# ELECTROLYTIC CONDUCTANCE-1

## Conductivity of Solutions

A measure of how well a solution conducts electricity.

Water with absolutely no impurities (does not exist): Conducts electricity very poorly

Impurities in water increase conductivity: So, when measure conductivity of water can estimate the degree of impurities.

The current is carried by dissolved ions.

The ability of an ion to carry current is a function of:

- Ion's charge (more charge, more current)
- Ion's mass or size (larger ions, conduct less)

Electrolytes: Substances whose aqueous solution is a conductor of electricity

- Strong electrolytes: All the molecules of the electrolyte are dissociated into ions.
- Weak electrolytes: A small percentage of the molecules are dissociated into ions.
- Nonelectrolytes: No molecular dissociation in aqueous solution occurs.

Role of the solvent: dielectric constant, viscosity coefficient, etc.

The strength of an electric current, $I$, flowing through a conductor is determined by the difference in potential, $V$, applied across the conductor and by the resistance, $R$, offered by the conductor to the current.

According to Ohm's law the relation among these three quantities is given by

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

From this equation it is evident that the current strength is directly proportional to the difference in potential and inversely proportional to the resistance.

By an appropriate choice of units, the constant of proportionality is made unity.

The quantities $I$, $R$ and $V$ may be expressed in

- electromagnetic units, based on the law of attraction or repulsion of magnets,
- electrostatic units, based on the Coulomb law of force between electric charges, or
- absolute practical units.

For convenience of comparison and standardization a system of units, known as the international, has been defined, and is the one generally employed in electrochemistry.

In this system the unit of current, or rate of flow of electricity, is the ampere which is defined as an invariable current of such strength that on passage through a water solution of silver nitrate it will deposit 0.00111800 gram of silver in 1 sec.

The unit of resistance, the ohm, is defined as the resistance at $0$°C of a column of mercury of uniform cross section, $106.300$ cm long, and containing $14.4521$ grams of mercury.

From these two units the unit of potential, the volt, follows from Ohm's law as the potential difference required to send a current of 1 amp through a resistance of 1 ohm.

The unit of quantity of electricity, or charge, is the coulomb.

A coulomb is the quantity of electricity necessary to deposit $0.00111800$ gram of silver from a solution of silver nitrate, no matter what the time is.

Consequently, a current of 1 amp is one which transports 1 coulomb of electricity per second.

Since the quantity of electricity carried by a current must equal rate of transport times the time, the charge $Q$ carried by a current $I$ in $t$ sec must be $Q = It$ coulombs.

Another unit of quantity of electricity which we shall employ frequently is the faraday, $F$. A faraday is equal to 96,500 coulombs.

The electrical work $w$ performed when a current of strength $I$ passes for $t$ sec through a resistance across which the potential drop is $V$ is given by Joule's law, namely,

$$w = VIt = VQ$$

Therefore, in

$$w = VIt = VQ$$

$w$ 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 1 amp flowing for 1 sec under a potential drop of 1 volt.

The work in joules is readily convertible to other energy units through the relations

$$1 \text{ joule} = 1 \times 10^7 \text{ergs} = 0.2389 \text{ cal}$$

The rate at which work is being done by an electric current is expressed in watts.

A watt is work performed at the rate of 1 joule per second, and is obviously a unit of electrical power.

∴ The power, in watts, delivered by a current follows as, $p = VI = VQ/t$.

The electronic versus the electrolytic conductors:

In electronic conductors, of which solid and molten metals and certain solid salts (cupric sulfide, cadmium sulfide) are examples, conduction takes place by direct migration of electrons through the conductor under the influence of an applied potential.

In electronic conductors, the atoms or ions composing the conductor are not involved in the process, and, except for a vibration about their mean position of equilibrium, they remain stationary.

The only noticeable effect produced by the current in the conductor is a heating resulting from the dissipation of electrical energy in the form of heat.

Another characteristic of electronic conductors is their increase in resistance as the temperature is raised.

Electrolytic conduction is encountered in solutions of strong and weak electrolytes, in fused salts, and also in some solid salts, such as sodium chloride and silver nitrate.

In distinction to electronic conductors, electron transfer in electrolytic conductors takes place not by the flow of free electrons, but by a migration of ions, both positive and negative, toward the electrodes.

This migration involves not only a transfer of electricity from one electrode to the other, but also a transport of matter from one part of the conductor to another.

Further, current flow in electrolytic conductors is always accompanied by chemical changes at the electrodes which are quite characteristic and specific for the substances composing the conductor and the electrodes.

While the resistance of electronic conductors increases with temperature, that of electrolytic conductors always decreases as the temperature is raised.

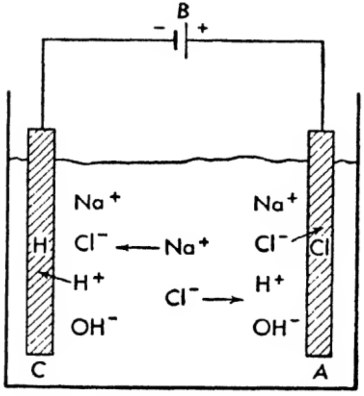
**Mechanism of Electrolytic Conduction:**

Consider a cell, composed of two inert electrodes, in this case platinum, connected to a source of current $B$ and dipping into an aqueous solution of sodium chloride.

The electrode $C$, connected to the negative side of $B$, is called the cathode.

This is the electrode by which electrons from $B$, say a battery, enter the solution.

In turn, electrode $A$, connected to the positive side of the battery, is termed the anode.



Note that, oxidation takes place at the anode, and reduction takes place at the cathode.

$2Cl^-(aq) = Cl_2(g) + 2e^-$ (Oxidation, at anode)

$2H^+(aq) + 2e^- = H_2(g)$ (Reduction, at cathode)

Thus, the electrons enter the solution at the cathode $C$ by combining with hydrogen ions in solution to form monatomic hydrogen.

Again, the electrons leave the solution at the anode $A$ by the discharge of chloride ions, with each chloride ion giving up one electron to the electrode and becoming a chlorine atom.

The electrons thus liberated flow through the external circuit from the electrode to the source of potential, while the nascent chlorine atoms combine with each other to form gaseous chlorine which escapes.

∴ Two electrons are removed from the cathode to form a molecule of hydrogen, and simultaneously two electrons are given up to the anode by chloride ions to form a molecule of chlorine.

The net result is a transfer of two electrons from the cathode side of the circuit to the anode side.

How the electrons get from the cathode to the anode when the circuit is closed?

The negative ions, or anions migrate toward the anode, while positive ions, or cations, migrate toward the cathode.

As these particles are charged, their motion constitutes a flow of electricity, or an electric current.

The anions move to the anode, and hence electrons are carried by these ions from the cathode to the anode.

Again, since transport of positive electricity to the left may be considered a flow of negative electricity to the right, the migration of cations to the cathode is equivalent to a flow of electrons in the opposite direction.

Consequently, the net result of the migration is a flow of electrons through the solution in the direction of the current, with each ion carrying part of the current and thus contributing its share to the transport of electricity through the solution.

The process of current passage through an electrolytic conductor with all the accompanying chemical and migratory changes is called **electrolysis**.

Thus, the electrons

- enter and leave the solution through chemical changes occurring at the electrodes, and
- pass through the solution by migration of ions.

Just as many electrons pass through the solution and leave it as entered it, no more, no less.

To establish that as many electrons pass through the solution and leave it as entered it, no more, no less, we will consider the **Faraday's laws of electrolysis**.

*The mass of a substance involved in reaction at the electrodes is directly proportional to the quantity of electricity passed through the solution*. (Faraday's first law of electrolysis)

This law holds very rigidly provided the passage of electricity takes place entirely by electrolytic conduction.

It applies to molten electrolytes as well as to solutions of electrolytes, and is independent of temperature, pressure, or the nature of the solvent, as long as the latter can promote ionization of the solute.

From Faraday's first law of electrolysis the quantity of electricity necessary to deposit one equivalent weight of silver may readily be calculated.

Since by definition 1 coulomb deposits $0.00111800$ gram of silver, and since the mass deposited is directly proportional to the quantity of electricity, the number of coulombs required for deposition of 1 gram atomic weight of silver, $107.88$ grams, must be

$$\frac{107.88}{0.00111800} = 96494 \text{ coulombs}$$

What mass of other substances will this quantity of electricity deposit or form?

