intorducing Poisson's equation and this equation in rectangular coordinates is

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} = -\frac{4\pi\rho}{D} \tag{9.35}$$

Where x, y and z are the coordinates of the point in the given volume element and D is the dielectric constant of the medium. Converting to polar coordinates, and making use of the fact that the terms containing ∂Ψ/∂θ and ∂Ψ/∂ϕ will be zero, since the distribution of the potential about any point in the electrolyte must be spherically symmetrical and consequently, independent of the angles θ and ϕ, Eq.(9.35) becomes

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = -\frac{4\pi\rho}{D} \tag{9.36}$$

Substituting the value of ρ from Eq.(9.34) in Eq.(9.36) we get

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = -\frac{4\pi}{D}\left(-\frac{\epsilon^2\Psi}{kT}\,\Sigma n_i Z_i^2\right)$$

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = \frac{4\pi\epsilon^2\Psi}{DkT}\,\sum_i n_i Z_i^2$$

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = k^2\,\Psi \tag{9.37}$$

where the quantity k(not to be confused with specific conduction) is defined by

$$k^2 = \frac{4\pi\epsilon^2 \sum_i n_i Z_i^2}{DkT}$$

or $$k^2 = \left(\frac{4\pi\epsilon^2 \sum_i n_i Z_i^2}{DkT} \right)^{1/2} \qquad (9.38)$$

where r denotes the distance from the central ion to the point where Ψ is determined, and $\frac{1}{k}$ has the dimensions of length. It is called Debye-Huckel reciprocal length. It is the distance over which electrostatic field of an ion extends with appreciable strength. k^{-1} is a measure of the thickness of the ionic atmosphere.

The differential equation Eq.(9.37) can be solved, and the solution has the general form

$$\Psi = \frac{Ae^{-kr}}{r} + \frac{Be^{kr}}{r} \qquad (9.39)$$

Where A and B are integration constants, whose values are determined by applying the boundary conditions. Since Ψ must approach zero as r increases, because the potential at infinite distance from the given point in the solution must be zero

$$0 = \frac{A\,e^{-\infty}}{\infty} + \frac{B\,e^{\infty}}{\infty}$$

$$0 = 0 + B\frac{e}{\infty}$$

$$e^{\infty} = \infty$$

$$e^{-\infty} = 0$$

$$\frac{1}{e^{\infty}} = 0$$

This can be only true if B = 0, since $\frac{e^{\infty}}{\infty} \neq 0$, hence Eq.(9.39) becomes

$$\Psi = \frac{A\,e^{-kr}}{r} \qquad (9.40)$$

The value of A can be calculated by the fact that for very dilute solution $\sum_i n_i Z_i^2$ is almost zero and hence k is also zero. The value of potential Ψ_i at the point under consideration will be

$$\Psi_i = \frac{A}{r} \qquad (9.41)$$

In case of dilute solutions the potential in the neighbourhood of an ion will be due to that ion alone, since other ions are too far away to have any influence. If the ion is being regarded as being a point charge, the potential at small distance will be

$$\Psi_i = \frac{Z_i\epsilon}{Dr} \qquad (9.42)$$

Eliminating Ψ_i between Eq.(9.41) and Eq.(9.42), we get

$$\frac{A}{r} = \frac{Z_i \in}{Dr}$$

or

$$A = \frac{Z_i \in}{D} \tag{9.43}$$

Substituting the value of A into Eq. (9.40), we get

$$\Psi = \frac{Z_i \in}{Dr} e^{-kr} \tag{9.44}$$

The value of Ψ represented by Eq.(9.44) is the mean value of the potential at point r produced by the ionic atmosphere and the central ion. Real solutions are characterized by the potential of the ionic atmosphere which is found as the difference between Ψ and Ψ_i

$$\Psi_{ia} = \Psi - \Psi_i$$

$$\Psi_{ia} = \frac{Z_i \in}{Dr} e^{-kr} - \frac{Z_i \in}{Dr}$$

$$\Psi_{ia} = \frac{Z_i \in}{Dr} (e^{-kr} - 1)$$

$$\Psi_{ia} = \frac{Z_i \in}{Dr} (-kr)$$

$$\Psi_{ia} = -\frac{Z_i \in k}{Dr} \tag{9.45}$$

$$\therefore \quad e^{-kr} = 1 - kr$$

$$1 - e^{-kr} = [1 - kr] = kr$$

$$e^{-kr} - 1 = 1 - kr - 1 = -kr$$

The Eq.(9.45) is independent of r and hence it may be assumed to hold even when r is zero, so that the potential on the ion itself, due to ionic atmosphere is given by above equation. The net charge of the ionic atmosphere is $-Z_i \in$, because it is equal in magnitude and opposite in sign to that of the central ion itself. If this charge were placed at a distance 1/k from the ion, the potential produced at it, would be $-Z_i \in k/D$, which is identical with the value given by equation (9.45). The quantity 1/k can thus be regarded as a measure of the thickness of the ionic atmosphere in a given solution. According to the definition of k, the thickness of the ionic atmosphere will depend on the number of ions of each kind present in unit volume and on their valence. If C_i is the concentration of the ions of the ith kind expressed in moles (gram-ions) per liter, then

$$n_i = C_i \frac{N}{1000}$$

where N is the Avogadro number, hence from Eq.(9.38)

$$\frac{1}{k} \left(\frac{DT}{\Sigma C_i Z_i^2} \frac{1000\,k}{4\pi \in^2 N} \right)^{1/2}$$

The value of universal constants are as follow: k is 1.38 × 10^{-16} e.g. per degree, ε is 4.80 × 10^{-10} esc and N is 6.025 × 10^{23}, hence

$$\frac{1}{k} = 2.81 \times 10^{-10}\left(\frac{DT}{\Sigma C_i Z_i^2}\right)^{1/2} \text{cm}$$

For water as solvent at 25°C, D is 78.6 and T is 298, so that

$$\frac{1}{k} = \frac{4.31 \times 10^{-8}}{(\Sigma C_i Z_i^2)} \text{cm}$$

The thickness of the ionic atmosphere is this seen to be of the order of 10^{-8} cm or 10^{-10} m. It decreases with increasing concentration and valence of the ions present in the electrolyte, and increases with increasing dielectric constant of the solvent an with increasing temperature.

9.16. DEBEY-HUCKEL-ONSAGER'S EQUATION

According to Debye-Huckel theory of strong electrolytes each ion is surrounded by an ionic atmosphere of opposite charge. A moving ion under the influence of applied electrical field is un-symmetrically surrounded by the ionic atmosphere of opposite charge. The charge density is greater in the rear than in the front of ion. As the ionic atmosphere is not symmetrical, it results in the retardation of the ion moving under the influence of applied field. This influence on the speed of ion is called asymmetric or relaxation effect. A viscous resistance of the solvent also acts on the moving ion. It is similar to the resistance acting against the movement of the colloidal particles in an electric field. It is called electrophonic affect Both asymmetric and electrophonic effects retard the speed of the central moving ions and ultimately decrease the conductance.

Debye and Huckel made an attempt to calculate the magnitude of the process which oppose the motion of the ions in solution. They supposed the ions to travel through the solution in straight lines, neglecting the zigzag Brownian motion brought about by the collisions of surrounding solvent molecules. This theory was improved in 1926 by the Norwegian-American physical chemist Lars. Onsager (1903-1976) who took Brownian motion into account. They applied stockes,s law and derived the following expression for electrophoretic effect for an ion of the ith kind.

$$\text{Electrophoretic force} = \frac{\in Z_i k\, K_i V}{6\pi\eta} \tag{9.46}$$

Where K_i is the coefficient of frictional resistance of the central ion with reference to the solvent, η is the viscosity of the medium, V is the applied potential gradient, ∈ in the electronic charge, Z_i is the valence of the i^{th} ion, k is the reciprocal of the thickness of the ionic atmosphere. The same result was derived in an attractive manner by Onsager, who showed that it is not necessary for the Stokes,s law to be strictly applicable in the immediate vicinity of an ion.

