**conductance**

**Introduction**:

Conducting ability of electrolytic solution provides a direct proof of the **existence** of ions in solutions. The experimental determinations of the conducting properties of electrolytic solutions are very important as they can be used to study quantitatively the **behaviour** of ions in solutions. Further, conducting properties can also be used to determine the values of many physical quantities such as solubilities and solubility products of sparingly soluble salts, ionic products of self-ionizing solvents, hydrolysis constants of salts, dissociation constants of weak acids and bases and to form the basis of conductometric titration methods.

Before the main topic, it is better to discuss the basics of Electrochemistry.

**BASICS OF CONDUCTANCE** —

**Metallic Conduction**:

The electrons can flow through metals, and this property is known as **metallic** or **electronic** **conduction**.

When electrons from an **external** **source** () are **forced into one end** of a metallic wire, it displaces the electrons of the metallic lattice at the point of entry. The **displaced** **electrons**, in turn, assume new positions by pushing neighbouring electrons ahead, and this effect is **transmitted** right down to the other end of the wire where they are forced out and sent back to the external source. The rate at which electrons enter from one end of the wire is always equal to that of transmission from the other end. At any position in the wire, the electrical **neutrality** is maintained.

The **quantity** of **electric** charge is measured in **coulombs**. One **coulomb** is **defined** as the charge carried by electrons. The rate of **current** flow is given in **amperes**; one ampere is . We can therefore write —

Where: the current in ampere,

 The chare transported in coulomb, and

 The time in second,

The current is forced through the circuit by an electrical **potential difference**, which is measured in **volts**. It takes of work to move from a lower to higher potential when the potential difference is . Thus, —

Thus,  **volt coulomb** is a unit of **energy** and equals joule.

**Important Note**: In ***CGS*** system **unit** of **charge** and **work** is and respectively

One electrostatic unit of charge (***esu***) is defined as the charge that will repel another like charge at a distance of by a force of

One is the work done when a force of acts through a distance of . Thus,

**Ohms Law:** Metallic conductors as well as electrolytes obey Ohm’s law, which states that —

“***The strength of current*** () ***flowing through a conductor is directly proportional to the potential difference*** () ***between its two ends***.” Thus, —

The **proportionality** constant “” is known as the **resistance** () of the conductor. Equation () is known as the Ohm’s law.

**Unit of Resistance ()**: Unit of resistance is . Thus —

**Effect of Temperature on Resistance**:

Resistance to current flow in a metal is caused by the vibration of the metal ions about their lattice positions; such vibrations interfere with the motion of the electrons and consequently retarded the flow of current. On **increasing** **temperature**, the thermal motion of metal ions increases and thus, offers **more resistance** against the flow of electrons. Hence, metals become **poorer** **conductors** with **rise** in the **temperature**.

**Electrolytic Conduction**:

In electrolytic conduction, charge is carried by ions of the electrolyte either in its molten stage or in its aqueous solution.

The principles of electrolytic conduction can be well explained by considering an **electrolytic** **cell** as shown in the figure given below for the electrolysis of .



**Working of an Electrolytic Cell**: The electrons are received from the end of the external battery by the electrode (**cathode**). These electrons are used up in the **reduction** reaction at the cathode. The numbers of electrons received at the electrode (terminal) are given back to the end of the external battery from the electrode (anode) of the cell where electrons are released as a result of oxidation reaction. Within the cell, current is carried by the **movements of ions**: **cations** towards the  **electrode** (cathode) and **anions** towards the  **electrode** (anode).

**Factors Affecting Electrolytic Conduction**:

The movement of ions of an electrolyte in an electrolytic cell to the oppositely charged electrodes is known as the electrolytic conduction. Electrolytic conduction depends on the mobility of ions and anything that inhibits the motion of ions causes resistance to current flow. Factors that influence the electrolytic conductivity of solutions of electrolytes include —

1. Interionic attraction,
2. Solvation of ions, and
3. Viscosity of the solvent.

All these factors depend on the attraction of solute-solute, solute-solvent and solvent-solvent during electrolysis. Further, the average kinetic energy of the solute ions increases as the temperature is raised and, therefore, the resistance of the electrolytic conductors generally decreases (*i.e*. conduction increases) as the temperature is raised.

**Note**: In the case of —

1. Metallic conductor we use the term **resistance** ()
2. Electrolytic solution we use the term **conductance** ()

Thus, both are same but used in different field.

**Electrolysis**:

The electrolysis of molten salts produces ions which are characteristic of the salt. When certain aqueous solutions are electrolysed, water is, however, involved in the electrode reactions rather than the ions derived from the solute. Hence, the current-carrying ions are not necessarily discharged at the electrodes.

The cathodic and anodic reactions involved in the electrolysis of aqueous solutions of some salts are given below —

**Faraday’s Law of Electrolysis**:

The **quantitative** relationships between **electricity** and the **chemical** **change** were first described by Michael Faraday. These are —

1. *The mass of a chemical substance involved (deposited) at an electrode is directly proportional to the amount of current passed through the cell.*
2. *The mass of different substances produced by a given amount of current are proportional to the equivalent masses of the substances*.

These two laws have been shown to hold very rigidly provided the passage of electricity takes place entirely by electrolytic conduction. Bothe the laws are applicable for —

1. Molten electrolytes as well as solutions of electrolytes, and
2. Independent of temperature, pressure or the nature of the solvent.

**Mathematically**, **Faraday’s law** may be represented as —

Here, ‘’ is the mass of the species having molar mass deposited or liberated in an electrode on passing a current ‘’ for time ‘’ and is the stoichiometric number of electrons involved in the reduction or oxidation reaction involved in the electrode.

**Conductance:** (In relation to electrolytes, the term conductance, is used more frequently than resistance)

Conductance implies the ease with which electric current can flow through a conductor. It is therefore, defined as the reciprocal of resistance (). Thus,

Since, is expressed in ohms (), therefore, conductance () for a sample is expressed is , also called .

However, the official unit or designation of is , and

**Resistance () and Resistivity or specific resistance**:

The resistance, of a conductor is —

1. Directly proportional to its length ( - in cm) and
2. Inversely proportional to its cross-sectional area ().

Hence,

The proportionality constant “” is called the **specific resistance or resistivity** of the sample.

Hence, **resistivity can be defined** as the resistance of a uniform column of the material of the conductor having a length of and a cross section of .

**Unit of specific resistance ()**: Since —

**Specific Conductance or Conductivity ()**: (Kappa)

The reciprocal of specific resistance () is called specific conductance or conductivity. Thus,

In the **case of solution**, definition will be the same as of a conductor. In simple words, it is defined as —

“The conductivity offered by a solution of length and area of unit cross section () *i.e*.  **solution**.

**Unit of specific conductance or conductivity ()**: Since —

Though, the unit is , but units is more convenient.