If two cells, one composed of silver electrodes in silver nitrate, the other of copper electrodes in copper sulfate, are connected in series, any current passed through one cell must also pass through the other.

With such a setup it can be shown that the weight of copper deposited per $0.001118$ gram of silver, i.e., per coulomb of electricity, is $0.0003294$ gram.

∴ The quantity of electricity necessary to deposit 1 gram atomic weight of copper, $63.57$ grams, follows as

$$\frac{63.57}{0.0003294} = 192988 = 2 \times 96494 \text{ coulombs}$$

However, since copper is divalent, an equivalent is $63.57/2$ grams.

Consequently, to deposit one equivalent of copper only one-half the above amount of electricity is required, or again $96{,}494$ coulombs.

Prom a series of such experiments Faraday arrived at his second law of electrolysis, namely, that *the masses of different substances produced during electrolysis are directly proportional to their equivalent weights*.

*The same quantity of electricity will produce chemically equivalent quantities of all substances* resulting from the process.

A direct consequence of Faraday's second law is that during electrolysis $96{,}494$ coulombs of electricity will yield one equivalent weight of any substance.

To honor the man who discovered these laws, the name faraday (algebraic symbol $F$) has been given to this quantity of electricity, i.e., 1 faraday = 96,494 coulombs.

For ordinary calculations $1\ F = 96500$ coulombs will be sufficiently exact.

Millikan and others have established that the charge on the electron is equal to $1.60 \times 10^{-19}$ coulombs of electricity.

∴ The number of electrons constituting $1F = 96494/1.60 \times 10^{-19} = 6.03 \times 10^{23}$, which is the Avogadro's number.

Thus, $1F$ of electricity is associated with $6.03 \times 10^{23}$ particles of unit charge, or, in general, with one equivalent of a chemical substance.

One equivalent of positive ions lacks this number of electrons, while one equivalent of negative ions has this number of electrons in excess.

When $1F$ of electricity is passed through a solution, Avogadro's number of electrons is removed from the cathode by reduction of one equivalent of substance, and exactly the same number of electrons is donated to the anode as a result of some oxidation.

## ELECTROLYTIC CONDUCTANCE-2

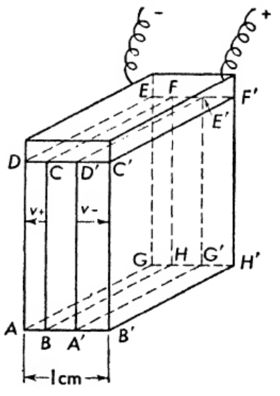
The same quantity of electricity will produce chemically equivalent quantities of all substances resulting from the process. A direct consequence of Faraday's second law is that during electrolysis $96{,}494$ coulombs of electricity will yield one equivalent weight of any substance. For ordinary calculations $1\ \mathrm{F} = 96500$ coulombs will be sufficiently exact. Millikan and others have established that the charge on the electron is equal to $1.60 \times 10^{-19}$ coulombs of electricity.

$\therefore$ The number of electrons constituting $1\mathrm{F} = 96494/1.60 \times 10^{-19} = 6.03 \times 10^{23}$, which is the Avogadro's number. Thus, $1\mathrm{F}$ of electricity is associated with $6.03 \times 10^{23}$ particles of unit charge, or, in general, with one equivalent of a chemical substance. One equivalent of positive ions lacks this number of electrons, while one equivalent of negative ions has this number of electrons in excess. When $1\mathrm{F}$ of electricity is passed through a solution, Avogadro's number of electrons is removed from the cathode by reduction of one equivalent of substance, and exactly the same number of electrons is donated to the anode as a result of some oxidation. As Faraday's laws are obeyed so rigidly, they may be utilized to determine the quantity of electricity passing through a circuit by observing the chemical changes produced by the same current in a suitable electrolytic cell. A cell used for this purpose is called a **coulometer**. The coulometer is placed in the circuit in series with any other apparatus, and is allowed to remain there as long as the current is flowing. It is then removed, and the chemical changes produced by the current are estimated by some appropriate means. The coulometer commonly employed for precise work is the silver coulometer. The electrolyte is an aqueous solution of purified $\mathrm{AgNO_3}$.

### Transference (or Transport) and Transference Numbers (or Transport Numbers)

Although current is transported through a solution by migration of positive and negative ions, the fraction of the total current carried by each is not necessarily the same for the two ions. For example, in a dilute $\mathrm{MgSO_4}$ solution, $38\%$ of the total current is carried by the $\mathrm{Mg^{2+}}$ and the rest $62\%$ is carried by $\mathrm{SO_4^{2-}}$. Similarly, in an aqueous $\mathrm{HNO_3}$ solution, $84\%$ of the total current is carried by the $\mathrm{H^+}$ and the rest $16\%$ is carried by $\mathrm{NO_3^-}$.

$\therefore$ The sulfate and hydrogen ions transport the greater fraction of the total current because in their respective solutions they move faster than the other ions present. If both ions in a solution moved with the same speed, each would transfer past any fixed plane in the solution the same quantity of electricity in any given time.



Consider two parallel plates, 1 cm apart, across which is applied a potential of 1 volt, and between which is contained some volumes of an electrolyte. Say,

$v_+ =$ velocity of the cation in cm/sec.
$z_+ =$ charge on the cation.
$n_+ =$ number of cations in the solution.

Similarly,

$v_- =$ velocity of the anion in cm/sec.
$z_- =$ charge on the anion.
$n_- =$ number of anions in the solution.

Then the quantity of electricity transported by the cation in 1 sec, i.e., the current due to the cation, is going to be all the electricity possessed by all the cations that lie within a distance $v_+$ of the negative plate, or, in other words, all those which lie within the volume $ABCDEFGH$. The number of these ions is obviously the fraction $v_+$ of the total or $n_+v_+$. Again, since the charge of each ion is $z_+$, and the quantity of electricity associated with unit charge is $c$, the electronic charge, the current carried by the positive ions, must be

$$I_+ = n_+ v_+ z_+ e$$

Similarly, the current carried by the anions to the positive plate must be that corresponding to all the electricity possessed by the anions in the volume $A'B'C'D'E'F'G'H'$, namely,

$$I_- = n_- v_- z_- e$$

∴ The total current carried by both is,

$$I = I_+ + I_- = n_+ v_+ z_+ e + n_- v_- z_- e$$

But, the condition for electroneutrality of the solution demands that the total charge of the cations must be equal to that of the anions, namely,

$$n_+ z_+ = n_- z_- = nz \text{ (say)}$$

Hence,

$$I = n_+ v_+ z_+ e + n_- v_- z_- e = nze(v_+ + v_-)$$

Thus, the fraction of the total current carried by the cations, $t_+$, is

$$t_+ = \frac{I_+}{I} = \frac{n_+ v_+ z_+ e}{n_+ v_+ z_+ e + n_- v_- z_- e} = \frac{v_+}{v_+ + v_-}$$

Similarly, the fraction of the total current carried by the anions, $t_-$, is

$$t_- = \frac{I_-}{I} = \frac{n_- v_- z_- e}{n_+ v_+ z_+ e + n_- v_- z_- e} = \frac{v_-}{v_+ + v_-}$$

$t_+$ and $t_-$ are called the **transport** or **transference numbers** of the cation and anion respectively. These numbers give the fraction of the total current carried by a given ion in a solution. Also,

$$\frac{t_+}{t_-} = \frac{v_+}{v_-}$$

and hence the transport numbers of the ions, and therefore the fractions of the total current they carry, are directly proportional to their absolute velocities. When these are equal, that is, $t_+ = t_-$, both ions contribute equally to the transport of current. No matter what the ratio between $t_+$ and $t_-$ may be, since the two ions carry between them all of the current, the sum of the two transference numbers must be unity, i.e.,

$$t_+ + t_- = 1$$

Thus, the knowledge of one of the transport numbers helps in determining the other.

## 6.2.4 Conductometric Titrations

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtuse, a small error in the conductance data can cause a large deviation. The following approximate rules will be found useful.

- The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity (Table 4.2 of Unit 4).
- The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte.
- Throughout a titration the volume of the solution is always increasing, unless the conductance is corrected for this effect, non linear titration curves result. The correction can be accomplished by multiplying the observed conductance either by total volume $(V+V')$ or by the factor $(V+V')/V$, where $V$ is the initial volume of solution and $V'$ is the total volume of the reagent added. The correction presupposes that the conductivity is a linear function of dilution, this is true only to a first approximation.
- In the interest of keeping $V$ small, the reagent for the conductometric titration is ordinarily several times more concentrated than the solution being titrated (at least 10-20 times). A micro burette may then be used for the volumetric measurement.