In the first derivation of the relaxation force Debye and Hückel did not take into account the natural Brownian movement of the ions but Onsager also considered this movement for the derivation of relaxation force. According to Onsager

$$\text{Relaxation force} = \frac{\epsilon^3 Z_i k}{6DkT} wV \qquad (6.47)$$

Where D is the delectric constant of the medium, k is Boltzmann constant, T is the absolute temperature K is same as in previous equation, Z_i is the value of the ion, V is the applied potential and w is defined as

$$w = z_+ z_- \frac{2q}{1+q^{1/2}}$$

$$\text{When } q = \frac{z_+ z_-}{z_+ + z_-} \frac{\lambda_+ + \lambda_-}{z_+\lambda_- + z_-\lambda_+} \qquad (9.41)$$

λ_+ and λ_- are the ionic conductance's of +Ve and –Ve ions.

Let us suppose that an ion of ith kind is moving through a solution with a steady velocity Ui. The driving force acting an the ion of ith kind due to applied electrical field is

$$\text{Driving force} = \in Z_i V \qquad (9.49)$$

It is now possible to equate the forces acting on anion of ith kind when it is moving through a solution with a steady velocity; the diving force due to applied electrical field is opposed by the frictional force of the solvent (K_iU_i), together with the electrophoretic and relaxation forces hence.

$$\in Z_i V = K_i U_i + \frac{\in z_i k}{6\pi\eta} K_i V + \frac{\in^3 z_i k}{6DkT}.wV$$

dividing throughout by KiV and rearranging, we get

$$\frac{\in z_i}{K_i} = \frac{U_i}{V} + \frac{\in z_i k}{6\pi\eta} + \frac{\in^3 z_i k}{6DkT}.\frac{w}{K_i}$$

$$\text{or} \quad \frac{Ui}{V} = \frac{\in z_i}{K_i} + \frac{\in z_i k}{6\pi\eta}.\frac{\in^3 z_i k}{6DkT}.\frac{w}{K_i}$$

Multiply the above equation throughout by V

$$\frac{U_i}{V} = \frac{\in z_i V}{K_i} - V\left(\frac{\in z_i k}{6\pi\eta}.\frac{\in^3 z_i k}{6DkT}.\frac{w}{K_i}\right)$$

$$Ui = \frac{\in z_i V}{K_i} - V \in k\left(\frac{Z_i}{6\pi\eta} + \frac{\in^2 z_i}{6DkT}.\frac{w}{K_i}\right) \qquad (9.50$$

If the potential gradient is taken as one volt per cm

$$\therefore \quad 1\ \text{volt}/\text{cm} = \frac{1}{300}\ \text{esu}$$

Since the forces of attraction are electrostatic in nature.

$$U_i = \frac{\in z_i}{300\,K_i} - \frac{\in k}{300}\left(\frac{z_i}{6\pi\eta} + \frac{\in^2 z_i}{6\,DkT}\cdot\frac{w}{K_i}\right) \tag{9.51}$$

At infinite dilution k is zero, so the above equation reduces to

$$U_i = \frac{\in z_i}{300\,K_i} \tag{9.52}$$

But $\quad U_i^o\,F = \lambda_i^o \quad$ so $\quad U_i^o = \frac{\lambda_i^o}{F}$

Hence $$\frac{\lambda_i^o}{F} = \frac{\in z_i}{300 K_i} \tag{9.53}$$

Since ions behave independently at infinite dilution, therefore ionic conductance at infinite dilution can be written as according to Kohlraushes law $\lambda_+^o = FU_+^o$ and $\lambda_-^0 = FU_-^0$

Again we know that $U_i = \frac{\lambda_i}{\alpha F}$

When α is the degree of dissociation. Substituting the value of U_i and U_i^o into Eq. (9.51), we get

$$\frac{\lambda_i}{\alpha F} = \frac{\lambda_i^o}{F} - \frac{\in k}{300}\left(\frac{z_i}{6\,\pi\eta} + \frac{\in^2 z_i}{6\,DkT}\cdot\frac{w}{K_i}\right) \tag{9.54}$$

When the electrolyte is fully ionized, i.e. $\alpha = 1$, then

$$\lambda_i = \lambda_i^o - \frac{\in k}{300}\left(\frac{z_i F}{6\pi\eta} + \frac{\in^2 z_i F}{6\,DkT}\cdot\frac{w}{K_i}\right) \tag{9.55}$$

we know that $\frac{\lambda_i^o}{F} = \frac{\in z_i}{300\,K_i}$

$$\therefore \quad \lambda_i^o\ 300\ K_i = \in z_i F$$

Substituting this value in above equation we get

$$\lambda_i = \lambda_i^o - \frac{\in k}{300}\left(\frac{z_i F}{6\pi\eta} + \frac{\in 300 \lambda_i^o}{6\,DkT}.w\right) \tag{9.56}$$

But $$K = \left(\frac{4\pi\epsilon^2}{DkT}\sum_i n_i Z_i^2\right)^{1/2} \qquad \text{(cf Eq.9.38)}$$

Where n_i is the number of ions present for unit volume. Substituting this value in Eq. (9.56), we get.

$$\lambda_i = \lambda_i^o - \frac{\epsilon}{300}\left(\frac{4\pi\epsilon^2}{DkT}\sum_i n_i Z_i^2\right)^{1/2}\left(\frac{Z_i F}{6\pi\eta} + \frac{300\epsilon\lambda_i}{6DkT}.w\right)$$

$$\lambda_i = \lambda_i^o - \frac{\epsilon}{300}\left(\frac{4\pi\epsilon^2 N}{DkT \times 1000}\sum c_i Z_i^2\right)^{1/2}\left(\frac{Z_i F}{6\pi\eta} + \frac{300\epsilon\lambda_i^o w}{6DkT}\right)$$

Hence $$ni = \frac{CiN}{1000}$$

The value of universal constant an as follows: K is 1.38×10^{-16} erg per degree ϵ is 4.802×10^{-10} esu and N is 6.025×10^{23}, hence.

$$\lambda_i = \lambda_i^o - \left[\frac{29.15Zi}{(DT)^{1/2}\eta}\left(\sum ciZi^2\right)^{1/2} + \frac{9.9 \times 10^5}{(DT)^{3/2}}\lambda_i^o w\left(\sum CiZi^2\right)^{1/2}\right]$$

$$\lambda_i = \lambda_i^o - \left[\frac{29.15Zi}{(DT)^{1/2}\eta} + \frac{9.9 \times 10^5}{(DT)^{3/2}}\lambda_i^o w\right]\left(\sum CiZi^2\right)^{1/2} \qquad \text{—9.57}$$

For 1:1 electrolyte, $C_i = C_+ + C_-$, $Z_i = Z_+ + Z_-$

$$\lambda_i = \lambda_i^o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9 \times 10^5}{(DT)^{3/2}}\lambda_i^o w\right](C_+Z_+^2 + C_-Z_-^2)^{1/2}$$

The quantities C_+ and C_- represent the concentrations of the ions in moles per liter, then may be replaced by the corresponding concentrations C in equivalent for liter, when C is the same for both ions i.e. $C_+ = C_- = C$

$$\lambda_i = \lambda_i^o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9 \times 10^5}{(DT)^{3/2}}\lambda_i^o w\right]\sqrt{C}(Z_+^2 + Z_-^2)^{1/2}$$

The equivalent conductance of an electrolyte is equal to the sum of the conductance's of the constitute ions, and so to follows from above equation.

$$\Lambda = \Lambda_{ov} - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9 \times 10^5 \Lambda_o^w}{(DT)^{3/2}}\right]\sqrt{C}\left(Z_+^2 + Z_-^2\right)^{1/2}$$

For 1:1 electrolyte, $Z_+ = Z_- = 1$ and $w = 2 - \sqrt{2}$, so

$$\Lambda = \Lambda_0 - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9 \times 10}{(DT)^{3/2}} \Lambda_0 \, 2 - \sqrt{2} \right] \sqrt{2C}$$

$$\Lambda = \Lambda_0 - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.2 \times 10^5}{(DT)^{3/2}} \Lambda_0 \right] \sqrt{C} \qquad (9.58)$$

$$\Lambda = \Lambda_0 - [A + B\,\Lambda_0] \sqrt{C} \qquad (9.59)$$

When A and B are constants dependent upon the nature of solvent and temperature.