**Determination of Specific Conductance or Conductivity ()**:

Because of the complicated distribution of current, it is inconvenient to calculate directly from the resistance () of the sample and cell dimensions . In practice, the cell is calibrated using a sample (normally an aqueous solution of ) of known , and a cell constant ‘’ (*i.e.* the ratio of ) is determined from —

Where is the resistance of the standard aqueous solution of . Now, if the same cell is used for a solution of resistance , then the conductivity of the solution will be —

**Classification of Conductance** — Conductances are basically of **two** types —

1. **Molecular conductance** (), **[**actually for ionic molar conductance, we use small form of lambda, for the molecule as a whole we use the capital form of lambda, **]**
2. **Equivalent conductance** (), **[**here again, for ionic equivalent conductance, we use small form of Equivalent, for the molecule as a whole we use the capital form of lambda, **]**

**Molar or Molecular conductance, is defined as —** The conductance of a solution containing of the electrolyte when placed between two sufficiently large electrodes placed apart. Mathematically —

Where is the specific conductance () and ‘’ is the molar concentration of the added electrolyte**.** Molar or Molecular conductance (), is usually expressed in .

**Practical relation —** Since, ‘’ is normally available in and molar concentration () in , so the practical relation is —

**Note**:

 Sp conductance Volume of the solution in containing of the electrolyte

**Equivalent conductance () is defined as —** The conductance of a solution containing of an electrolyte placed between two sufficiently large electrodes which are apart.

 Mathematically —

Where is the specific conductance () and ‘’ is the concentration of the added electrolyte in **.** Equivalent conductance (), is usually expressed in .

**Practical relation —** Since, ‘’ is normally available in and equivalent concentration () in , so the practical relation is —

**Note**:

 Sp conductance Volume of the solution in containing of the electrolyte

**Problem (1)**: The molar conductivity of . The measured resistance in a conductivity cell was . The resistance was , when the same cell contained . Calculate the molar conductivity of at that concentration.

[**Method**: First we need to determine the cell constant, and then use this constant and the given resistance to calculate the conductivity of the test solution. The molar conductivity is then found by dividing the conductivity by the molar concentration.]

**Solution**: The conductivity () of a () solution,

It follows that the cell constant () is —

Therefore, for () solution —

The molar conductivity of () is therefore —

**Problem (2)**: The molar conductivity of and a resistivity . The resistance was , when the same cell contained . Calculate the molar conductivity of at that concentration.

**Solution**: The conductivity or specific conductance () of a () solution,

It follows that the cell constant () is —

Therefore, for () solution —

The molar conductivity of () is therefore —

**Problem (3)**: When a conductance cell was filled with a aqueous solutions of , which had a specific conductance of , it had a resistance of at room temperature. When the same cell was filled with a solution of its resistance was . Calculate the cell constant and specific conductance of at this concentration.

**Solution**: For the aqueous solution —

Therefore, the cell constant of the cell —

Now, for the aqueous solution of —

**Problem (4)**: A cell, whose resistance when filled with a solution is was found to be when filled with solution at . Calculate —

1. Cell constant,
2. The specific and equivalent conductivities of solution and
3. The degree of dissociation of solution at this dilution.

(Given: Specific conductivity of is at . Equivalent conductance of solution and - ions at are respectively )

**Solution**: Cell constant of the cell used is —

Specific conductance of solution is —

But for solution —

Therefore, equivalent conductance,

Now,

**Problem (5)**: At , the specific conductance of pure water is . The ionic conductances of ions at this temperature are respectively. Calculate the value of ionization constant of water.

**Solution**: Since, we have —

But, conc. of

Therefore, equivalent conductance,

If the dissociation of water were completed, then the conc. of ions would have been - . But actual degree of dissociation is , then —

**Problem (6)**: The molar conductivity of solution of is at . A cell with electrodes that are in surface area and apart is filled with solution. How much current will flow when the potential difference between two electrodes is .

**Solution**: Molar conductivity of solution,

Concentration of solution,

Therefore, the conductivity of solution will be —

Again, the conductance of solution will be —

Resistance offered by the solution is given by —

The current flowing through the electrode is given by Ohm’s law —

**Problem (7)**: The conductivity of solution is . When an equal volume of solution is added, the conductivity decreases to . A further addition of solution, the volume of which is equal to that of the first portion added, the conductivity increases to . Calculate () () for .

**Solution**: Molar conductivity of solution—

On adding equal volume of solution, the total volume becomes double and the conc. of the salt formed will be .

Molar conductivity of solution will be —

On further addition of equal volume of the acid, the solution will become and . The conductivity of this solution will be given by —

Given that

Substituting these values in the above equation, we have —

On solving for , we will get —

 **Problem (8)**: A conductivity cell filled with solution at has a measured resistance of . Calculate the cell constant if the conductivity for solution is and conductivity water with is used to make up the solution. When the cell is filled with , the cell resistance is . Calculate the molar conductivity of acetic acid at this concentration.

**Solution**: Since, the cell constant —

Now, the conductivity of solution will be —

Therefore, the conductivity due to acetic acid alone will be —

Hence, the molar conductivity of solution will be —

**Problem (9)**: A sample of water from a large swimming pool has a resistance of at when placed in a certain conductance cell. When filled with solution, the cell has a resistance of at . Five hundred grams of were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of . Calculate the volume of water in the pool. Given: Molar conductivity of at that concentration is and molar conductivity of at is .

**Solution**: Molar conductivity of solution,

The resistance offered by solution

Conductivity of solution will be —

So, the cell constant —

Now, the conductance of water —

Again, conductance of water on adding —

Therefore, conductance due to alone will be —

Again, the conductivity of is—

And, the conc. of in the swimming pool will be —

Mass of in solution

Finally, the total volume of water in the swimming pool containing will be —

**Variation of Conductivity and Molar Conductivity with Concentration**:

Both the conductivity and molar conductivity of a solution vary with concentration. The **conductivity** **increases** with **increase** in *conc*. whereas **molar** **conductivity** **increases** on **dilution** (*i.e*. decrease in *conc*.). For strong electrolytes, **conductivity** () increases sharply with increase in conc. while for weak electrolytes, conductivity starts at lower values in dilute solutions and increases much more gradually. In both the cases, this increase is due to the increase in the number of ions per unit volume of the solution. For strong electrolytes, the number of ions per unit volume increases in proportion to the conc. and that is why the increase in conductivity is very rapid. In weak electrolytes, however, the increase in the number of ions is basically due to the change in the partial ionization of the solute, and consequently, the conductivity increases gradually.

The, molar conductivity () of both strong and weak electrolytes has been found to increase on dilution. The basic reason for this is that the decrease in conductivity is more than compensated by increase in the value of on dilution.

The variation of molar conductivity on dilution for strong and weak electrolytes shows together different behaviour as can be seen from the **figure** given below, where has been plotted against . For strong electrolytes, the variation is almost linear in dilute solutions while that for weak electrolytes, the variation is very rapid.



As the molar conductivity is a measure of the conducting power of all the ions that are available **in of the substance**, it is, therefore, obvious that the number of ions that are available for conductance increases on dilution. The **increase** in the **number of ions** in the case of weak electrolytes is due to the increase in 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.