The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric endpoint can be successfully applied.

Application: Acid-base titration, especially at trace levels. Relative precision better than 1% at all levels. There are also few disadvantages with this technique. As you know the conductance is a non-specific property, concentration of other electrolyte can be troublesome.

The electrical conductance of a solution is a measure of its currents carrying capacity and therefore determined by the total ionic strength. It is a non-specific property and for this reason direct conductance measurement are of little use unless the solution contains only the electrolyte to be determined or the concentrations of other ionic species in the solution are known. Conductometric titrations, in which the species in the solution are converted to non-ionic for by neutralization, precipitation, etc. are of more value.

**Some Typical Conductometric Titration Curves are:**

1. **Strong Acid with a Strong Base, e.g. HCl with NaOH:** Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as $H^+$ ions react with $OH^-$ ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of $OH^-$ ions (Fig. 6.2).

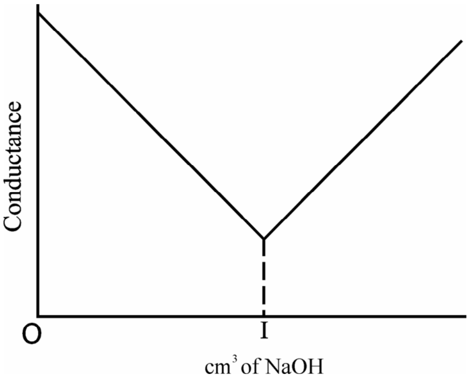


**Fig. 6.2: Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)**

2. **Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of $H^+$ by $Na^+$ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated $CH_3COOH$ to $CH_3COONa$ which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt $CH_3COONa$. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting $OH^-$ ions (Fig. 6.3).

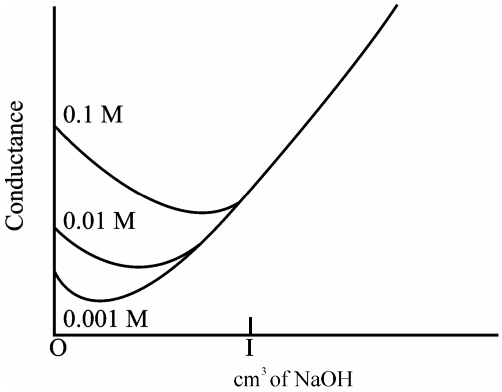


**Fig. 6.3: Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)**

3. **Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia**: Initially the conductance is high and then it decreases due to the replacement of $H^+$. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate (Fig. 6.4).

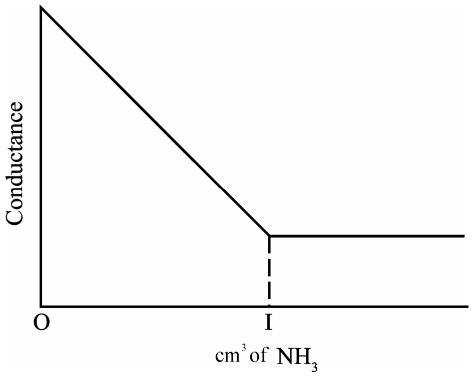


**Fig. 6.4: Conductometric titration of a strong acid ($H_2SO_4$) vs. a weak base ($NH_4OH$)**

4. **Weak Acid with a Weak Base**: The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting (Fig. 6.5).

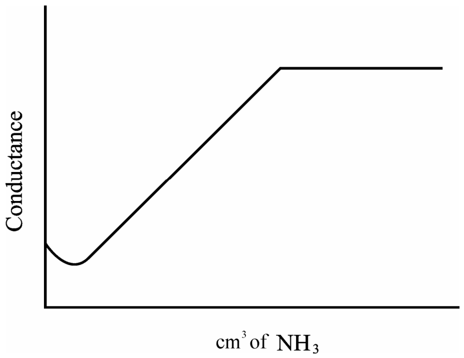


**Fig. 6.5: Conductometric titration of a weak acid (acetic acid) vs. a weak base ($NH_4OH$)**

5. **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base**: In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of $OH^-$ ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to Fig. 6.5 (Fig. 6.6).

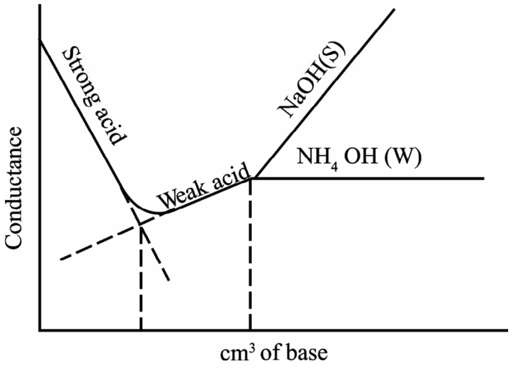


**Fig. 6.6 Conductometric titration of a mixture of a strong acid (HCl) and a weak acid ($CH_3COOH$) vs. a strong base (NaOH) or a weak base ($NH_4OH$)**

6. **Displacement (or Replacement) Titrations**: When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the strong acid and weak acid itself is liberated in the undissociated form. Similarly, in the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is generated in the undissociated form. If for example, M-HCl is added to 0.1 M solution of sodium acetate, the curve shown in Fig.6.7 is obtained, the acetate ion is replaced by the chloride ion after the endpoint. The initial increase in conductivity is due to the fact that the conductivity of the chloride ion is slightly greater than that of acetate ion. Until the replacement is nearly complete, the solution contains enough sodium acetate to suppress the ionization of the liberated acetic acid, so resulting a negligible increase in the conductivity of the solution. However, near the equivalent point, the acetic acid is sufficiently ionized to affect the conductivity and a rounded portion of the curve is obtained. Beyond the equivalence point, when excess of HCl is present (ionization of acetic acid is very much suppressed) therefore, the conductivity arises rapidly. Care must be taken that to titrate a 0.1 M-salt of a weak acid, the dissociation constant should not be more than $5 \times 10^{-4}$, for a 0.01 M -salt solution, $K_a < 5 \times 10^{-5}$ and for a 0.001 M-salt solution, $K_a < 5 \times 10^{-6,}$ i.e., the ionization constant of the displace acid or base divided by the original concentration of the salt must not exceed above $5 \times 10^{-3}$. Fig. 6.6. Also includes the titration of 0.01 M- ammonium chloride solution versus 0.1 M - sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the displacement of ammonium ion of grater conductivity by sodium ion of smaller conductivity.

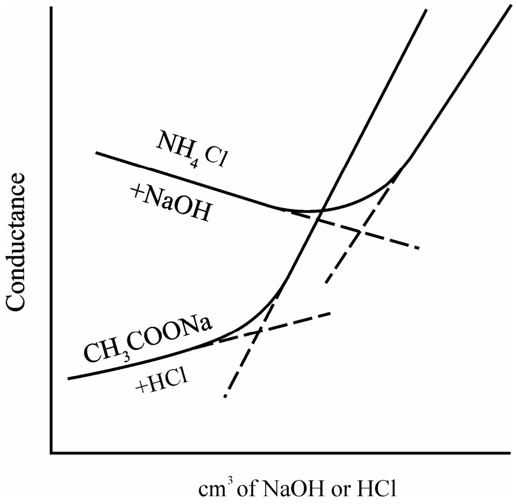


**Fig. 6.7: Conductometric titration of a salt of weak acid (sodium acetate) vs. strong acid (HCl); salt of a weak base ($NH_4Cl$) vs. a strong base (NaOH)**

7. **Precipitation Titration and Complex Formation Titration**: A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex . The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate). If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by *AB* and not the observed *AC*. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portion of the two arms of the curve until they intersect (Fig. 6.8).