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

and $$B = \frac{8.2 \times 10^5}{(DT)^{3/2}}$$

Equation (9.58) and (9.59) represents the forms of the Debye Huckel-Onsager conductance equation, these relationship are based on the assumption that the dissociation of the electrolyte is complete. This equation accounts for the falling off of equivalent conductance at appreciable concentrations in terms of decrease in ionic velocity resulting from inter ionic forces. The decrease of conductance due to these forces is represented by the quantities in the square brackets. The first term gives the effect due to electrophoretic force and the second term represents the influence of asymmetric force. It is apparent from the equation that for a given solved at a definite temperature, the magnitude of the interionic forces increases with increasing valences of the ions and with increasing concentration of the electrolyte.

Validity of Debye-Huckel Onsager Equation:

Assuming complete dissociation of 1:1 electrolyte the D.H.O equation may be written in the form.

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

Where A and B are constants dependent only on the nature of the solvent and temperature. The above equation is an equation of straight line. In order to test the validity of above equation, the experimental value of Λ of very dilute solution of a strong electrolyte are plotted against $\sqrt{C}$. A straight line is obtained with slope equal to $A + B\Lambda_0$ and intercept Λ_0 as shown in Fig-9.6. This equation is obeyed.

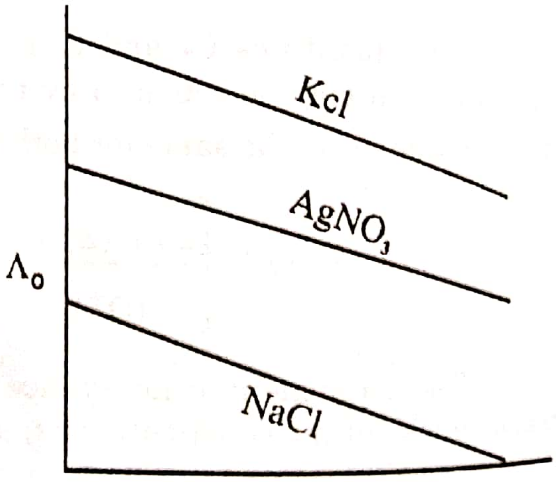


Fig. 9.6. Test of Debye- Huckel-Onsager equation

at the concentration of about 2×10^{-3} equivalent per liter. This equation is also applicable to non-aqueous solvents. This equation hold good for certain electrolytes like NaCl, $AgNO_3$, KCl, HCl etc. Marked deviations are observed for 2:2 solutes, and for solutions prepared in solvents having lower dielectric constants. Negative deviations from theoretical values of conductance may be due to incomplete dissociation.

It has been observed that smaller ions, possessing higher valence, show marked deviation in a medium of low dielectric constant.

D.H.O. equation also show deviation of higher concentration of solutes. Bjerrum was the first man who tried to explain this observation. He said that when electrolyte concentration is increased, the ions become close to each other and the forces of attraction between opposite charges are increased. At higher concentration, individual ions, associate into electroneutral ion pairs (B^+A^-) which an unable to conduct electricity. As a result of the combination of charge particles, the conductance decreases.

9.17. WIEN AND DEBYE-FALKENHAGEN EFFECTS

The conductance of completely dissociated electrolytes is independent of the electric field strength in the range of moderate field strengths. At higher field strengths of the order 10^7 Vm^{-1}, however, Wien (1922) observed an increase in the conductance with increasing field strength. The increase is more intense for more concentrated solutions and for polyvalent ions the conductance always approaches a limiting value with increasing field strength. This effect of field strength on the conductance is called *Wien effect*. This effect can easily be interpreted by making use of the ion-ionic atmosphere interaction model. Under condition of high field strength, the ionic mobility is so large that the ionic atmosphere is unable to rearrange itself fully around the moving central ion. Consequently, both the electrophoretic and twie-relaxation effects exert no influence on the moving ion, and the observed conductance rises above the value found for low field strength.

A second phenomenon, also observed by Wien under conditions of high field strength deals with the influence of the electrical field on the dissociation constant of the weak electrolytes. A high field strength affects the dissociation positively and, consequently, affects the equilibrium dissociation constant (dissociation equilibrium constant) of such an electrolyte. The theoretical interpretation of this very important observation, as given by Onsager (1934) and Bass (1968) is based an the fact that at high electrical field strengths the probability of ion-pair and triple-ion formation is much lower than at low field strengths.

If a high frequency alternating current is applied to an electrolyte, and the time of oscillation is equal to or less than the relaxation time of the ionic atmosphere, the asymmetrical charge distribution usually associated with an ion in motion cannot form completely. The retardation of the ionic velocity due to asymmetric effect is thus reduced, and the conductance of the solution should be greater than the normal value P. Debye and H.Falkenhagen (1928) deduced theoretically the existence of high frequency effect on the conductivity of the ion. In 1928 Sach proved experimentally that this is really so at frequencies exceeding 5 MHz, where the equivalent conduct approaches a value some what lower than Λ_α. The value must be lower than Λ_α

because the high frequency field eliminates the time relaxation effect only; it has no influence on the electrophoretic effect.

It is important to emphasize that the influence of high frequency currents and high voltages provides strong arguments in favor of the view that under normal conditions ionic velocities, and hence conductances are below those for infinite dilution because of the effect of the ionic atmosphere which increases with increasing concentration.

9.18. IONIC STRENGTH:

When we dissolve an electrolyte into aqueous solution, it dissociates into positive and negative ions. When the concentration of the electrolyte increases in the solution, there occurs an interaction between positive and negative ions. Because of this interaction the ions behave differently from those in dilute solutions. The behavior of ions in solution is influenced by a number of factors, chief among which are the natural attraction of ions unlike charge and repulsion of ions of like charge (Coulomb's law) and the influence of thermal agitation (Boltzmann distribution law) to counteract the electrical attraction and repulsion. The effects are dependent upon the total ionic composition of the solution, which is expressed by G.N. Lewis in a concept called ionic strength of the solution. Ionic strength is a useful concept because it allows us to consider same general expressions that depend only on ionic strength and not on the identities of the ions themselves. This quantity is a measure of electrical environment in the solution.

Ionic strength is given the symbol μ and is defined as half the sum of the terms obtained by multiplying the molality (or concentration) of each ionic species present in the solution by the square of its valence; thus

$$\mu = \frac{1}{2}\sum m_i Z_i^2 \qquad (9.60)$$

When m_i is the molality of the ion and Z_i is its ionic change. The product $m_iz_i^2$ is summed for all the ions in the solution then divided by two to give the ionic strength.

If a solution contains a number of ionic species indicated by the subscripts 1,2,3, etc. so that their respective molalities are m_1, m_2, m_3, etc. in gram ions per 1000 gram of solvent, and Z_1 Z_2 an Z_3 etc. are the corresponding valencies, then the ionic strength is given by

$$\mu = \frac{1}{2}\left(m_1z_1^2 + m_2z_2^2 + m_2z_3^2 + ...\right) \qquad (9.61)$$

For a single electrolyte such as sodium chloride or potassium sulfate, the above equation reduces to two terms, one for positive and one for negative ion, viz.

$$\mu = \frac{1}{2}(m_+z_+^2 + m_-z_-^2) \qquad (9.62)$$

When m_+ and m_- are the molalities and Z_+ and Z_- are the valences of positive and negative ions. Ionic strength is an empirical relationship and is expressed terms of molal concentration of the ions rather than in SI unit of ions per cubic meter.