**Ion Transport and Conductivity:** [**Repetitions** of the basics of conductance: **Levine** 471]

Electrical conduction is a transport phenomenon in which electrical charge (carried by electrons or ions) moves through the system. The **electric current** () is **defined** as the rate of flow of charge through the conducting material. Thus, —

Here, is the amount of electrical charge passes through a cross section area in time .

The electric ***current density*** () is the electric current per unit cross-sectional area () —

The **SI unit** of **current** () is **ampere** () and equals **one coulomb** () **per second** —

Although the **charge is more fundamental** than the **current** , it is easier to measure current ; it is easier to measure current than charge. (That’s why in ***SI system ampere*** is used as one of its **fundamental** units.) The ***ampere is defined*** — as the current that when flowing through two long, straight parallel wires exactly apart will produce a **force per unit length** between the wires of exactly . [Once current produces a magnetic field which exerts a force on the moving charges in the other wire] The force between two current carrying wires can be measured accurately using a **current balance** (***Halliday*** and ***Resnick***).

The **Coulomb is defined** as the charge transported in by a current —

Charge flows because it experiences an electric force, so there must be an **electric field**  in a current carrying conductor. The **conductivity** (**Kappa**, formerly called **specific conductance**, of a substance is defined by —

Here ‘’ is the magnitude of the **electric field**. The higher the conductivity ‘’, the greater the current density ‘’, that flows for a given applied electric field. The reciprocal of the conductivity is the **resistivity ()** —

Variation of electric field with **electric potential** () along - direction is given by —

Hence, from —

Current can flow in a conductor only if when there is a gradient of **electric potential** (), in the conductor. Such a gradient can be produced by attaching the ends of the conductor to the terminals of a battery.

Equation () resembles with the **Fick’s law** of transport equations *viz*. —

Let us consider a **current-carrying conductor** that has a homogenous composition and a constant **cross-sectional area** . Then the **current density**  will be constant at every part in the conductor. From , the **field strength**  is constant at every point, and the equation —

Integrates to —

Hence, —

Hence, the equation , becomes —

Let, , be the length of the conductor. Then is the magnitude of the **electric potential difference** between the ends of the conductor, and we have, —

The quantity is often called the **“*Voltage*”**. The ***resistance*** ‘’ of the **conductor** is defined by —

From equations () & (), we have —

From equation (), ‘’ has the **unit of volts per ampere**, the ***SI* unit** is ***ohm***, ‘’ *i.e*.

Thus the **SI unit** of resistivity is , also called “”, but the universally accepted name is ***Siemens*** (). Thus, —

[Note: ]

The **conductivity** () and its **reciprocal** (**resistivity**) depends on the composition of the conductor but not on its dimensions. From equation (), the resistance () depends on the dimensions of the conductor as well as the material that composes it.

For many substances, in equation () is **independent** of the magnitude of the applied electric field and hence, is **independent** of the magnitude of the **current density**. Such substances are said to obey **Ohm’s law** — *i.e*. remains constant as changes. Thus, for substances that **obey** **Ohm’s law**, a plot of will be a straight line with **slope** ‘’. **Metals obey Ohm’s law**, solutions of **electrolytes** also **obey Ohm’s law**, provided ‘’ is not **extremely high** and provided **steady-state** conditions are maintained.

**Metals** have very **low resistivity** () and **very high - values**. Concentrated aqueous solutions of **strong electrolytes** have rather **low** - values. An **electrical insulator** (For example glass) is a substance with **very low** - values. **A semiconductor** () is a substance with ‘’ intermediate between of metals and insulators. **Semiconductors** and **insulators** generally do **not** **obey Ohm’s law**; their conductivity increases with increasing applied potential difference . **~~//~~**

**Problem** (): The conductivity of a solution at is . Find the molar conductivity in this solution.

**Solution**: We have —

**Arrhenius Theory of Electrolytic Dissociation**:

According to the **Arrhenius** theory of electrolytic dissociation, there exists an equilibrium between the undissociated molecule and the ions which result from the dissociation of the molecule. Thus, —

This equilibrium is characterized by the equilibrium constant, defined as —

If ‘’ is the degree of dissociation and ‘’ is the initial concentration of the weak electrolyte , then concentrations of various species are —

Since, for weak electrolytes, , hence, we can write . Therefore, equation () reduces to —

The expression is known as the ***Ostwald dilution law***, according to which ***the*** ***degree of dissociation increases as ‘’ decreases***. As ‘’ is increased, the concentrations of the ions are also increased. Thus, the decrease of conductance for a weak electrolyte is primarily due to the increase in the number of ions on dilution.

**Expression of Degree of Dissociation**:

According to Arrhenius, the degree of dissociation of an electrolyte can be calculated by using the following expression —

Here is the molar conductivity of the solution at a given concentration and is that at infinite dilution.

Therefore, the expression for dissociation constant becomes —

From equation (), it is evident that the plot of versus will be a straight line with slope equal to . Thus, this graphical method provides a way to determine the value of the dissociation constant for a weak electrolyte.

**Molar conductance and its Temperature dependence**:

Since, the solvents viscosity decreases as the temperature increases, the ionic mobility increase as increases, hence molar conductance also increase with the increase in temperature.

 

Figure shows the variation of with temperature () for

[**Note**: We generally use for individual ions and for the solution of the electrolyte]

**Kohlrausch’s Law: Kohlrausch law of independent migration of ions** —

Kohlrausch law of independent migration of ions **states** that at **infinite dilution**, where **ionization** of all electrolytes is **completed** and where all **inter-ionic effects** are **absent**, each ion migrates **independently** of its **co-ion**, and contributes a definite share to the **total** **equivalent** **conductance** of the electrolyte, *i.e*. —

The equivalent conductance at infinite dilution for any electrolyte, where its ionization is complete, is the **sum** of **equivalent conductance** for the **cation** and **anion** at **infinite** **dilution**.

**Mathematically, Kohlrausch law** can be written as —

Here are the **equivalent** **conductance** of the **cation** and **anion** respectively at infinite dilution.

The law suggests that at infinite dilution the conductance of an electrolyte say , **depends** on the independent contributions from . The independence of these contributions is seen from the difference between - values of electrolytes containing a common ion say (where is in common with ).

Similarly, —

Thus, the **difference is constant**. The same is also true for salts with a common cation, which also would be a constant.

**Comparison of Molar Conductivities of Alkali-Metal ions**:

It is very interesting to compare the conductivities of the alkali-metal ions —

Ion

Conductivity,

These values can be well explained by **Stokes’ law** —

On the basis of Stokes’ equation we would be forced to conclude that the - ion is larger than that of - ion. In fact, the crystallographic radius of - ion is much smaller than that of - ion. However, in solution, these ions are solvated. The number of water molecules attached to any ion depends upon its charge density. Larger the charge density of an ion, larger will be the number of water molecules attached to the ion. Since, the crystallographic radii of the follows the order —

The charge density will follow the order —

Since, **- ion** has the **maximum** charge density, it follows that it will be more extensively hydrated than the rest of the ions, and as a result, it has the **largest ionic radius**. Thus, the actual ionic radii of these ions in **solution** follow the order —

And, therefore, the order of molar ionic conductivities should be —

In practice, this is the correct order of the molar ionic conductivities.