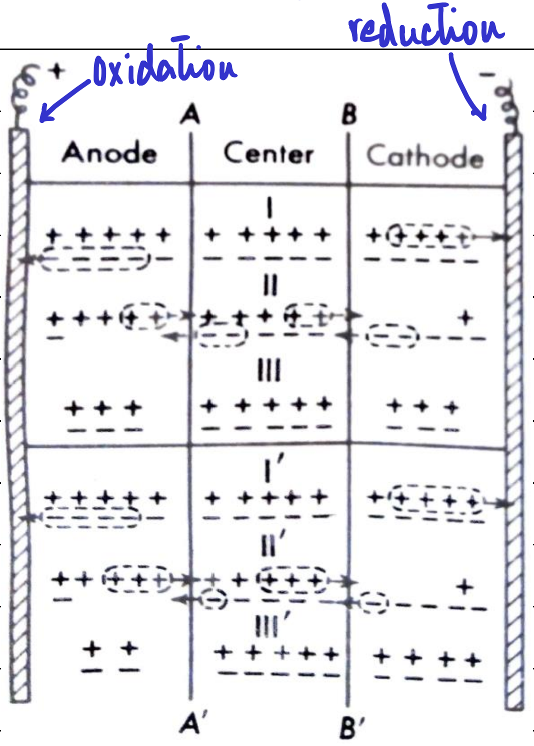
## Experimental determination of transport/transference no.

- * Hittorf's method
- * Moving Boundary method

1 Faraday (F) = 96494 Coulombs
≅ 96500 Coulombs

1 F ≡ 1 equivalent

## Hittorf's method/rule



When current is passed through a solution, the changes in concentration are directly related to the velocities of the ions that take place in the vicinity of the electrodes.

* Relationship between changes in concn. and velocities of the ions.

* Say each compartment contains 5 equivs. of cation and anion each.

* Assumption: speeds of cations and anions are equal.

* Say: 4F of electricity is passed.

① 4 equivs. of cations in the cathode compartment will accept electrons from the electrode and deposit.

② 4 equivs of anions in the anode compartment will give electrons to the electrode and deposit.

③ Migration: as the anions and the cations move with the same speed, each carry half of the total current across AA′ and BB′

Cations must transport 2F of electricity from left to right

anions must transport 2F of electricity from right to left.

∴ from migration, no change in concn. in the central compartment.

* Assumption: Speed of the cations = 3×speed of the anions.

Say: 4F of electricity is passed

① 4 equivs. of cations deposited at cathode

② 4 equivs. of anions deposited at anode

③ Migration: as the cations carry 3 times more current as the anions, 3 equivs. of cations must migrate from anode to the centre and from centre to cathode.

1 equiv. of anions leaves cathode and only 1 equiv. leaves the centre for anode.
from migration: no change in concn. in the central compartment.
∴ Unequal concn. change at the two electrodes.

Concn. change in anode = 3x Concn. change in cathode

* a parallelism between concn. loss due to migration and the velocity of the ion responsible

$$\frac{\text{Loss of cation equivs. at anode due to migration}}{\text{Loss of anion equivs. at cathode due to migration}} = \frac{v_+}{v_-} = \frac{t_+}{t_-}$$

∵ Total current passed through the cell ∝ $t_+ + t_- = 1$

$$\frac{\text{Loss of cation equivs. at anode due to migration}}{\text{Equivs. of current passed}} = \frac{t_+}{1} = t_+$$

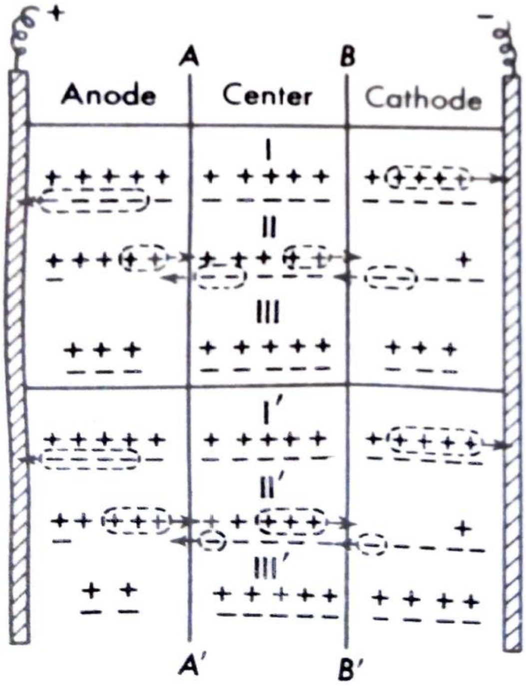
Similarly,

$$\frac{\text{Loss of anion equivs. at cathode due to migration}}{\text{Equivs. of current passed}} = \frac{t_-}{1} = t_-$$

**Experimental Determination of Transport Number**

**1. Hittorf's Rule**

When current is passed through a solution, the changes in concentration is directly related to the velocities of the ions occur in the vicinity of the electrodes. The relationship between the changes in concentration and velocities of the ions that are responsible for this change is expressed by means of the Hittorf's rule. Imaginary planes $AA'$ and $BB'$ divide the cell into three imaginary compartments – anode, centre and cathode. Say, each compartment contains 5 equivalents of cation and anion each.



We also assume that the speeds of the ions to be equal. Say, $4F$ of electricity are passed through the cell. Thus, for $4F$ of electricity are passed, $4$ equivalents of cations in the cathode compartment will accept electrons from the electrode and deposit. Also, $4$ equivalents of anions in the anode compartment will give up their electrons to the anode and will also deposit. The results of these are shown in $II$.

While these changes occur at the electrodes, the ions migrate through the solution. Since in this case both ions move with the same speed, each must carry one-half the current across the planes $AA'$ and $BB'$. That is, past the planes $AA'$ and $BB'$, cations must transport $2F$ of electricity from left to right, the anions $2F$ of electricity from right to left. Thus, $2$ equivalents of cations must move from the anode compartment into the centre, and $2$ equivalents from the centre into the cathode compartment. At the same time, $2$ equivalents of anions must move from the cathode compartment to the centre, and $2$ equivalents from the centre into the anode compartment. When these migrations are added to the changes at the electrodes, the final result is $III$.

∴ The concentration in the central compartment remains unchanged upon the passage of current. The concentration in both anode and cathode compartments has decreased by the same amount of $2$ equivalents. However, the situation is different when the speeds of the ions are not the same. Say, the speed of the cations $=$ $3$ ×the speed of the anions. As $4F$ of electricity is passed, just as before, $4$ equivalents of each ion are deposited at the corresponding electrodes. But, since the cation carries here $3$ times as much current as the anion, $3$ equivalents of cation must migrate from anode to the centre, and from centre to the cathode compartments. At the same time only $1$ equivalent of anions leaves the cathode section, and only $1$ equivalent of anions leaves the centre for the anode compartment. As given in $III'$, and just as before, there is no change in the concentration in the central compartment. There are concentration changes at the two electrodes, and these changes are unequal.

The concentration changes in the anode $= 3 \times$ the concentration change in cathode. By repeating the above argument for various ionic speed ratios, it can be readily shown that the changes in concentration at the electrodes as a result of electrolysis will be equal only when the ionic speeds are the same. When these are different, so are the concentration changes at the electrodes. When $v_+ : v_- = 1$, due to migration, the loss in concentration of cations from the anode compartment $=$ the loss in concentration of anions from the cathode compartment. When $v_+ : v_- = 3$, due to migration, the loss in concentration of cations from the anode compartment $= 3 \times$ the loss in concentration of anions from the cathode compartment. This parallelism between concentration loss due to migration and the velocity of the ion responsible leads to the Hittorf's rule.

$$\frac{\text{Loss in cation equivalents at anode due to migration}}{\text{Loss in anion equivalents at cathode due to migration}} = \frac{v_+}{v_-} = \frac{t_+}{t_-}$$

Since the total current passed through the cell, expressed in equivalents, is proportional to $t_+ + t_- = 1$, direct consequences of this rule are also the statements:

$$\frac{\text{Loss in cation equivalents at anode due to migration}}{\text{Equivalents of current passed}} = \frac{t_+}{1} = t_+$$

$$\frac{\text{Loss in anion equivalents at cathode due to migration}}{\text{Equivalents of current passed}} = \frac{t_-}{1} = t_-$$

## Application of Hittorf's method

To determine the transport numbers of the ions in an exactly 0.2 molal solution of $CuSO_4$, the cell was filled with the solution and electrolyzed between copper electrodes for some time. The cathode solution was found to weigh 36.4340 g and to contain 0.4415 g of copper. Further, the cathode in the coulometer showed an increase in weight of 0.0405 g due to deposited silver. From these data it is required to calculate the transport number of the copper and sulfate ions.