For uni-univalent electrolyte such as NaCl or KCl of molality m, the ionic strength is equal to its molality.

$$\mu = \frac{1}{2}(m \times 1^2 + m \times 1^2)$$

$$\mu = \frac{2m}{z} = m$$

Na^{+1} Cl^{-1}

1 : 1

Na^{+1}, $m \times 1^2$

$\mu = \frac{1}{2}(2m) = \mu = \frac{2m}{2}$

$\mu = m$

Thus for 1:1 electrolyte μ is equal to its m. One should reminder that ionic strength is a property of the solution and not of any particular ion.

Example 9.4

Calculate the ionic strength of (i) 0.1 molal NaCl (ii) 0.2 molal K_2SO_4 (iii) a solution containing 0.1 m KCl and 0.2 m K_2SO_4 (iv) 0.2 m $BaCl_2$ solution.

Solution:

(i) $m_+ = m_- = 0.1$, $Z_+ = Z_- = 1$, so

$$\mu = \frac{1}{2}(0.1 \times 1^2 + 0.1 \times 1^2)$$

$$\mu = 0.1$$

(ii) K_2SO_4 produces two K^+ ions and one SO_4^{2-} ion

$m_+ = 2 \times 0.2 = 0.4$, $Z_+ = 1$

$m_- = 0.2$ $Z_- = 2$

$$\mu = \frac{1}{2}(0.4 \times 1^2 + 0.2 \times 2^2)$$

$$= 0.6$$

(iii) In a mixture of solution containing 0.1m KCl and 0.2m K_2SO_4, total molality of K^+ ion $= m_1 = 0.1 + 0.4 = 0.5$

molality of Cl^- ion $= m_2 = 0.1$

molality of SO_4^{2-} ion $= m_3 = 0.2$

$$\mu = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2)$$

$$= \frac{1}{2}(0.5 \times 1^2 + 0.1 \times 1^2 + 0.2 \times 2^2)$$

$$= 0.7$$

(iv) $BaCl_2$ produces one Ba^{2+} ion and two Cl^- ions

$$m_+ = 0.2,\ Z_+ = 2$$

$$m_- = 2 \times 0.2 = 0.4,\ Z_- = 1$$

$$\mu = \frac{1}{2}(0.2 \times 2^2 + 0.4 \times 1^2)$$

$$= 0.6$$

9.19. ACTIVITIES AND ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES:

The thermodynamic and other properties of the solutions of non-electrolytes can be adequately expressed in terms their concentrations, even at moderate concentrations. But the solutions of electrolytes exhibit marked deviation even at relatively low concentrations. Dilute ionic solutions have concentration of 0.001 m or even less. According to Debye-Huckel theory of interionic attraction, the electrostatic attractions between the ions in the solution of an electrolyte have significant influence on the mobility of ions. The ionic concentrations in case of weak electrolytes, being low do not show appreciable deviation from the ideal behavior. But in solutions of strong electrolyte the ionic concentrations are large, so interionic forces cannot be neglected. Due to electrostatic attraction between fractions of cations and anions, the solution exhibits the properties of one in which the effective or apparent concentrations of the ions less than the theoretical concentrations. Depending on the relative importance of factors, such as ion-ion attractions and ion-solvent interactions, the effective concentration of the solute dissolved in water may appear to be less than, equal to or greater than the molal concentration. This effect becomes more significant at higher concentrations and increasing valence of the ions.

This effect becomes G.N. Lewis suggested due to restricted mobility of the ions in solutions of strong electrolytes the ions do not exert their full effect for showing their behavior. He proposed the term activity in place of concentration term molarity, molality, formality, mole fraction), so as to explain the departure of electrolyte solution from ideal behavior. To distinguish between molar or molal or formal concentration of a substance and the effective concentration of a substance which accounts non-ideal behavior, the latter is called the activity of the species. So the affective concentration of an ion in a solution is called its activity. It is customary to relate the activity of a species to its concentration through the expression.

$$a_i = \gamma_i m_i \tag{9.63}$$

in which a_i is the activity of the substance i, γ_i, in the activity coefficient of the substance i and m_i is the molal concentration of the substance i. Activity coefficient (γ) is not a constant and its value varies with the concentration. For aqueous solutions, both activity and concentration are expressed in the same units, so that the activity coefficient is dimension less. [For dilute solutions, the molarity is almost numerically equal to molality, which is preferred unit for colligative properties (because then the solution properties do not depend on the identity of the solute). Therefore, we can shift from molarity concentration units to molality concentration units).

For dilute solutions (< 0.001m), the electrostatic attractions can be neglected, so

$$a_i = m_i$$

and value of γ_i becomes unity. For an electrolyte, such as NaCl, the activity of Na^+ and Cl^- ions can be written as

$$a_+ = \gamma_+ m_+$$

and $$a_- = \gamma_- m_-$$

Since it is not possible to get only positive or negative ions in the solution of an electrolyte, there is no experimental method available to determine the activity or activity coefficient of individual ionic species. The reasons is that the solutions are electrically neutral and we cannot increase the number of cations without an equal increase in the number of anions. Since we cannot study separately the effect of cations or anions in the presence of each other in a neutral solution, it is therefore, not possible to measure the individual ion activities. Fartunately for most proposes, it is sufficient to know the mean ionic activity $(a_\pm)$ and mean activity coefficient $(\gamma_\pm)$.

Since it is not possible to substitute concentrations for activities in ionic solutions, it is essential to consider how the ionic concentrations may be converted to the activities and how such activities can be evaluated. In order to introduce some definitions commonly employed in dealing with the activities of strong electrolytes. Consider on electrolyte A_xB_y which ionizes in the solution according to

$$A_xB_y = xA^{Z+} + yB^{Z-}$$

When Z+ and Z- are the charges on the cation and anion respectively. The activity of the electrolyte as a whole, a_2, is defined in terms of the activities of the two ions, a_+ and a_- as

$$a_2 = a_+^x a_-^y \tag{9.64}$$

If V is the total number of the ions furnished by one molecule of the electrolyte, i.e., V = x + y, this mean activity is defined as

$$a_\pm = (a_2)^{1/V} = (a_+^x a_-^y)^{1/V} \tag{9.65}$$

The activities of the ions one related to their concentrations through the relation.

$$a_+ = \gamma_+ m_+ \tag{9.66}$$

$$a_- = \gamma_- m_- \tag{9.67}$$

When m_+ and m_- are the molalities of the cation and anions and γ_+ and γ_- are the corresponding activity coefficients. There activity coefficients are appropriate factors which when multiplied by the molalities of the respective ions yield their activities. Introducing Eq (9.66) and (9.67) into Eq (9.64), we obtain for a_2

$$a_2 = (m_+\gamma_+)^x\ (m_-\gamma_-)^y$$

$$a_2 = (m_+^x\, m_-^y)^x\ (\gamma_+^x\, \gamma_-^y) \tag{9.68}$$

and for mean activity from Eq. (9.65)

$$a_\pm = (a_2)^{1/v} = (m_+^x m_-^y)^{1/v}\, \gamma_+^x\, \gamma_-^y)^{1/v} \tag{9.69}$$

The factor $(m_+^x\, m_-^y)^{1/v}$ is defined as the mean molality of the electrolyte.