**Problem** (): The crystallographic radii of are . Estimate the ionic conductivities using Stokes law, . Compare the values obtained with the experimental values of .

**Solution**: We have

Substituting the values of for the in Stokes law —

[Experimental value is ]

[Experimental value is ]

**Applications of Kohlrausch’s law (or Conductance Measurements)**:

Following are the important and practical applications of Kohlrausch’s law of independent migration of ions —

[] **Calculation of Equivalent conductance at infinite dilution () for weak electrolyte** —

By graphical method we can’t determine the equivalent conductance of weak electrolyte at infinite dilution, as these are ionised very feebly. But indirectly, by applying **Kohlrausch law** we can determine the value of for weak electrolytes. ***For example*** —

Equivalent conductance at infinite dilution, for **acetic acid** () can be calculated from the equivalent conductance of (all are **strong electrolytes**) at infinite dilution as follows —

Adding equation () & () and from the result, subtracting equation (), we get —

[] **Calculation of degree of dissociation of Weak electrolyte ()**—

The value of equivalent conductance at infinite dilution () helps to calculate the degree of dissociation and dissociation constant of weak acids and bases (electrolytes). ***For example***, the degree of dissociation of a weak electrolyte is —

 Equivalent or molar conductivity of the electrolyte at a given *conc*. and,

 Equivalent or molar conductivity of the electrolyte at infinite dilution

The above ratio is called the ***conductance ratio***.

Again, the dissociation constant () of a ***weak acid*** is —

 

[] **Calculation of Ionic Product of Water ()** —

The ionic product of water () can be determined as follows —

The electrolytic conductivity of extremely pure water is determined at by using a very sensitive ***Wheatstone bridge circuit*** (from this the molar conductivity of water is calculated). The molar conductivity at **infinite** **dilution** or **zero** **concentration** () is calculated by applying **Kohlrausch’s law**. From these two values, the degree of ionization of water () is obtained (), by knowing the value of - we can know the value of .

Since, the ionization of pure water can be represented as —

Since, for pure water. , therefore we can calculate

**Electrolytic** **conductivity** for **pure** water is, at .

Since, water has a volume of its conc. is . Thus, the molar conductivity of water is given by —

Now, —

Thus, —

Hence, —

[] **Determination of Solubility Product ()** —

To determine , the solubility product, the following procedure has been adopted—

To find the solubility product of (sparingly soluble salt), the electrolytic conductivity of a saturated solution of is found at . Its accurate value has found to be . To get the ***electrolytic conductance*** of pure the conductance due to pure water ( at ) is subtracted, when we get the value as at the same temperature.

If the solubility of is , then its will be , because is only sparingly soluble, so it can be assumed that are the same. Then, —

But, —

Thus, —

[**Few more applications see page 54**]

**Problem ():** The molar conductivity of and measured resistance of the conductivity cell was found to be . By using the same cell, the resistance of a solution was measured at to be . Find the degree of ionization of the acid at this concentration and its .

**Solution**: The specific conductance of is —

So the cell constant, —

Now, for , —

Now, —

So, the degree of ionization, —

Again, for acetic acid () —

 Initial concentration:

 Equilibrium concentration:

Now, —

**Problem ():** The values for are respectively. Calculate for . The resistance of conductivity cell is when filled with and drops to when enough solid is added to make the solution as well. Calculate the cell constant and conc. of the solution ( for ).

**Solution**: We have —

The specific conductance of 1st solution is —

Again, the specific conductance of 2nd solution is —

The difference in these two gives specific conductivity resulting from which should be equal to —

According to question —

The ion concentration in solution is then —

**Problem ():** At of certain conductivity cell was found to be when it is filled with water, when filled with and when filled with water saturated with . The equivalent conductivity of is calculated to be and that of . Calculate —

1. Cell constant,
2. Specific conductivity of saturated solution of and
3. Solubility of .

**Solution**: () For solution —

() For the saturated solution of , is given by —

() Again, due to water is —

Therefore, net due to is

Finally, the concentration is given by, —

**Problem (4):** The specific conductivity of solution is and rises to if the solution is saturated with . The equivalent conductivities are for ions respectively. Calculate the solubility product of .

**Solution**: The increase in - values is due to the presence of

Thus, —

Hence, —

**Problem (5):** The following data are obtained in an experiment to determine the dissociation constant of the weak acid —

 ***Solution*** ***Conductivity***

 Calculate and the degree of dissociation of . ***Given***:

**Solution**: On mixing solution and solution, we get the salt formation , the conc. of which is . The molar conductivity of this solution is given by —

Since, the salt formed is a strong electrolyte and the solution is fairly diluted, this value of can be assumed to be .

Hence, according to ***Kohlrausch law***, we have —

Since, , therefore,

The molar conductivity at infinite dilution of the weak acid () is —

The apparent molar conductivity of will be —

The degree of dissociation is given by —

**Problem (6):** Calculate the molar and equivalent conductivities at infinite dilution of the salt . Given the ionic conductivities at infinite dilution of as and , respectively.

**Solution**: We have —

Since of contains - equivalents of the salt, the equivalent conductivity of this salt will be half of the molar conductivity, *i.e*. —

**Problem (7):** How will you calculate the molar conductivity and equivalent conductivity at infinite dilution of potash alum?

**Solution**: The potash alum is . Thus, at infinite dilution of potash alum will produce . Hence, we can write —

Since the total charge carried by of potash alum is , therefore one equivalent of the salt (it is a double salt) will be equal to of .

Since

Hence, we will have —

**Problem (8):** The values of for are, respectively. The resistance of a conductivity cell is when filled with and drops to when enough is added to make the solution in as well. Calculate the cell constant and hydrogen-ion concentration of the solution.

***Given*** —

**Solution**: Resistance of

 Resistance of

 Conductance due to solution is —

Conductivity of solution is —

Therefore, the cell constant will be —

Now, the molar conductivity of solution is —

According to Kohlrausch law, is given by —

Therefore, the degree of dissociation acetic acid is given as —

 The hydrogen-ion concentration of solution is —

Thus, of the solution will be —

 The increase in - values is due to the presence of

**The Mobilities of Ions**

To interpret **conductivity** measurements **accurately** we need to know —

1. Why different ions move at different rates —
2. Why different ions have different molar conductivities and
3. Why the molar conductivities of strong electrolytes decreases with the square root of conc.

Answer of all these questions lies in the central idea that —

“***The greater the mobility of an ion in solution, the greater is its contribution to the conductivity***”

In order to explain the actual phenomenon of mobilities of ions, following terms are usually encountered —

**The Drift Speed ()**: If is the potential difference between two electrodes separated by a distance ‘’, then the **ions in the solution** between them experience an uniform electric field of magnitude —

In such a field an ion of charge (we will disregard the sign of ion to avoid notational complications) experience a force of magnitude —

In the solution when an ion **migrates** towards **oppositely** **charged** **electrodes**, it experiences a frictional retarding force , that is proportional to its speed (), *i.e*.