Solution: $Cu^{2+}(aq.) + 2\bar{e} \rightarrow Cu(s)$

Given: 36.4340 gm of cathode solution contains 0.4415 gm Cu.

That is, $\frac{MW(CuSO_4)}{AW(Cu)} \times 0.4415 = 0.4415 \times \frac{159.609}{63.546} = 1.1089$ gm $CuSO_4$

∴ Wt. of water in the cathode solution = 36.4340 − 1.1089 = 35.3251 gm

∵ Before electrolysis the $CuSO_4$ soln. was 0.2 molal.

⇒ Each gram of water had associated with it $\frac{0.2 \times MW(CuSO_4)}{1000 \text{ gm}}$ of $CuSO_4$

∴ 35.3251 gm of $H_2O$ had associated with them initially

$(35.3251 \times 0.2 \times 159.609)/1000 = 1.1276$ gm of $CuSO_4$

∴ loss in wt. of $CuSO_4$ in cathode = (1.1276 − 1.1089) gm = 0.0187 gm

= $(2 \times 0.0187)/159.609 = 0.000234$ equiv

total current passed through the cell is given by 0.0405 gm of Ag = $\frac{0.0405}{107.87}$

= 0.000375 equiv.

∴ Loss in $CuSO_4$ due to deposition of Cu on the cathode should be 0.000375 equiv.

But the actual loss is only 0.000234 equiv.

∴ The difference of the two must have been involved in migration

⇒ 0.000375 − 0.000234 = 0.000141 equiv. must have migrated

As the ion that migrates towards cathode is $Cu^{2+}$, this no. of equiv. must have been transported by this ion

$$t_{Cu^{2+}} = 0.000141/0.000375 = 0.376$$

$t_{SO_4^{2-}} = 0.624$

To determine the transport numbers of the ions in an exactly $0.2$ molal solution of $\mathrm{CuSO_4}$, the cell was filled with the solution and electrolyzed between copper electrodes for some time. The cathode solution was found to weigh $36.4340$ g and to contain $0.4415$ g of copper. Further, the cathode in the coulometer showed an increase in weight of $0.0405$ g due to deposited silver. From these data it is required to calculate the transport number of the copper and sulfate ions.

Given that, the $36.4340$ g cathode solution contained $0.4415$ g of Cu. This is equivalent to

$$0.4415\times\frac{\mathrm{MW(CuSO_4)}}{\mathrm{AW(Cu)}}=0.4415\times\frac{159.609}{63.546}=1.1089\ \mathrm{g\ CuSO_4}$$

∴ The weight of water in this solution was then $36.4340-1.1089=35.3251$ g

∵ Before electrolysis the $\mathrm{CuSO_4}$ solution was $0.2$ molal, that is, each gram of water had associated with it $0.20\times\mathrm{MW(CuSO_4)}/1000$ g of the salt.

∴ $35.3251$ g of water had associated with them initially

$$35.3251\left(0.20\times\frac{\mathrm{MW(CuSO_4)}}{1000}\right)=\frac{35.3251\times0.20\times159.609}{1000}=1.1276\ \mathrm{g\ CuSO_4}$$

∴ The loss in weight of $\mathrm{CuSO_4}$ in the cathode compartment $=1.1276-1.1089=0.0187$ g, or $2\times0.0187/159.609=0.000234$ equivalent. The total current passed through the cell is given by $0.0405$ g of silver, or $0.0405/107.87=0.000375$ equivalent. So, the loss in $\mathrm{CuSO_4}$ due to deposition of Cu on cathode should have been this number of equivalents. But the actual loss was only $0.000234$ equivalent.

∴ The difference $0.000375-0.000234=0.000141$ equivalent must have migrated into this compartment.

As the ion that migrates towards the cathode is $\mathrm{Cu^{2+}}$, this number of equivalents must have been transported by this ion, and therefore its transport number is

$$\mathrm{t_{Cu^{2+}}}=\frac{0.000141}{0.000375}=0.376,$$

so that the transport number of $\mathrm{SO_4^{2-}}$ ion is $\mathrm{t_{SO_4^{2-}}}=1-0.376=0.624.$

## Moving boundary method

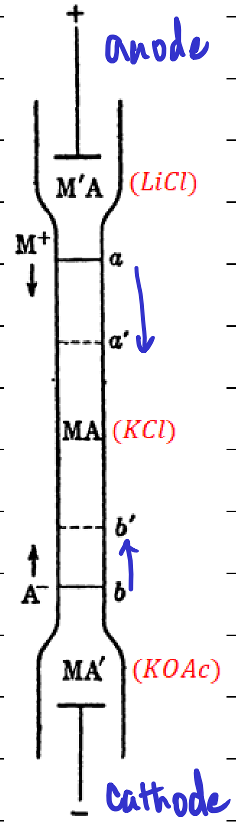
for an electrolyte, $MA \rightarrow M^+ + A^-$ (say, KCl) → test electrolyte

$\boxed{M'A,\ MA'}$ indicator electrolytes

$M' + A^-$ $\quad$ $M^+ + A'^-$

KCl → LiCl $\quad$ $M^+$ $\quad$ $M'^+$

KCl → KOAc



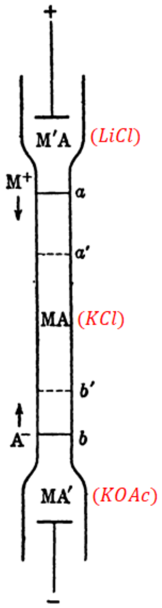
speed of $M'^+$ < speed of $M^+$ } Boundaries remain distinct
speed of $A'^-$ < speed of $A^-$ }

$$\frac{aa'}{aa'+bb'} = \frac{u_+}{u_+ + u_-} = \frac{t_+}{t_+ + t_-} = t_+$$

$$\frac{bb'}{aa'+bb'} = \frac{u_-}{u_+ + u_-} = t_-$$

### 2. The Moving Boundary Method

Say we want to determine the transport numbers of the ions constituting an electrolyte MA (say, KCl).
Two other electrolytes, M′A (say, LiCl) and MA′ (say, KOAc), each having an ion common with MA are available. MA is the experimental electrolyte, while M′A and MA′ are the indicator electrolytes. Say we place the solution of MA between the indicator electrolyte solutions in such a manner so as to form sharp boundaries at a and b.



The anode is inserted in the solution M′A, and the cathode in that of MA′. To maintain distinct boundaries between the solutions during the passage of current, we must have that

- the speed of the ion $M'^+ <$ the speed of the ion $M^+$, and
- the speed of the ion $A'^- <$ the speed of the ion $A^-$.

If these conditions hold, then

- $M'^+$ ions do not overtake $M^+$ ions at a, and
- $A'^-$ ions do not overtake $A^-$ ions at b.

∴ The boundaries remain distinct (do not get blurred).
∵ The indicator ions are slow to move, they are also called following ions. Under the influence of an applied electric field,

- the boundary a moves to a′, while at the same time,
- the boundary b moves to b′.

The distances aa′ and bb′ depend on the speeds of the ions $M^+$ and $A^-$.
∵ There is a uniform potential gradient through the central solution MA,

- the distance $aa' \propto u_+$, the ionic velocity of $M^+$, and
- the distance $bb' \propto u_-$, the ionic velocity of $A^-$.

Therefore,

$$\frac{aa'}{aa'+bb'} = \frac{u_+}{u_+ + u_-} = t_+$$

and

$$\frac{bb'}{aa' + bb'} = \frac{u_-}{u_+ + u_-} = t_-$$

so that the transport numbers can be determined from observations on the movements of the boundaries a and $b$. If $1F = 96500$ coulombs of electricity is passed, $t_+$ equivalent of the cation must pass any given point in one direction. If $C$ equivalents per unit volume is the concentration of the solution, in the vicinity of the boundary formed by the $M^+$ ions, this boundary must sweep through a volume of $t_+/C$ while $1F$ is passing.
∴ The volume $\phi$ swept out by the cations for the passage of $Q$ coulombs is,

$$\phi = \frac{Qt_+}{FC}$$

If the cross-section of the tube in which the boundary moves is $A$ cm$^2$, and the distance through which it moves during the passage of $Q$ coulombs is $l$ cm, then $\phi = lA$, and hence,

$$lA = \frac{Qt_+}{FC} \Rightarrow t_+ = \frac{lAFC}{Q}$$

Since the number of coulombs passing can be determined, $t_+$ may be calculated from the rate of movement of one boundary.