$$m_\pm = (m_+^x\, m_-^y)^{1/v}$$

Similarly $(\gamma_+^x\, \gamma_-^y)^{1/v}$ is known as mean activity coefficient

$$\gamma_\pm = (\gamma_+^x\, \gamma_-^y)^{1/v}$$

In terms of mean molality and mean activity coefficient, Eq (9.68) an (9.69) may be written as

$$a_2 = a_\pm^v = m_\pm\gamma_\pm \tag{9.70}$$

$$a_\pm = a_2^{1/v} = (m_\pm\gamma_\pm)^v \tag{9.71}$$

Finally since for any electrolyte of molality m, we have

$$m_+ = xm$$

$$m_- = ym$$

Eqs. (9.70) and (9.71) then take the form

$$a_\pm = (m_+^x\, m_-^y)^{1/v}\ \gamma_\pm$$

$$= \left[(xm)^x\,(ym)^y\right]^{1/v}\ \gamma_\pm$$

$$= \left[\left(x^x m^x\right)\left(y^y m^y\right)\right]^{1/v}\ \gamma_\pm$$

$$= \left[\left(x^x y^y\right)^{1/v}\left(m^{x+y}\right)\right]^{1/v}\ \gamma_\pm$$

$$= \left(x^x y^y\right)^{1/v} m\ \gamma_\pm \tag{9.72}$$

and $$a_2 = (a_\pm)^\nu = \left[(x^x y^y)^{1/\nu} m\, \gamma_\pm\right]^\nu$$

$$= \left(x^x y^y\right) m^\nu \gamma_\pm^\nu \qquad (9.73)$$

Equation (9.72) and (9.73) are the expressions needed for converting activities to molalities, or vice versa. Thus for 1:1 electrolyte such as KCl, of molality m, we have x = 1, y = 1, V = 2 and therefore

$$a_\pm = (1 \times 1)^{1/2} m\, \gamma_\pm$$

$$a_2 = a_\pm^2 = m^2 \gamma_\pm^2$$

Again for an electrolyte of the 2:1 type, such as $BaCl_2$, we have x = 1, y = 2 and V = 3.

$$a_\pm = \left(1 \times 2^2\right)^{1/3} m\, \gamma_\pm$$

$$= (4)^{1/3} m\, \gamma_\pm$$

$$a_2 = a_\pm^3 = 4m^3 \gamma_\pm^3$$

Example 9.5.

Calculate the mean and total activity of the following electrolytes: (i) CuSO (ii) Na_3PO_4 (iii) $Ca_3(PO_4)_2$

Solution:

(i) $CuSO_4$ x = 1, y = 1, and V = 1 + 1 = 2

$$a_\pm = (1 \times 1)^{1/2} m\, \gamma_\pm$$

$$= m\gamma_\pm$$

$$a_2 = (a_\pm)^2 = m_2 \gamma_\pm^2$$

(ii) Na_3PO_4 x = 3, y = 1, V = x + y = 4

$$a_\pm = (3^3 \times 1^1)^{1/4} m\, \gamma_\pm = (27)^{1/4} m\gamma_\pm$$

$$a_2 = (a_\pm)^4 = 27m^4 \gamma_\pm^4$$

(iii) $Ca_3(PO_4)_2$ x = 3, y = 2, V = x + y = 3 + 2 = 5

$$a_\pm = (3^3 2^2)^{1/5} m\, \gamma_\pm = (108)^{1/5} m\, \gamma_\pm$$

$$a_2 = 108 m^5 \gamma_\pm^5$$

Example 9.6. Calculate the mean activity of the ions and activity of the electrolyte in 0.1m NaCl solution. The $\gamma_{\pm}$ is 0.778.

Solution:

$$m = 0.1 \text{ and } \gamma_{\pm} = 0.778$$

$$a_{\pm} = m\gamma_{\pm}$$

$$= 0.1 \times 0.778 = 0.0778$$

$$a_2 = (a_{\pm})^2$$

$$= (0.0778)^2 = 6.05 \times 10^{-3}$$

9.20. DEBYE- HUCKEL LIMITING LAW:

One of the most significant contributions to our understanding of the behavior of electrolyte solutions is the Debye-Huckel limiting law. Debye and Huckel (1923) derived an equation which offers quantitative calculation of mean activity coefficients of strong electrolytes. The values obtained theoretically were in good agreement with the experimental values as long as the concentrations are kept low. The equation which they derived is known as Limiting Law equation. The name signifies that its application is limited to dilute solutions of strong electrolytes only. This limiting law is based on the following assumptions:

(i) Electrolytes are completely dissociated into ions in solution.

(ii) The solutions are dilute, with a concentration of 0.01m or lower.

(iii) The interactions between ions of solute are electrostatic in character. Electrostatic forces are strictly long rang interactions.

(iv) The ions in the solution are subject to random thermal motion which disrupts the orientation of oppositely charged species caused by the interionic attractions.

(v) Each ion is regarded as point charge and is surrounded by ions of opposite charge, forming an ionic atmosphere.

(vi) The dielectric constant of an electrolyte solution is uniform and independent of the actual concentration of the dissolved solute.

The energy associated with the ionic atmosphere is electrical in origin. It therefore, most be a function of charge density and the potential produced by the ionic atmosphere. According to Debye-Huckel theory the energy of ionic interaction is electrostatic in origin and may be defined as the energy of charging a central ion in the electric field of an ionic cloud.

The energy of a charged body, that is the work expanded in the process of charging, is half the product of its charge and potential. Hence for an ion of charge + $Z_i \in$ the energy it possesses by virtue of its ionic atmosphere is given as

$$E_i = \frac{1}{2} \text{(charge) (potential)}$$

$$E_i = \frac{1}{2}(Z_i \in)\left(\frac{-Z_i \in k}{D}\right)$$

$$E_i = -\frac{Z_i^2 \in^2 k}{2D}$$

The corresponding energy for a 1 g ion is obtained on multiplying by the Avogadro number, N, so that

$$E_i = -\frac{NZ_i^2 \in^2 K}{2D} \tag{9.74}$$

According to the definition of chemical potential the chemical potential of a particular ion in an ideal solution is given by

$$\mu_i = \mu_i^o + RT\ln x_i \tag{9.75}$$

When x_i is mole fraction in the given solution. For a non-ideal solution one can write

$$\mu_i = \mu_i^o + RT\ln a_i$$

$$\mu_i = \mu_i^o + RT \text{ in } a\, x_i + RT \ln \gamma_i \quad (\therefore a_i = \gamma_i x_i) \tag{9.76}$$

Where a_i is the activity and γ_i the activity coefficient of ionic species. The difference between Eqs (9.75) and (9.76) is $RT\ln\gamma_i$ which is equal to the difference in free energy change accompanying the addition or removal of 1g ion of the given species from a large volume of real and ideal solution respectively. This difference of free energy may be regarded an, equivalent to the electrical energy of the ion due to its atmosphere; that is to say, the departure from ideal behavior is ascribed entirely to interionic forces. Hence Eq. (9.74) became as.

$$RT\ln\gamma_i = -\frac{NZ_i^3 \in^2 k}{2D}$$

$$\ln\gamma_i = -\frac{NZ_i^3 \in^2 k}{2DRT} \tag{9.77}$$

From Eq. (9.38), we know

$$k = \left(\frac{4\pi \in^2 \sum n_i Z_i^2}{DkT}\right)^{1/2}$$

or

$$k = \frac{4 \in (\pi)^{1/2} (\sum n_i Z_i^2)^{1/2}}{(DkT)^{1/2}}$$

Where n_i is the number of ions per ml. It may be replaced by $NC_i/1000$, where C_i is the number of gram ions dissolved per liter, k is the Boltzmann constant, $k = R/N$

$$k = \frac{2\in(\pi)^{1/2}\left(\sum \frac{NC_i}{100} Z_i^2\right)^{1/2}}{\left(\frac{DRT}{N}\right)^{1/2}}$$

$$k = \frac{2\in\left(\frac{\pi}{1000}\right)^{1/2}(N)^{1/2}\left(\sum C_i Z_i^2\right)^{1/2}}{\left(\frac{DRT}{N}\right)^{1/2}}$$

$$k = \frac{2\in\left(\frac{\pi}{1000}\right)^{1/2} N\left(\sum C_i Z_i^2\right)^{1/2}}{(DRT)^{1/2}} \tag{9.68}$$