Here, (***Stockes law*** in a microscopic scale, *i.e*. ), and

 Radius of the sphere

If the two forces act in **opposite directions** and the ions reach a **terminal speed**, called **the drift speed**. Thus, when **accelerating force** is balanced by the **viscous drag** , then —

This drift speed governs the rate, at which charge is transported; we might expect the conductivity of bulky ions (such as ) but not for small ions.

**Ion Mobilities**

We know that the **ions** in a solution **migrate** in **oppositely** charged **electrodes** with a terminal or drift speed, because of two oppositely directed forces *viz*. —

 () Accelerating electric field —

() Viscous or dragging force —

Thus, ***drift speed*** () of an ion is ***directly proportional*** to the ***strength*** of ***applied electric field*** (), *i.e*. —

Where the ***coefficient of proportionality***, is called the ***mobility of ions***

Since, the ***drift speed*** for an ion of charge , moving in solution in an electric field is, —

Comparing equation () and (), we have —

Again, from equation (), we have —

***So, we can define ionic mobility as*** —

***The velocity with an ion would move under a potential gradient of ( ) in a solution is called its ionic mobility***. The ***limiting*** value of ionic mobility is obtained when the solution is at ***infinite dilution***, so that no ***inter-ionic attraction***, *etc*., would arise.

**Units of Ionic Mobility** —

**Relation between Mobility () and Conductivity () of Ions** —

The relation between an ions mobility () and its molar conductivity () is —

Where Charge of the ion, and

 Faraday’s constant ()

**Proof of Equation ()**: **To prove**  —

Consider a solution of strong electrolyte () at a molar . Let, each formula unit of the electrolyte gives rise to cations of charge and anions of charge . The *conc*. of each type of ion is therefore and the number of density of each type is . The number of ions of one kind that passes through an imaginary window of area (as shown in the **figure**) during an interval of time is equal to the number within the distance , and therefore to the number in the volume . The number of ions of that kind in this volume is equal to . The flux through the window (the number of this type of ions passing through the window per unit area per unit time) is therefore, —

But each ion carries a charge , and so, the ***flux of charge*** is —

Since, , the flux is —

The current ‘’ through the window due to ions we are considering is the charge ***flux times the area*** —

But the electric field () is proportional to the potential gradient, so we can write —

But, according to ***Ohms law***, —

Comparing equations () and (), we get,

Dividing both sides of equation () by the **molar concentration of the ions** (), we get,

 This is the required equation. **Proved** //

**Transport Numbers** () and **Conductivity** ():

Since, the relation between an ions mobility () and its molar conductivity () is —

Where Charge of the ion, and

 Faraday’s constant ()

Equation () applies to the cations and anions. Therefore, for the solution itself in the limit of zero concentration (where there is no ***inter-ionic*** interaction), thus —

For a symmetrical electrolyte (for example, ), the equation simplifies to —

Again, (Kohlrausch law)

But,

Therefore, we can write —

Here, are the **transport numbers** of cations and anions respectively.

**Problem** (): A potential of is applied to two electrodes placed apart; how far would an ammonium ion be expected to move in in a dilute solution ammonium salt at . Given:

**Solution**: We have ionic mobility for cation —

For - ion

Potential gradient

Since,

Therefore, the distance moved in will be —

**Problem** (): For , the values of are . Calculate the mobilities and velocities of these ions if they are in a cell in which the electrodes are apart and to which a potential of is applied.

**Solution**: Ionic mobility of (or any cation, with ) is —

Potential gradient

The actual velocity with which - ion moves is given by —

Similarly, the ionic mobility of is —

The actual velocity with which - ion moves is given by —

**The Walden’s Rule**:

When an ion in solution is subjected to an electric field, it moves with a constant velocity (drift velocity). The ion attains this constant velocity when the accelerating electric force becomes equal to the retarding frictional force (**Stockes law**). These two forces are given as —

 Electrical force acting on the ion

 Frictional force as given by **Strokes law**

Where: the charge carried by the ion,

 Radius of the ion,

 Velocity with which the ion moves, and

 Viscosity of the medium

On equating these two forces, we get —

Thus, the ionic mobility will be —

Now, the molar conductivity of the solution is given by —

 Since,

Substituting the values of from equation (), in the above equation, we get —

The only quantity on the right-hand-side of equation () which depends on the medium is ‘’. Thus, for an electrolyte in different medium, we must have —

Equation () is known as the **Walden’s rule**.

When equation () is applied to a specific electrolyte in several different solvents, it is found that except for electrolytes containing very large ions, the product of is not constant. This arises from the fact that the ions are solvated. An ion is attracted to molecules of solvent which are carried along with the ion as it moves. The effective radius of the ion is therefore larger than its crystallographic radius and is different in each solvent. The amount of solvent held to the ion is less with larger ions, so that the effective radius is more nearly the same in various solvents, consequently Walden’s rule is more accurate for large ions. **~~//~~**

**Transport Numbers or Hittrof Numbers ()**:

The transport number “” is **defined** as the **fraction** of the **total current** carried by the **ions** of a specified type. For a solution of two kinds of ion, the cation transport number is —

Here, is the current carried by the cation and is the total current passed through the solution. Similarly, the anion transport number is, —

Here, is the current carried by the anion.

 Since,

The limiting transport number ‘ ’ is defined in the same way but for the limit of zero *conc*. of the electrolyte solution (where there is no ionic interaction). //

**Relation between Transport Numbers () and Ionic Mobilities ()**:

The required relationships between the transport number () and ionic mobility are —

We can **prove these** relations as follows —

If is the charge carried by an ion, “” is their numbers and be their mobilities, then —

The (total) **current carried by cations**, , and

The (total) **current carried by anions**,

 Hence, the total current,

Since, the solution is being **electrically neutral**, hence —

Therefore, transport number of cation will be —

Similarly, the transport number for anion will be —

Equation () and () provides the relation between transport number () and ionic mobility.

**Relation between Conductance (Ionic, ) with** :

We know that the relation between the ionic mobility () and molar conductivity () is —

 Where:

At the infinite dilution (*i.e*. no interionic interactions), conductance of cation is —

And, that for anion is

Since,

Since, the solution is electrically neutral,

Therefore, we may have —

Similarly, for **anion**, we will get —

Here, are the transport numbers of cations and anions respectively at infinite dilution. //

**The Measurement of Transport Numbers**:

There are two methods exclusively used for the measurement of transport numbers—

1. **Moving Boundary method**, and
2. **Hittrof method**

**Moving Boundary Method**:

The most accurate method for the measurement of transport numbers is the moving boundary method, in which the motion of a boundary between two ionic solutions having a common ion is observed as current flows.