## Ways to define electrolytic conductance

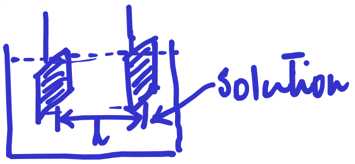
Conventional definition of resistance, $R = \rho\left(\frac{l}{a}\right)$

$\rho$ = specific resistance/resistivity = resistance of a conducting wire of unit (1 cm) length and unit cross-sectional area (1 $cm^2$).

$\therefore \frac{1}{R} = \frac{1}{\rho}\left(\frac{a}{l}\right) \Rightarrow L = L_s\left(\frac{a}{l}\right)$

L = conductance; $L_s$ = specific conductance/conductivity may be considered the conductance of 1 cm cube (not cc) of material.

Say, 1 equiv. mass of an electrolyte is dissolved in vol. V of the solution. Say, this whole solution is placed in a conductivity cell.



Cell constant
$\lambda$ : lambda (lc)
$\Lambda$ = Lambda (uc)

$L = L_s\left(\frac{a}{l}\right)$

or, $L = L_s\left(\frac{al}{l^2}\right)$ or, $Ll^2 = L_s(V_{eq}/eq^{-1})$

$V_{eq}$ has units of $m^3 eq^{-1}$

$\boxed{Ll^2/eq}$: equivalent conductivity = $\Lambda_{eq}$

$$\Lambda_{eq} = \frac{Ll^2}{eq} = L_s V_{eq}$$

$\Lambda_{eq}$ is defined as the conductance of a vol. of solution containing one equiv. mass of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution.

$\Lambda_{eq} = (\Omega^{-1} cm^{-1})(cm^3 eq^{-1}) = \Omega^{-1} cm^2 eq^{-1} = S\, cm^2 eq^{-1}$

If $C_{eq}$ = concn. of the soln. in equiv. per unit vol., then

$V_{eq}(m^3 eq^{-1}) = 1/C_{eq}$ $\therefore \Lambda_{eq} = L_s V_{eq} = L_s \frac{1}{C_{eq}}$

$\Lambda_m$ = molar conductivity, defined as the conductance of a vol. of soln. containing one mole of a dissolved substance when ----whole soln.

$\Lambda_m = L_s V_m = L_s (1/C_m) = L_s / C_m$

$C_m$ = molar concn. of the soln.

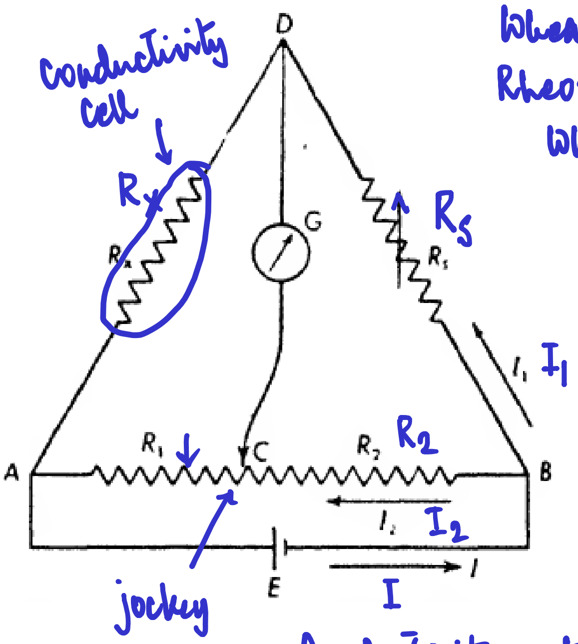
$\Lambda_m = (\Omega^{-1} m^{-1})(m^3 mol^{-1}) = \Omega^{-1} m^2 mol^{-1}$
$= S m^2 mol^{-1}$.

## Determination (experimental) of conductance

Wheatstone bridge
Rheostat

Cell constant
0.1 }
0.01 }

When no current flows through the circuit



$R_s I_1 = R_2 I_2$

$R_x I_1 = R_1 I_2$

$\frac{R_x}{R_s} = \frac{R_1}{R_2} \Rightarrow R_x = (R_1/R_2) R_s$

$L = L_s (a/l)$

Conductivity meter reading → L }
cell constant (known) } $L_s$ is determined

$\Lambda_{eq} = 1000 L_s / c$ ; $\Lambda_{eq}$ is determined

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

α = degree of dissociation

$c(1-\alpha) \quad c\alpha \quad c\alpha$

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

## Variation of conductance with concentration

(a) variation of $L_s$ with concentration
(b) " " $\Lambda$ " "

$K - K\alpha = c\alpha^2$ or, $c\alpha^2 + K\alpha - K = 0$

$ax^2 + bx + c = 0$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\boxed{\alpha = \alpha_1, \alpha_2}$

Debye-Hückel theory of interionic interactions

**Electrolyte Conductance**

The resistance of an electrolytic conductor to current passage can be determined by the application of Ohm's law to such conductors. However, instead of the resistance, it is customary to speak of the conductance which is merely the reciprocal of the electrical resistance. As is well known, the resistance of any conductor is proportional directly to its length and inversely to its cross-sectional area, namely,

$$R = \rho \frac{l}{a}$$

where R is the resistance in ohms, l the length in centimeters, and a the area in square centimeters. The constant of proportionality ρ is the resistance of a conductor 1 cm in length and with a cross-sectional area of 1 sq cm. and is called the specific resistance or the resistivity. The value of ρ depends on and is characteristic of the nature of the conductor. We define the conductance, $\mathrm{L}$, as the reciprocal of $\mathrm{R}$, as

$$\mathrm{L}=\frac{1}{\mathrm{R}}=\frac{1}{\rho}\left(\frac{\mathrm{a}}{\mathrm{l}}\right)=\mathrm{L_s}\left(\frac{\mathrm{a}}{\mathrm{l}}\right)$$

where $\mathrm{L_s}=1/\rho$ is the specific conductance or the conductivity. This quantity may be considered the conductance of $1$ cm cube (not cc) of material, and is expressed in reciprocal ohms or mhos.

Since the charges of solute ions determine the conductance of a solution, the comparison of conductance data is made between values for solutions corresponding to a total of unit charge on each ion of the solute. It is because of this that the equivalent conductivity of the solution is employed for comparison purposes.

Suppose 1 equivalent mass of an electrolyte is dissolved in volume $\mathrm{V}$ of the solution. Let this whole solution be placed in a conductivity cell. Multiplying and dividing the right side of the equation

$$\mathrm{L}=\mathrm{L_s}\left(\frac{\mathrm{a}}{\mathrm{l}}\right)$$

by $\mathrm{l}$, we get

$$\mathrm{L}=\mathrm{L_s}\left(\frac{\mathrm{al}}{\mathrm{l}^2}\right)\Rightarrow \mathrm{Ll}^2=\mathrm{L_s}\left(\mathrm{V_{eq}}/\mathrm{eq}^{-1}\right)$$

$\mathrm{V_{eq}}$ carry the units of $\mathrm{m}^3\ \mathrm{eq}^{-1}$. The term $\mathrm{Ll}^2/\mathrm{eq}$ is known as **equivalent conductivity**, abbreviated as $\Lambda_{\mathrm{eq}}$. Thus, we have,

$$\Lambda_{\mathrm{eq}}=\mathrm{Ll}^2/\mathrm{eq}=\mathrm{L_s}\mathrm{V_{eq}}$$

The equivalent conductivity of an electrolyte may be defined as **the conductance of a volume of solution containing one equivalent mass of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution**. The equivalent conductivity thus gives the conducting power of the ions produced by 1 equivalent mass (i.e., mass corresponding to a total of unit charge on each ion) of an electrolyte at any particular concentration. The unit of $\Lambda_{\mathrm{eq}}$ in the CGS system is

$$\Lambda_{\mathrm{eq}}=(\Omega^{-1}\mathrm{cm}^{-1})(\mathrm{cm}^3\mathrm{eq}^{-1})=\Omega^{-1}\mathrm{cm}^2\mathrm{eq}^{-1}=\mathrm{S\ cm}^2\mathrm{eq}^{-1}$$

If $\mathrm{C_{eq}}$ is the concentration of the solution (in equivalent per unit volume), then $\mathrm{V_{eq}}$ (which carry a unit of $\mathrm{m}^3\ \mathrm{eq}^{-1}$) will be equal to $1/\mathrm{C_{eq}}$. Hence, we may write $\Lambda_{\mathrm{eq}}=\mathrm{L_s}\mathrm{V_{eq}}$ as,

$$\Lambda_{\mathrm{eq}}=\mathrm{L_s}\left(1/\mathrm{C_{eq}}\right)=\mathrm{L_s}/\mathrm{C_{eq}}$$

In SI units, the concentration, C is expressed as the amount of substance per unit volume instead of equivalent of substance per unit volume, and thus one uses the term **molar conductivity** as defined below.