Substituting this value of into Eq. (9.77), we get

$$\text{In}\,\gamma_i = \frac{-NZ_i^2\in^2}{2\,DRT}\cdot\frac{2\in\left(\frac{\pi}{1000}\right)^{1/2} N\left(\sum C_i Z_i^2\right)^{1/2}}{(DRT)^{1/2}}$$

Multiplying both sides by negative and on rearranging we get

$$-\text{In}\,\gamma_i = \frac{N^2Z_i^2\in^3}{DRT}\cdot\frac{\left(\frac{\pi}{1000}\right)^{1/2}\left(\sum C_i Z_i^2\right)^{1/2}}{(DRT)^{1/2}}$$

$$-\log\gamma_i = \frac{N^2\in^3\left(\frac{\pi}{1000}\right)^{1/2}}{2.303\,R^{3/2}}\cdot\frac{Zi^2\left(\sum C_i Z_i^2\right)^{1/2}}{(DT)^{3/2}} \tag{9.79}$$

The term in the large parentheses consists of several constants, only and may be replaced by A'.

$$-\log\gamma_i = \frac{A'\,Z_i^2\sqrt{\sum C_i Z_i^2}}{(DT)^{3/2}} \tag{9.80}$$

Further, we know that

$$\mu = \frac{1}{2}\sum C_i Z_i^2 .$$

$$2\mu = \sum C_i Z_i^2 \tag{9.81}$$

Substituting the value of $\sum C_i Z_i^2$ from Eq. (9.81) into Eq. (9.80) we get

$$-\log \gamma_i = \frac{A' Z_i^2 \sqrt{2\mu}}{(DT)^{3/2}}$$

$$-\log \gamma_i = \frac{A' \sqrt{2} Z_i^2 \sqrt{\mu}}{(DT)^{3/2}}$$

$$-\log \gamma_i = \frac{A'' Z_i^2 \sqrt{\mu}}{(DT)^{3/2}} \tag{9.82}$$

For a given solvent and temperature, D and T have definite values which may be inserted into Eq. (9.82) to give

$$\log \gamma_i = -A\ Z_i^2 \sqrt{\mu} \tag{9.83}$$

By inserting the values of N, E, π, R, D, and T, the value of A is found to be 0.509 at 25°C, hance

$$-\log \gamma_i = 0.509\ Z_i^2 \sqrt{\mu} \tag{9.84}$$

Eqs. (9.83) and (9.84) represent the Debye-Huckal limiting law. This expresses the variation of the activity coefficient of an ion with the ionic strength of the solution. It is expected to hold for dilute solutions of electrolytes as is clear from the fact that the expression for the potential on an ion due to ionic atmosphere was derived assuming dilution being approached. Moreover, from Eq (9.84). It follows that activity coefficient of an ion should decrease with increasing ionic strength of the solution.

Since the individual activity or activity coefficient, of an ion cannot be determined experimentally, it is not possible to make direct test of Eg. (9.83) However, it is possible to relate the individual ion activities to the measurable mean activities of the ions. If one molecule of a binary electrolyte dissociates into V ions of which V+ are cations and V- anions, then the mean activity coefficient is related to individual ionic activity coefficient γ_+ and γ_- by

$$\gamma_\pm = (\gamma_+^{v+} \gamma_-^{v-})^{1/v}$$

$$\log\gamma_\pm = \frac{1}{v} \log (\gamma_+^{v+} \gamma_-^{v-})$$

$$= \frac{1}{v}\left[\log \gamma_+^{v+} + \log \gamma_-^{v-}\right]$$

$$= \frac{1}{v}\left[V_+ \log \gamma_+ + V_- \log \gamma_-\right] \tag{9.58}$$

If the valences of the ions are Z_+ and Z_- respectively, then by the relationship between the valve and the number of ions, i.e., $v_+ z_+ = v_- z_-$, it follows that

$$\frac{V_+}{V_-} = \frac{Z_-}{Z_+}$$

$$\log \gamma_\pm = \frac{1}{v_+ + v_-}[Z_- \log \gamma_+ + Z_+ \log \gamma_-]$$

$$\log \gamma_\pm = \frac{1}{v_+ + v_-}\left[Z_-\left(-AZ_+^2\sqrt{\mu}\right) + Z_+(-AZ_-^2\sqrt{\mu}\right]$$

$$\log \gamma_\pm = -\frac{AZ_+Z_-\sqrt{\mu}\,(Z_+ + Z_-)}{Z_- + Z_+}$$

$$\log \gamma_\pm = -A\, Z_+ Z_- \sqrt{\mu} \qquad (9.86)$$

Equation (9.86) also represents the Debye-Huckal limiting law for dilute solutions. According to this law the department from the ideal behavior in a given solvent is gourmed by the ionic strength of the medium and valence of the ions of electrolyte, but is independent of their chemical nature.

Verification of the Debye-Huckel Limiting Law:

The mean activity coefficients of various electrolytes can be determined experimentally by a number of methods, e.g. measurement of vapour pressure, freezing point, solubility or electromotive force. In general, it is found that the mean activity coefficient of an electrolyte decrease with increasing concentration, but at higher concentration range it is frequently found that the mean activity coefficient increase with increasing concentration, thus passing though a minimum.

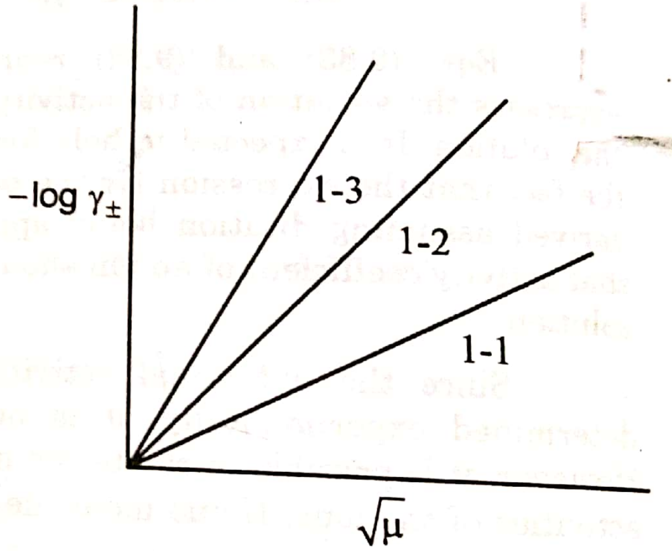


Fig. 9.7. Test of Debye-Huckel limiting law for diffent electrolytes.

The law can be tested by plotting a graph between $-\log \gamma_\pm$ and $\sqrt{\mu}$, at room temperature. All electrolytes should give a straight line passing through the origin. The slope of the line depends on z_+ and z_- values of the given electrolytes. For electrolytes this slope should be A, for 1-2 or 2-1 type electrolytes 2A for 1-3 or 3-1 electrolytes 3A etc.

Example 9.7. Calculate the mean activity coefficient of (i) a 1-1 electrolyte, e.g., NaCl at a molility of 0.01 and of (ii) 1-2 electrolyte, e.g., Na_2SO_4 at a molality of 0.001 in aqueous solution of 25°C.