**[**In the moving boundary method for the measurement of transport numbers, the distance moved by the boundary is observed as a current is passed. All the - ions (as shown in the **figure**) in the volume between must have passed through , if the boundary moves from **]**

Let, be the salt of interest and a salt giving a denser solution. The solution of is called the **indicator solution**; it occupies the lower part of a vertical tube (as shown in the **figure**). The solution, which is called the **leading solution**, occupies the upper part of the tube. There is a sharp boundary between the two solutions (). The **indicator** solution must be **denser** than the **leading** solution, and the **mobility** of - ions must be **greater** than that of - ions. Thus, if any - ions diffuse into the lower solution, they will be pulled upwards more rapidly than the - ions around them, and the boundary will reform. The interpretation of the experiment leads the relation between the distances moved by the boundary in the time “” for which a current “” is passed as follows —

When current “” is passed for a time , the boundary moves from , and so all the - ions in the volume between must have passed through . That number is , so the charge they transfer through the plane is . However, the total charge transferred when a current “” flows for an internal is . Therefore, the fraction due to the motion of the - ions, which is their transport number, is —

Hence, by measuring “”, the volume from the distance moved, the transport number and hence the conductivity and the mobility of the ions can be determined. **~~//~~**

**Hittrof Method**:

In the Hittrof method, an electric cell is divided into three compartments and an around of electricity is passed. An amount of cations is discharged at the cathode, but an amount of cations migrates into the cathode compartment. The net change is the amount of cations in the compartment is therefore —

Hence, by measuring the charge of composition in the cathode compartment, the anion transport number can be deduced. Likewise, the charge in composition of anode compartment is, , which gives the cation transport number . //

**High Conductivity of Proton**:

The proton, though it is very small, has a very high molar conductivity (). The explanation is that the proton conducts current by a mechanism that does not involves its actual motion through the solution. According to the **chain mechanism or Grotthus mechanism** of proton migration, instead of a single, highly solvated proton moving through the solution, there is an effective motion of a proton that involves the rearrangements of bonds in a group of water molecules (as shown in the figure). The conductivity is governed by the rates at which the water molecules can rotate into orientations in which they can accept or donate protons and the rate at which the proton tunnel from one end of a hydrogen bond to another.

 

**Problem ()**: Calculate the ionic mobilities of cation in a . Given that its transference number as and .

**Solution**: We have —

**Problem ()**: At , the mobilities of ions are respectively. Calculate the equivalent conductance of and transport numbers of the ions.

**Solution**: We have —

The transport number would be —

Since,

**Problem ()**: In a solution, . Find out the mobility of and the migration speed of in the field strength .

**Solution**: We know —

Now,

**Problem ()**: A cylindrical tube of long and in cross section is fitted with . A potential difference across the length of the cell is now applied such that a current of flows. If (and for ), find out the velocity of the ions in .

**Solution**: Total current

Out of it, a fraction is carried by and thus current carried by will be —

The velocity is given by —

[Since, ]

**Problem ()**: A solution of was electrolysed in a **Hittrof** apartment with - electrodes. After electrolysis the molality of cathode solution was found to be in and in . Find out the transport number of the if the cathode reaction is —

**Solution**: Because, the solution after electrolysis is in ; thus if of electricity passed through the cell per of water in cathode chamber that migrates into this (cathode) chamber will be —

Since, - ions carry per mole into cathode chamber. Hence —

**Solutions of Electrolytes [Non-ideal Solution i.e. Real Solution]**:

**[The Chemical Potentials in non-ideal systems are usually expressed in terms of Activities and Activity Coefficients]**

**Activities () and Activity Coefficients () of Electrolyte Solutions (non-ideal)**:

The chemical potential () of an ideal or ideally dilute solution is given by —

Here, is the chemical potential of the **pure** component “” and is the mole-fraction of the component in the solution.

Equation () can also be written as —

The activity of the substance “” in any solution is defined as —

Thus the activity, replaces the mole-fraction, in the expression for in a ***non-ideal*** solution. From equation () and (), we can write —

When the solution component “” is in its standard state, *i.e*.

And, thus from equation (), we have —

The **difference** between **real solution** **chemical potential** in equation () and the corresponding **ideal solution** in equation () is —

The ratio is thus, a measure of the **departure** from **ideal behaviour**. We therefore, **define** the activity coefficient () of the component “”, as —

Thus, for any solution,

The **activity coefficient**, measures the degree of departure of “” behaviour from ideal or ideally dilute behaviour. The **activity** can be **viewed** as being obtained from the **mole-fraction**, by correcting for non-ideality. In an ideal or ideally dilute solution —

From equation () and (), the chemical potential in a **non-ideal solution** of **non-electrolyte** are —

Since, depends on , hence depends also on these variables, *i.e*.

**Determination of activity:**

Considering an **-** electrolyte of type (), who’s ionization can be expressed as —

The equilibrium constant —

Where: The activity of the cation,

 The activity of the anion, and

 The activity of the undissociated electrolyte,

Since, it is impossible to isolate the individual ions from the solution, hence experimental determination of is not practically possible, however, it is possible to determine the **mean activity** of the two ions (), which may be considered as the **geometric mean** of the activities of the respective ions. Thus —

We separate activity coefficient for the ions as —

Hence, the mean activity coefficient —

Where The mean ionic concentration

Now, let us considering a general electrolyte , dissociates into - cations and - anions:

Here are the valencies of the ions (cations & anions)

If represents the activities of the cations, anions and undissociated electrolytes respectively, then —

The **mean activity** is then —

Here Total number of ions

Since,

Again, Mean ionic concentration, and

 Mean activity coefficient

Since, we determine experimentally, and hence these quantities are important for the determination of (mean **activity)**. //

**Ionic Strength ()**: [See also **below** for alternative and **best** definition]

Electrolytes which contain ions with multiple charges have great effect on activity coefficient of ions, than the electrolytes only slightly charged ions. Depending on the charges of the ions, the electric field created by these ions will be different. The intensity of electric field in an electrolytic solution is expressed by the term ionic strength , which is defined by the following relation —

 Where is the molality of type of ion and is their charges

The greater the ionic charge the lower will be the activity coefficient of the ions. For example, the ionic strength of a solution will be —

**Ionic Strength ()**: [**Alternative definition**]

Ionic strength () is the measure of the electrical intensity due to the presence of ions in the solution. It is given by the half of the sum of all the ions obtained by multiplying the molality of each ion by the square of its valency. **Mathematically**, we have,

Where are the molalities and are the valency of each ions present in the solution.

For single electrolyte, for example, the above equation contains only two terms, one for cation and other for anion. Hence,

Here are the valencies of the cation and anion respectively and are their corresponding molalities.

**Question (1)**: Determine the ionic strength of solution.

**Solution**: Since —

**Question (2)**: Determine the ionic strength of solution.

**Solution**: Since —

**Question (3)**: Determine the ionic strength of solution.

**Solution**: Since —

**Question (4)**: Calculate the ionic strength of solution of and .

**Solution**: Since —

 Again —

**Question (5)**: Calculate the ionic strength of a electrolyte whose conc. is .

**Solution**: For electrolyte, for example, for —

For electrolyte, for example, for —

**Question (6)**: Calculate the mean molality and Ionic Strength of , , and solution.

**Solution**: For —

Again —

For —

Again —

For —

Again —

For —

Again —

**Question (7)**: The molalities of are ; assuming complete ionization, calculate the ionic strength of the solution.

**Solution**: Here, for —

Further, for —

Hence, the total molality of -

Therefore, the ionic strength of the solution of salt mixture will be, —

**Question (8)**: Calculate the ionic strength for —

1.
2. A solution which is

**Solution**:) For —

) For —

) For —

) For a mixture of —

Here, for —

Further, for —

Hence, the total molality of -

Therefore, the ionic strength of the solution of salt mixture will be, —

**Debye-Hückel-Onsager Theory** — **the Physical Concepts of Strong Electrolytes**

**[Effects of Ion-Ion & Ion-Solvent Interactions on the Migration of Ions under the Influence of an Applied Electric Field]**

To explain the variation of equivalent conductance with concentration for strong electrolytes which also exists in ionic form in molten state, Debye and Hückel proposed their famous interionic attraction theory, which is then (1927) improved by Onsager, hence the name Debye – Hückel – Onsager theory. According to this theory, each ion in solution is surrounded by counter – ions, which greatly affect the ionic mobilities, so it is called “interionic effects”.