The molar conductivity, $\Lambda_{\mathrm{m}}$, of an electrolyte may be defined as **the conductance of a volume of solution containing one mole of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution**. Thus, it gives the conducting power of the ions produced by 1 mole of an electrolyte at any particular concentration.

$$\Lambda_{\mathrm{m}}=\mathrm{L_s}\mathrm{V_m}=\mathrm{L_s}(1/\mathrm{C})=\mathrm{L_s}/\mathrm{C}$$

where $\mathrm{V_m}$ is the volume of the solution containing one mole of the substance and C is the resultant molar concentration. Note $\mathrm{V_m}$ carries the unit of $\mathrm{m}^3\ \mathrm{mol}^{-1}$. The unit of $\Lambda_{\mathrm{m}}$ will be

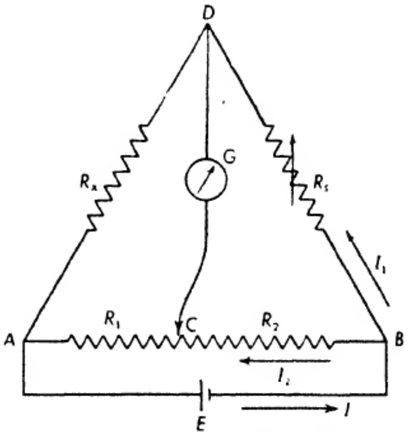
$$\Lambda_{\mathrm{m}}=(\Omega^{-1}\mathrm{m}^{-1})(\mathrm{m}^3\mathrm{mol}^{-1})=\Omega^{-1}\mathrm{m}^2\mathrm{mol}^{-1}=\mathrm{S\ m}^2\mathrm{mol}^{-1}$$

If $\mathrm{n_+z_+}$ (or $\mathrm{n_-}\ |\mathrm{z_-}|$) is the total charge number of the cations (or magnitude of the charge number of the anions) of a single molecule of an electrolyte, it follows that $1\ \mathrm{mol}\equiv(\mathrm{n_+z_+})(1\ \mathrm{eq})$. Hence,

$$\Lambda_{\mathrm{m}}=\mathrm{L_s}/\mathrm{C}\ \text{and}\ \Lambda_{\mathrm{eq}}=\mathrm{L_s}/\mathrm{C_{eq}}=\frac{\mathrm{L_s}}{\mathrm{n_+z_+\ eq\ mol^{-1}}\times\mathrm{C}}\Rightarrow\Lambda_{\mathrm{eq}}=\frac{\Lambda_{\mathrm{m}}}{\mathrm{n_+z_+\ eq\ mol^{-1}}}$$

### Determination of Conductance

The equivalent conductance of an electrolyte is always calculated from specific conductance values through $\Lambda=1000\mathrm{L_s}/\mathrm{C}$. Consequently, the problem of obtaining $\Lambda$ reduces itself to a determination of the specific conductance of the electrolyte, and this, in turn, to a measurement of the resistance of the solution. For measuring resistances of electrolytic solutions, the Wheatstone bridge method is employed. $\mathrm{R_x}$, the unknown resistance whose value is to be determined, is placed in one arm of the bridge, a variable known resistance $\mathrm{R_s}$ in the other. $\mathrm{AB}$ is a uniform slide wire across which moves a contact point $\mathrm{C}$. To balance the bridge the contact is moved along this resistance until no current from the battery $\mathrm{E}$ flows through the galvanometer $\mathrm{G}$, and hence no deflection of it is observed.



When this condition is reached, $R_s$, the resistance from A to C, $R_1$ and that from C to B, $R_2$, are read.
$R_x$ is then calculated from these according to the following considerations. When the current I from the battery reaches point B it divides into two parallel paths and into the two currents, $I_1$ and $I_2$. These currents lead to potential drops across the resistances they traverse. The purpose of balancing the bridge is to find a point along AB, namely C, such that the potential drop from B to C is equal to that from B to D. When this point is found, D and C are at the same potential and no current flows through the branch containing the galvanometer. The condition for bridge balance is, then,

$$R_sI_1 = R_2I_2$$

But when these potential drops are equal, those from D to A and from C to A must also be equal.

$$\therefore R_xI_1 = R_1I_2$$

Dividing now the second of these equalities by the first, we obtain

$$\frac{R_x}{R_s} = \frac{R_1}{R_2} \Rightarrow R_x = R_s\left(\frac{R_1}{R_2}\right)$$

By reading $R_s$, $R_1$ and $R_2$ for the bridge balance, $R_x$ can be calculated. We define the conductance, L, as the reciprocal of R, as

$$L = \frac{1}{R} = \frac{1}{\rho}\left(\frac{a}{l}\right) = L_s\left(\frac{a}{l}\right)$$

where $L_s = 1/\rho$ is the specific conductance or the conductivity. The equation, $L = L_s(a/l)$ needs special attention. From the equation,

$$L = L_s\left(\frac{a}{l}\right)$$

we may write, $L_s = (l/a)L$.
∴ As before, $L_s$ can be calculated from the measured resistance (R), which gives the conductance L, and the ratio $(l/a)$ for the particular cell used is required. For any given cell this ratio of distance between electrodes to their cross-sectional area is a fixed quantity, and is therefore called the **cell constant** K. To obtain the value of the cell constant it is not necessary to determine l and a. Instead, a solution of known $L_s$ is placed in the cell, the resistance is measured, and K is calculated. To determine cell constants either 1 (N), 0.1 (N), or 0.01 (N) solutions of potassium chloride are used. A 1 (N) solution is a solution containing 1 gram mole of salt per $dm^3$ of solution at 0°C. The conductance values of these 1 (N), 0.1 (N), or 0.01 (N) solutions are measured with great accuracy in cells with electrodes of definite area and definite spacing, and their specific conductance values are well known.
The basic unit of conductance is $\text{ohm}^{-1}$ (or mho) which is now called Siemens (S). Specific conductance is expressed in the units of Siemens per cm (S/cm).

**ELECTROLYTIC CONDUCTANCE [SEMESTER-III (H); C5T]**
Google Meet Link: https://meet.google.com/isc-odcs-gnw
Date: 25/02/2024

1. Given that, at 25 °C, $\Lambda_{\mathrm{LiI}} = 117\ \mathrm{cm^2 equiv^{-1} \Omega^{-1}}$, $\lambda_{\mathrm{H^+}} = 350\ \mathrm{cm^2 equiv^{-1} \Omega^{-1}}$ and $\Lambda_{\mathrm{LiCl}} = 115\ \mathrm{cm^2 equiv^{-1} \Omega^{-1}}$, and $t_+$ for LiCl is 0.34. Calculate (a) $\Lambda_{\mathrm{HI}}$, (b) $t_+$ for HI, and (c) the specific conductivity of a solution which is 0.1 (M) in LiI and 0.2 (M) in LiCl.