Solution:

(i) For 1-1 electrolyte, the ionic strength is equal to its molality, hence $\mu = 0.01$, $Z_+ = Z_- = 1$, so

$$\log \gamma_\pm = -0.509 \times 1 \times 1\sqrt{0.01}$$

$$\log \gamma_\pm = -0.0509$$

$$\gamma_\pm = -0.889$$

(ii) For 0.001 molal 1-2 electrolyte.

$$\mu = \frac{1}{2}(0.002 \times 1^2 + 0.001 \times 2^2)$$

$$\mu = 0.003$$

$$\log \gamma_\pm = -0.509 \times 1 \times 2\sqrt{0.003}$$

$$\log \gamma_\pm = -0.0558$$

$$\gamma_\pm = 0.879$$

9.21. DETERMINATION OF ACTIVITY COEFFICIENTS OF ELECTROLYTES

The mean activity coefficients of various electrolyte can be determined experimentally by a number of methods. Some of them one:

(i) Solubility method

(ii) Vapour pressure method

(iii) Freezing point method

(iv) Electromotive force method

(v) Equilibrium constant method.

It is important to note that activity coefficient of a single ion cannot be determined experimentally, because it is impossible to isolate an ion in free state. Hence only mean activity coefficient of various electrolytes, are usually determined. We shall discuss here some of these methods.

(i) Solubility Method:

This method is particularly used for sparingly soluble salts. When a solution is saturated with a salt there is an equilibrium between the excess solid and the ions in the solution. To consider a simple case, such as that of sparingly soluble salt silver chloride in contact with its saturate solution, the equilibrium may be represented by

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

Where Ag^+ and Cl^- ions refer to the hydrated ions in the solution. The corresponding equilibrium constant is given as

$$K = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}} \tag{9.87}$$

Since the silver chloride is present in the solid state, its activity is taken as unity by convention.

$$K.(a_{AgCl}) = (a_{Ag^+})(a_{Cl^-}) \qquad \therefore a_{AgCl} = 1$$

$$K_S = (a_{Ag^+})(a_{Cl^-}) \tag{9.88}$$

Where the constant, K_s is known the solubility product constant of the silver chloride.

In general for any electrolyte having the general formula AB(s), in contact with its saturated solution, the equilibrium between the solid and the ions in solution is

$$AB_{(s)} \rightleftharpoons A^+ + B^-$$

and the solubility product constant is given by

$$K_s = (a_{A^+})(a_{B^-}) \tag{9.89}$$

This expression is the basis of the solubility product principle which states that when a solution is saturated with a given salt, the product of the activities (or concentrations) of its constituent ion, raised to the appropriate powers, must be constant, irrespective of the nature of other electrolytes present in the solution.

If the activity of each ion is written as the product of its concentration in gram ions per liter and the corresponding activity coefficient, then the expression for the solubility product of $AB_{(s)}$ becomes.

$$K_S = \gamma_+[A^+]\,\gamma_-[B^-]$$

$$K_S = \gamma_+\gamma_-[A^+][B^-]$$

$$K_S = \gamma_\pm^2[A^+][B^-]$$

Taking logarithms an both sides we get (on rearranging)

$$\log K_S = \log \gamma_\pm^2 + \log [A^+][B^-]$$

$$\log K_S = 2\log \gamma_\pm + \log [A^+][B^-]$$

$$\log [A^+][B^-] = \log K_S = 2\log \gamma_\pm$$

The solubility 'S' of such a salt is equal to the moles per liter of the salt t dissolves, if no species of electrolyte $AB_{(S)}$ other than A^+ and B^- exist in solution.

$$[A^+] = [B^-] = S$$

Thus $\log S.S. = \log K_S - 2\log \gamma_\pm$

$$\log S^2 = \log K_S - 2\log \gamma_\pm$$

$$2\log S = \log K_S - 2\log \gamma_\pm$$

$$\log S = \frac{1}{2}\log K_S - \log \gamma_\pm \qquad (9.90)$$

Since K_s is solubility product, and is constant at a given temperature, so variation of mean activity coefficient i.e, $\gamma_\pm$, can be related with the solubility of that compound at a given temperature. In order to find the utility of last equation, now consider the data that are obtained when a sparingly soluble salt is dissolved in solutions that contain various amounts of neutral or non-reacting electrolyte, that do not contain the ions A^+ or B^- Debye-Huckel theory again suggests that at low ionic strength.

$$-\log \gamma_\pm = 0.5091\, Z_i^2 \sqrt{\mu}$$

$$-\log \gamma_\pm \propto \sqrt{\mu}$$

Hence we write the previous equation.

$$\boxed{\log S = \frac{1}{2}\log K_S + 0.5091\, Z_i^2 \sqrt{\mu}} \qquad (9.91)$$

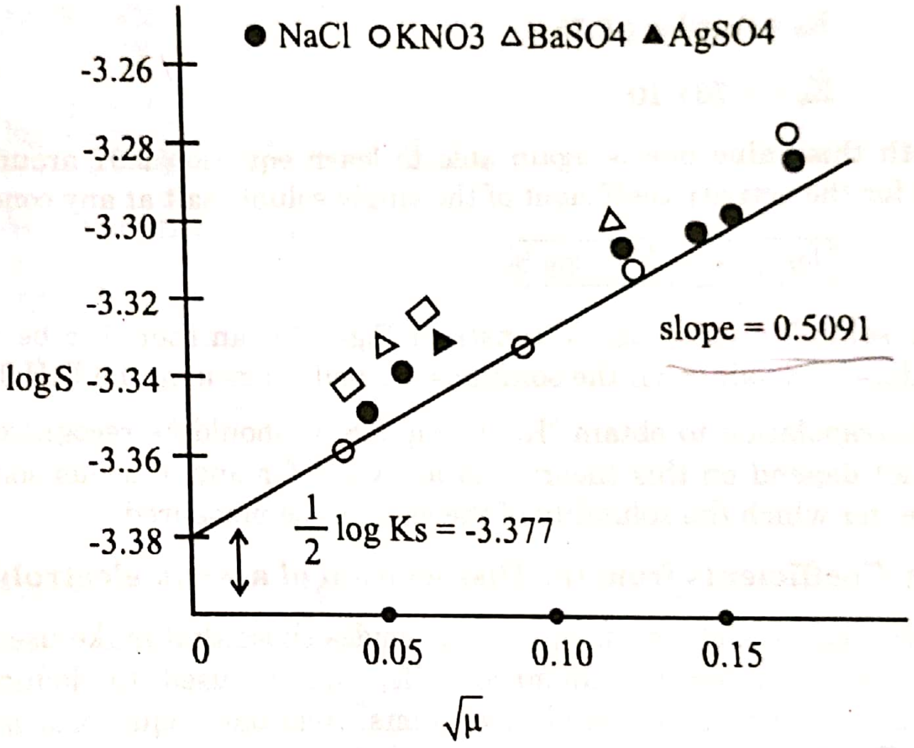


Fig. 9.8 calculation of K_s by extra-polation method

If "log S" is plotted against $\sqrt{\mu}$ by using a complicated but experimentally convenient salt $[Co(NH_3)_4C_2O_4][Co(NH_3)_2(NO_2)_2C_2O_4]$, a straight line is obtained, which supports Deby-Huckel predictions of linear relation and straight line has been drawn with predicted slope of 0.5091

The Fig 9.8 shows the effect of added salts on the solubility of a salt $[CO(NH_3)_4C_2O_4][CO(NH_3)_2(NO_2)_2C_2O_4]$ containing a singly charged cation and a singly charged anion. For this particular set of data that the linear relation is rather rough and that support for Debye-Huckel theory is given but is not very convincing here. It is just such difficulties that the theory frequently encounters particularly in solutions other than those of extremely low ionic strength.