There are **two interionic effects**, that affects the speed of an ion *viz*. —

1. Relaxation effect or Asymmetry effects or ion-ion interaction effects, and
2. Electrophoric effect or ion-solvent interaction.

**Ion-Ion Interaction Effects:**

In solution each ion is surrounded by an ionic atmosphere, which is perfectly symmetrical around the central ion in the absence of external electric field (Figure -).

The spherically symmetric ionic atmosphere with respect to the central ion destroys in presence of external electric field because of their movement towards the oppositely charged electrodes (Figure -). The motion of the central ion is retarded because of the unsymmetrical ionic atmosphere around it, *i.e*. more charges behind the charged central ion, as shown in the figure -, so because of the attraction between the oppositely charged ions, actual mobility of the central ion decreases. Since, the effect is due the asymmetry of the ionic atmosphere, so it is also called the asymmetry or relaxation effect.

 

**Ion-solvent Interaction Effects:**

Because of the interaction between the solvent and ions of an electrolytic solution, the motion of the ions retarded. In presence of external electric field along with the motion of ionic atmosphere and central ion to the oppositely charged electrodes, the solvent molecules associated with them are also moved. The flow of ionic atmosphere and the solvent molecules associated with them flows in a direction opposite to that for the central ion i.e. motion is retarded, what we call **electrophoric effect** in analogous to colloidal particle in an electric field.

Thus, both these effects accounts for the **decreased** value of **conductance** then the accepted one.

The quantitative formulation of these effects is far from simple, *i.e*. highly complicated, but the **Debye-Hückel-Onsager** theory is an attempt to obtain quantitative expression, almost accurately. The theory showed that because of the above two retarding factors viz. ion – ion and ion-solvent interactions, the equivalent conductance of the electrolyte decreases and these are concentration dependent. For a **-** electrolyte (), the following equation was derived by them —

Where: Equivalent conductance at a given concentration and temperature

 Equivalent conductance at infinite dilution,

 Dielectric constant of the solvent and

 Viscosity coefficient of the medium

Equation () can also be written as —

Equation () is the simplified form of Debye-Hückel-Onsager equation in the simplest form with two constants . Equation () is of the form of .

Thus, the plot of versus for strong electrolytes will be a straight line as shown in the figure (), which on extrapolating to , we will get the value of equivalent conductance at infinite dilution ().

**Debye-Hückel Limiting law:**

Oppositely charged ions attract each other, as a result, cations and anions are not uniformly distributed in solution: anions are more likely to found near cations, and vice-versa. Overall the solution is electrically neutral, but near any given ion, there is an excess of **counter-ions**, the ions of opposite charge. Averaged over time, **counter-ions** are more likely to be found by any given ion. This time-averaged, spherical haze, in which **counter-ions**, outnumber ions of the same charge at the central ion, has a net charge equal in magnitude but opposite in sign to that on the central ion and is called its ionic atmosphere.

The energy, and therefore the chemical potential, of any given central ion are lowered as a result of its electrostatic interaction with its ionic atmosphere. This lowering of energy appears as the difference between the **Gibbs energy** () and its **ideal value** in the solution, and hence can be identifies as —

This ionic model leads to the result that, at very low concentrations, the activity coefficients can be calculated from the **Debye-Hückel limiting law** —

Here, for an aqueous solution (of electrolyte) at (in general, depends on the **relative permittivity** and the **temperature**) and “” is the **ionic strength** of the solution.

Thus, the **Debye-Hückel limiting** law **expresses** the change in **activity coefficient** of an ion with the **ionic strength** of the medium and is applicable only at infinite dilution. Further, from the law it also follows that (only at **infinite dilution**) there is a decrease in the activity coefficient of an ion with an increase in ionic strength of the solution. //

**Problem (1)**: At the constants in the Onsager equation are and . Calculate the molar conductivities of solution and solution. ***Given that*** —

**Solution**: The molar conductivity of at infinite dilution is —

The value of from Onsager equation is —

And, the value of from Onsager equation is —

**Problem (2)**: Estimate the at mean activity coefficient of .

**Solution**: From the **Debye-Hückel limiting law**, we have —

Here,

Molality,

Therefore, the ionic strength of will be —

**Problem (3)**: Calculate the ionic strength and mean activity coefficient of aqueous solution of .

**Solution**: From the **Debye-Hückel limiting law**, we have —

Here,

Molality,

Therefore, the ionic strength of will be —

**Problem (4)**: The solubility of in water at is , calculate:

1. The standard reaction Gibbs energy for the reaction,
2. The solubility of

**Solution**: **Method for ()**: The thermodynamic equilibrium constant is expressed in terms of activities. ***For example***, for the dissociation of —

These may be obtained from the molalities of the ions (each of which is equal tomultiplied by the mean activity coefficient, which in turn obtained from **Debye-Hückel limiting law**, *viz*.

Now, the standard reaction Gibbs energy is obtained is obtained from —

**Method for ()**: Calculate the ionic strength ‘’, of the solution (the contribution of can be ignored as its **solubility is so low**), and interpret the **equilibrium constant** obtained in part () in terms of **new solubility** by using the mean activity coefficient calculated for this solution. Because the ions produce a favourable ionic atmosphere around the ions, and thus **lower their Gibbs energy**, we can expect the solubility of to be greater in **2nd solution** than in **pure water** *i.e*. aqueous medium. Now —

**Solution of (a)**: The equilibrium constant for the dissociation of is —

The ionic strength of the solution ( electrolyte) is —

It follows from **Debye-Hückel limiting law**, *viz*. —

Therefore, the equilibrium constant —

The standard reaction Gibbs energy is, therefore —

**Solution of (b)**: The ionic strength of solution is ()

The mean activity coefficient of ions in such a solution is obtained from the **Debye-Hückel limiting law** —

The solubility of in this solution is therefore, obtained from —

Thus, the new solubility is therefore //

**Conductivity at High Electric Field and High Frequencies**:

The **evidence** that there **exists** an **ionic atmosphere** around the ions is shown by the ***Wien effect*** and ***Debye-Falkenhagen effect***. These two effects are explained as follows —

***Wien Effect***: —

In very high electric fields, , an increase in conductivity is observed. This results from the fact that a finite time (the ***relaxation time***) is required for the ionic atmosphere to form around an ion. In very high electric fields, the ion moves so readily that it effectively loses its ionic atmosphere. As a result there is no time for the formation of ionic atmosphere to slow down the ionic motion. Thus, the **asymmetry effect** (as in ***Debye-Hückel-Onsager’s*** theory of strong electrolytes) **disappears** which results in the increase of conductance, and the corresponding phenomenon is known as ***Wien effect***.