Solution: Since $t_+(\mathrm{LiCl}) = 0.34 \Rightarrow \frac{\lambda(\mathrm{Li^+})}{\Lambda(\mathrm{LiCl})} = 0.34$ or, $\lambda(\mathrm{Li^+}) = 0.34 \times \Lambda(\mathrm{LiCl})$

or, $\lambda(\mathrm{Li^+}) = 0.34 \times 115\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}} = 39.1\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

Now, $\lambda(\mathrm{Li^+}) + \lambda(\mathrm{Cl^-}) = \Lambda(\mathrm{LiCl})$

$\therefore \lambda(\mathrm{Cl^-}) = (115 - 39.1)\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}} = 75.9\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

Also, $\lambda(\mathrm{I^-}) = \Lambda(\mathrm{LiI}) - \lambda(\mathrm{Li^+}) = (117 - 39.1)\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}} = 77.9\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

(a) $\Lambda(\mathrm{HI}) = \lambda(\mathrm{H^+}) + \lambda(\mathrm{I^-}) = (350 + 77.9)\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}} = 427.9\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

(b) $t_+(\mathrm{HI}) = \frac{\lambda_{\mathrm{H^+}}}{\Lambda(\mathrm{HI})} = \frac{350}{427.9} = 0.818$

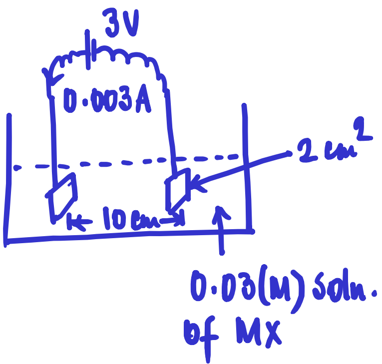
(c) Sp. conductivity, $L_s$ of a soln. which is 0.1(M) LiI and 0.2(M) LiCl

Now, $\Lambda = \frac{1000\,L_s}{C}$, C is in gm eq. per 1000 cm$^3$

$L_s = \frac{1}{1000}\Lambda C = \frac{1}{1000}\sum_i \lambda_i C_i = \frac{1}{1000}\left[0.1 \times 39.1 + 0.1 \times 77.9 + 0.2 \times 39.1 + 0.2 \times 75.9\right]\ \mathrm{eq\,cm^{-3}.\,cm^2\,eq^{-1}\,\Omega^{-1}}$

$= 0.0347\ \Omega^{-1}\,\mathrm{cm^{-1}}$

2. A conductivity cell has electrodes whose effective area is $2\ \mathrm{cm^2}$ and whose effective separation is $10$ cm. It is filled with a 0.03 (M) solution of a salt MX (univalent ions), and on application of 3 V potential difference, a current of 0.003 A flows. It is also known that the transference number of $\mathrm{M^+}$ in this solution is 0.4. Calculate
(a) the equivalent conductance of MX,
(b) the individual ionic equivalent conductivities of $\mathrm{M^+}$ and $\mathrm{X^-}$, and the resistance of the above cell attributable to $\mathrm{M^+}$ ions,
(c) the velocity in $\mathrm{cm\ sec^{-1}}$ with which $\mathrm{M^+}$ ions moved in the above experiment, and
(d) the diffusion coefficient of $\mathrm{M^+}$ ions in this solution at 25 °C.



Solution: (a) Eq. conductance, $\Lambda = \frac{1000\,L_s}{C}$

Now, $R = \rho\,(l/a)$ or, $\frac{1}{R} = L_s \cdot \frac{1}{(l/a)}$ $\therefore L_s = (l/a) \cdot \frac{1}{R}$

From Ohm's law, $V = IR$, $R = V/I = 3\mathrm{V}/0.003\mathrm{A} = 1000\ \Omega$

$l/a = 10\ \mathrm{cm}/2\ \mathrm{cm^2} = 5\ \mathrm{cm^{-1}}$

$\therefore L_s = \frac{5\ \mathrm{cm^{-1}}}{1000\ \Omega} = 0.005\ \Omega^{-1}\,\mathrm{cm^{-1}}$

$\therefore \Lambda = \frac{1000\,L_s}{C} = \frac{1000 \times 0.005\ \Omega^{-1}\,\mathrm{cm^{-1}}}{0.03\ \mathrm{eq\,cm^{-3}}}$

or, $\Lambda \cong 167\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

(b) Given, $t_{\mathrm{M^+}} = 0.4 \Rightarrow \frac{\lambda_{\mathrm{M^+}}}{\Lambda(\mathrm{MX})} = 0.4$ $\therefore \lambda_{\mathrm{M^+}} = 0.4 \times 167\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$
$= 66.7\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

$t_{\mathrm{X^-}} = 0.6 \Rightarrow \frac{\lambda_{\mathrm{X^-}}}{\Lambda(\mathrm{MX})} = 0.6$ or, $\lambda_{\mathrm{X^-}} = 0.6 \times 167\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}} = 100.3\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}}$

$\lambda_{\mathrm{X^-}} = \Lambda(\mathrm{MX}) - \lambda_{\mathrm{M^+}} = (167 - 66.7)\ \mathrm{cm^2\,eq^{-1}\,\Omega^{-1}} = 100.3\ \mathrm{cm^2\,eq^{2}\,\Omega^{-1}}$

Calculation of resistance: assignment

(c) velocity of $M^+$ ions, $v_{M^+}$

mobility: velocity of an ion under unit pot. gradient, $u_{M^+} = \frac{v_{M^+}}{(V/l)}$

a 3V pot. diff. is applied along a distance of 10 cm.

∴ pot. grad., $V/l = 3V/10\text{ cm} = 0.3\text{ V cm}^{-1}$

$u_{M^+} = \frac{\lambda_{M^+}}{F} = \frac{66.7\text{ cm}^2\text{ eq}^{-1}\,\Omega^{-1}}{96489\text{ Coulomb}}$   ∴ $v_{M^+} = u_{M^+}(V/l)$

or, $v_{M^+} = \frac{66.7\text{ cm}^2\text{ eq}^{-1}\,\Omega^{-1}}{96489\text{ Coulomb}} \times 0.3\text{ V cm}^{-1} = 2.07\times10^{-4}\text{ cm s}^{-1}$

(d) Diffusion coeff., $D_{M^+} = \frac{\lambda_{M^+} RT}{z_{M^+} F^2} = \frac{66.7\times8.314\times298.15}{1\times(96489)^2} = 1.78\times10^{-5}\text{ cm}^2\text{ s}^{-1}$

3. A specific conductivity value of $3.82\ \Omega^{-1}\text{m}^{-1}$ was measured for a solution containing $0.1$ (M) KCl and $0.2$ (M) MCl (a strong electrolyte). Calculate $\lambda$ for $\text{M}^+$, given the values of $\lambda$ for $\text{K}^+$ and $\text{Cl}^-$ are $7.4\times10^{-3}\ \text{m}^2\text{equiv}^{-1}\Omega^{-1}$ and $7.6\times10^{-3}\ \text{m}^2\text{equiv}^{-1}\Omega^{-1}$, respectively.

Solution: Assignment   $\lambda_{M^+} = 4\times10^{-3}\text{ m}^2\text{ eq}^{-1}\,\Omega^{-1}$

4. A particular conductivity cell had a resistance of $468\ \Omega$ when filled with $0.001$ (M) HCl, a resistance of $1580\ \Omega$ when filled with $0.001$ (M) NaCl, and one of $1650\ \Omega$ when filled with $0.001$ (M) $\text{NaNO}_3$. The equivalent conductivity of $\text{NaNO}_3$ is $0.0121\ \text{m}^2\text{equiv}^{-1}\Omega^{-1}$. Neglecting changes in $\Lambda$ values with concentration, calculate
   (a) the specific conductivity of $0.001$ (M) $\text{NaNO}_3$,
   (b) the cell constant, and
   (c) the resistance of the cell when filled with $0.001$ (M) $\text{HNO}_3$ and the equivalent conductivity of $\text{HNO}_3$.

Solution: Assignment (a) $L_s = 0.0121\ \Omega^{-1}\text{m}^{-1}$   (c) $R = 475\ \Omega$
(b) Cell constant $= 20\text{ m}^{-1}$

5. A silver nitrate solution was electrolyzed in a transport cell with silver electrodes. The anode compartment contained $0.1210$ g silver ions before electrolysis and $0.1652$ g after electrolysis. During electrolysis, $0.0854$ g of Ag was deposited in the cathode. Calculate $t_+$ and $t_-$. Given, the atomic weight of silver 107.8.

Solution: 107.8 g of Ag is deposited at the cathode for the passage of 1 F.

∴ 0.0854 g of Ag is deposited for the passage of $\frac{0.0854}{107.8}$ F.

∴ Amount of charge sent $= \frac{0.0854}{107.8}$ F

Gain in the wt. of Ag in the anode chamber for the passage of $\frac{0.0854}{107.8}$ F

$= (0.1652 - 0.1210)\text{g} = 0.0442\text{ g} = \frac{0.0442\text{ g}}{107.8\text{ eq}^{-1}} = \frac{0.0442}{107.8}\text{ g eq}$

Gain in g eq. of Ag in the anode chamber for the passage of 1 F

$= \frac{0.0442/107.8}{0.0854/107.8} = 0.52 = t_-$   ∴ $t_+ = 0.48$