An extrapolation can be mad in Fig 9.8 with/ without D.H.T and one obtains for the L.H.B of equation (9.91) at zero ionic strength, the value −3.377. Again the limit of zero ionic strength corresponds to the complete absence of ionic interactions. Therefore,

$$\gamma_\pm = 1 \text{ and } \log \gamma_\pm = 0$$

At this limit equation 9.91 gives

$$\frac{1}{2} \log K_s = -3.377$$

$$\log K_s = -6.754$$

$$K_s = \text{Antilog}(-6.754)$$

$$K_s = 1.76 \times 10^{-7}$$

With this value one is again able to learn equation 9.91 around to give an expression for the activity coefficient of the singly soluble salt at any concentration.

$$\boxed{\log \gamma_\pm = -3.377 - \log S} \qquad (9.92)$$

The solubility data, use to construct Fig-(9.8) can therefore be made to give $\gamma_\pm$ for the dissolved salt in all the solutions studied. Although, the D.H.T was used to aid in the extrapolation to obtain "K_s" in Fig 9.8, it should be recognized that these results do not depend on this theory and are valid for any aqueous solution at this temperature, for which the solubility of the salt can be measured.

(ii) Activity Coefficients from the Dissociation of a weak electrolyte

Other studies of chemical equilibria besides those that make use of oxidation-reduction reactions in electro chemical cells, can be used to deduce in electro thermodynamic properties of non-ideal systems. Acid-base equilibria provide many illustrations. The traditional example is the equilibrium set up by the dissociation of acetic acid, CH_3COOH, here abbreviated HAc.

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

or $$HAc \rightleftharpoons H^+ + Ac^-$$

The thermodynamic equilibrium constant, denoted by K_{th} is given

$$K_{th} = \frac{(a_{H^+})(a_{AC^-})}{(a_{HAc})}$$

$$K_{th} = \frac{\gamma_+\gamma_-[H^+][Ac^-]}{\gamma_{HAc}\,[HAc]} \tag{9.93}$$

This expression is simplified when it is realized that the electrostatic interactions are primarily responsible for the non-ideality which produces activity coefficient different from unity. The uncharged HAc molecule should therefore behave relatively ideally, and we can set $\gamma_{HAc} = 1$

$$K_{th} = \frac{\gamma_\pm^2[H^+][Ac^-]}{[HAc]} \tag{9.94}$$

Taking log of the above expression and an rearranging we get

$$\log K_{th} = \log\left[\frac{\gamma_\pm^2\,[H^+][Ac^-]}{[HAc]}\right]$$

$$\log K_{th} = \log \gamma_\pm^2 + \log \frac{[H^+][Ac^-]}{[HAc]}$$

$$\log K_{th} = 2\log \gamma_\pm + \log \frac{[H^+][Ac^-]}{[HAc]}$$

$$\log \frac{[H^+][Ac^-]}{[HAc]} = \log K_{th} - 2\log \gamma_\pm \tag{9.95}$$

Since HAc is partially dissociated, so the concentration of dissociated and un-dissociated acetic acid may be substituted in the above expression by considering the degree of dissociation ($\propto$). Let

$$HAc \rightleftharpoons H^+ + Ac^-$$

1 mole	$0+0$	$t=0$
$(1-\alpha)$ mole	$\alpha+\alpha$	after $t-$sec

Where α=no of moles converted to ions and it is also known is degree of dissociation. Let the concentration of CH3COOH is taken as "C" moles liter. Then at equilibrium stage.

$$C(1-\alpha) \rightleftharpoons C\alpha + C\alpha$$

Substitute then values of concentration in Eq. (9.95) we get

$$\log \frac{C\alpha.\,C\alpha}{C(1-\alpha)} = \log K_{th} - 2\log \gamma_\pm$$

$$\log \frac{C\alpha^2}{(1-\alpha)} = \log K_{th} - 2 \log \gamma_{\pm} \tag{9.96}$$

For solutions that are very dilute in ions. One can still use the Arrhenius expression to obtain the degree of dissociation from the conductivity measurement.

$$\alpha = \frac{\Lambda}{\Lambda_o} = \frac{\text{equivalent conductance at given cancentration}}{\text{equivalent conductance at infinite dilution}}$$

In this way, the left side of Eq. (9.96) is determined for various acetic acid concentrations. The right side consists of a constant term log K_{th} and a term which the D.H. theory suggests will, at low concentrations, be proportional to the square root of the ionic strength.

$$-\log \gamma_{\pm} \propto \sqrt{\mu}$$

If the solution contains only the H^+ and Ac^- ions from the dissociation of HAc, one has

$$\mu = \frac{1}{2}\left[(C\alpha)(1)^2 + (C\alpha)\,(-1)^2\right]$$

$$\mu = C\alpha$$

and $$\sqrt{\mu} = \sqrt{C\alpha}$$

so $$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 2(0.5091\, Z_+ Z_- \sqrt{\mu})$$

$$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 1.018\, Z_+ Z_- \sqrt{C\alpha} \tag{9.97}$$

Equation (9.97) is an equation of straight-line,

$$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 1.018\sqrt{C\alpha} \quad \therefore \text{ electrolyte is 1:1 type } Z_+ = Z_- = 1$$

If a graph is plotted between log $\frac{C\alpha^2}{1-\alpha}$ v/s $\sqrt{C\alpha}$ a straight-live obtained with slope 1.018 and intercept log K_{th}.

Extrapolation to zero ionic strength, when $\gamma_{\pm} = 1$ and log $\gamma_{\pm} = 0$, gives

$$\log K_{th} = -4.7565$$

and $$K_{th} = \text{antilog}\,(-4.7565)$$

$$K_{th} = 1.752 \times 10^{-5}$$

$$K_{th} = 1.752 \times 10^{-5} \text{ (theoretical)}$$

$$K_{th} = 1.8 \times 10^{-5} \text{ (experimental)}$$

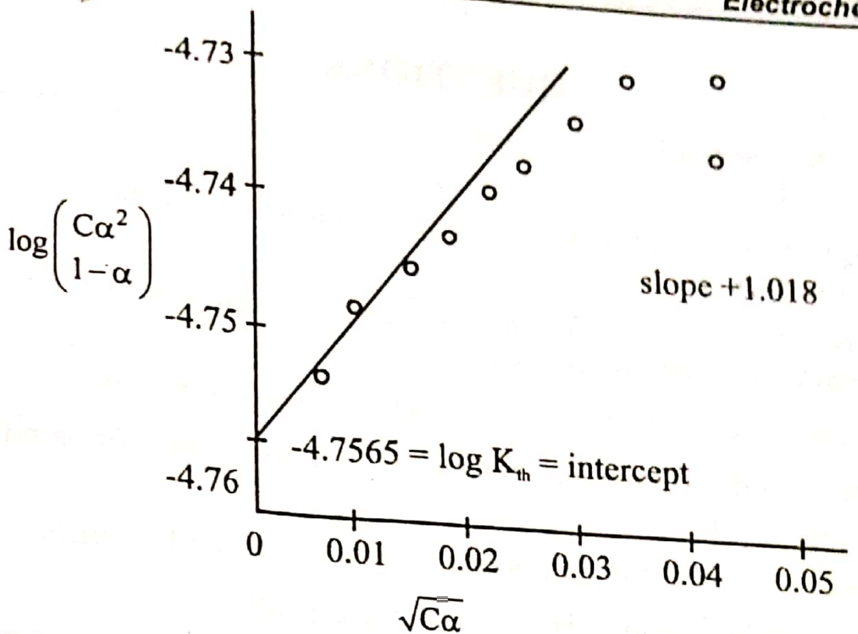


Fig. 9.9. Representation of experimented data for weak electrolyte

The value of K_{th} is very close to experimental value, so D.H.L can be used to calculate the thermodynamic equilibrium constant of weak electrolyte.

Equation (9.96) can also be now rearrange to give.

$$\log \gamma_{\pm} = \frac{1}{2} \log K_{th} - \frac{1}{2} \log \frac{C\alpha^2}{1-\alpha}$$

$$\log \gamma_{\pm} = -2.3782 - \frac{1}{2} \log \frac{C\alpha^2}{1-\alpha} \qquad (9.98)$$

From equation (9.98), we can determine $\gamma_{\pm}$ for the dissociation products of CH_3COOH at any concentrations for which values of α can be obtained.