***Debye-Falkenhagen Effect***: —

In Debye-Falkenhagen effect, conductivity of an electrolyte increases when high frequency is used (of the order of ). The ion changes its direction of motion so quickly that the more sluggish atmosphere cannot adjust and follow the motion of the ion. The ion moves as if it had no ionic atmosphere, and thus conductivity increases. In fact, at high frequency, both the **asymmetry** and **electrophoric** effects are **absent**, which results in the increase of conductance, and the corresponding phenomenon is known as ***Debye-Falkenhagen effect***.

**Stokes-Einstein Equation**:

We know that the flux ( ) is related to drift speed () by —

Flux , is obtained from **Fick’s first law** and is defined as the amount of molecules per unit area per unit time, *i.e*. —

Here, is the diffusion coefficient and is the slope of the molar *conc*. ().

Thus, all the particles within a distance , and therefore, in a volume , can pass through a window of area “”, in an interval “”. Hence, the amount of substance that can pass through the window in that interval is —

Now, in a solution where the activity of a particle is “”, the chemical potential is —

If the solution is not uniform, then the activity depends on the position and we can write —

The quantity is called the **thermodynamic force**.

If the solution is ideal, “” may be replaced by “”, and then —

Using equation () in equation (), we have —

But, an ion in solution has a **drift speed** , when it experiences a force, from an electric field of strength “” ().

Therefore, from equation (), we have —

This equation is known as **Einstein relation** between the diffusion coefficient and ionic mobility.

Again, since ionic mobility —

Where,

Equation () and () relate the mobility of an ion () to the frictional force () and to the diffusion coefficient () respectively. Thus —

Where,

This expression is called the **Stokes-Einstein equation**. If the frictional force is described by Stokes law, then —

An important feature of **Stokes-Einstein equation** is that it is independent of the change of diffusing species, hence is applicable in the limit of vanishingly small change and even to neutral molecules. Consequently, we may use viscosity measurements to estimate the diffusion coefficients for molecules in solution. //

**Problem (1)**: Calculate the diffusion coefficient, limiting molar conductivity, and effective hydrodynamic radius of () and () in water at .

 ***Given***: Ionic mobility,

 Viscosity of water,

**Solution**: From ***Stokes-Einstein equation***, we have —

Diffusion coefficient —

The ionic conductivity —

Again, from the ***Stokes-Einstein relation***, we have —

For ion we will put only, others are same as for - ion. //

XXXXX#XXXXXX

**Few more Applications of Conductometric measurements**:

 [From Page 21]

[] **Determination of Hydrolysis constant from Conductometric measurement**:

Hydrolysis constant of a salt can be determined from conductivity measurements. Let ‘’ be the *conc*. of the salt (formed from a weak base and strong acid) in the solution. The cation of this salt undergoes hydrolysis in the solution as —

Thus, if ‘’ is the degree of hydrolysis, then the concentrations of in the solution will be respectively. The conductivity of this solution is given by —

 Here, is the conductivity of the unhydrolyzed salt of concentration ‘’ and is the conductivity of the solution of concentration ‘’. An alternate form of equation () is —

Where: Molar conductivity of the hydrolyzed solution,

 Molar conductivity of the unhydrolyzed solution of concentration , and

 Molar conductivity of the solution of concentration

The values of can be determined experimentally by adding a large excess of base to the solution, which causes the equilibrium to shift to the left, *i.e*. it minimise the hydrolysis.

Knowing the value of ‘’ from either of the two equations, the hydrolysis constant can be obtained by using the expression —

 [] **Conductometric Titrations**:

The principle of conductometric titrations is based on the fact that during the titrations, one of the ions is replaced by the other and invariably these tow ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of titrations. ***For example***, —

[] **Strong Acid *versus* Strong Base**:

Considering the titration between a strong acid, , and a strong base, . Before is added, the conductance of solution has a high value due to the presence of highly mobile hydrogen ions (). As is added, - ions combine with ions to form undissociated water and thus, the faster moving - ions are replaced by relatively slower moving - ions. Consequently, the conductance of the solution decreases and this continues right up to the equivalence point where the solution contains only . Beyond the equivalence point, if more of is added, then the solution contains an excess of the fast moving ions with the result that its conductance is increased and it continues to increase as more and more of is added. If we plot the conductance value versus the amount of added, we get a curve of type shown below in figure (1). The descending portion represents the conductance before the equivalence point (solution contains a mixture of acid and the salt ) and the ascending portion represents the conductances after the equivalence point (solution contains the salt and the excess of ). The point ‘’ which represents the minimum conductance is due to the solution containing only with no free acid or alkali and thus represents the equivalence point. This point can, however, be obtained by the extrapolation of the lines , and, therefore, one is not very particular in locating this point experimentally as it is in the case of ordinary acid-base titrations involving the acid-base indicators.



[] **Weak Acid *versus* Strong Base**:

Let us consider the specific example of acetic acid () being titrated against . Before the addition of alkali, the solution shows poor conductance due to feebly ionized . Initially the addition of alkali causes not only the replacement of but also the suppressed the dissociation of acetic acid due to the common ion and thus the conductance of the solution decreased in the beginning. But, very soon the conductance starts increasing as addition of neutralizes the undissociated to , thus causing the replacement of non-conducting with strong conducting . The increase in conductance continues right up to the equivalence point. Beyond this point, conductance increases more rapidly with the addition of due to the highly conducting ions. The graph near the equivalence point is curved due to the hydrolysis of the salt . The actual equivalence point can, as usual, be obtained by the extrapolation of the curve obtained is shown in the figure () given below.



[] **Weak Base *versus* Strong Acid**:

In this case, description is exactly same as in [], and the graph is also same.

[] **Weak Base *versus* Weak Acid**:

Here, the nature of the curve before the equivalence point () is similar to that shown in **figure** () as shown above. After the equivalence point, conductance virtually remains the same as the weak base which is being added is feebly ionized and, therefore, is not very much conducting.

[] **Mixture of Weak & Strong Acids *versus* a Strong Base**:

In this case, the strong acid is first neutralized and only when this has been completely neutralized, the weak acid starts neutralizing. Thus, we have the neutralization reaction in two stages and the curve contains two breaks as shown in the **figure** () given below. The first break corresponds to the neutralization of the strong acid and the second corresponds to that of the weak acid. From these the individual concentrations of the strong acid and the weak acid can be calculated.

**Important Note/ Comments/ Extension**: The same concept can be used for the conductometric titration involving a mixture of weak and strong bases () against a strong acid () or a diprotic acid (oxalic acid) versus , involving a stepwise neutralization. All these exhibits two break curves as shown as in the **figure** () given above.



 The End

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