

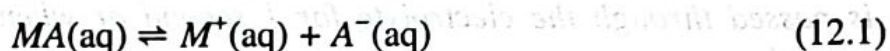
14.4 The Mechanism of Electrolytic Conduction

The first successful mechanism of electrolysis was put forward by R. Clausius (1857). He made the following assumptions:

- (i) in solution the electrolytes are automatically split into ions,
- (ii) the ions exist only for a short interval and an equilibrium exists between the ions and the undissociated molecules,
- (iii) the free ions carry charge and carry current during the short period of their existence.
- (iv) only a very small number of the molecules would be split up into ions,
- (v) as the ions are removed by discharge at the electrodes or recombination, fresh molecules break up into the ions in order to maintain the equilibrium.

This theory was satisfactory to a large extent, but there was no quantitative expression associated with it. The quantitative relationship was given by Arrhenius.

S. Arrhenius put forward his theory of electrolytic dissociation in 1887. According to this theory it is assumed that when an acid, base or salt is dissolved in water, a fraction of it breaks up spontaneously into positive and negative ions, and an equilibrium is established between the undissociated electrolyte molecules and the ions. Thus for the electrolyte MA,



The ions are free to move independently and randomly in the liquid medium. When an electric field is applied the ions are attracted towards the electrodes, the positive ions, called *cations*, going to the cathode and the negative ions, called *anions*, to the anode. At the electrodes the ions give up their charge and are liberated. By postulating that the fraction of the electrolyte dissociated increased when the solution was diluted Arrhenius was able to explain the concentration variation of conductance. Arrhenius gathered support for his theory from van't Hoff's investigation of the colligative properties of solutions (Section 9.20).

It is now believed that once electrolytes are placed in water the ions separate. The ions get surrounded by water molecules and oppositely charged ions which form what is called an ion atmosphere. When electricity is passed through the solution ions with their ion atmospheres move to electrodes with opposite sign (Section 14.13).

14.5 Faraday's Laws of Electrolysis

Micheal Faraday (1804) carried out a large number of experiments on electrolysis, and derived quantitative relationships between the quantity of electricity passed through the electrolyte and the amount of material liberated on the electrodes. The results of his experiments were expressed in the form of two laws. These are known as Faraday's Law of electrolysis

First Law of Electrolysis: *The amount of substance dissolved from or liberated at an electrode is proportional to the quantity of electricity passed through the electrolyte solution.*

The unit of the quantity of electricity is *Coulomb*. One Coulomb is the quantity of electricity when one ampere current flows through a conductor for one second. One coulomb is given the symbol *C*.

If *I* ampere current flows for *t* seconds then the quantity of electricity passed is

$$Q = I \times t \text{ coulombs} \quad (14.2)$$

Now if *m* is the mass in gram of substance liberated at an electrode by passing *Q* coulomb of electricity, according to Faraday's first law

$$m \propto I \times t$$

where *I* is the current in Ampere (A) and *t* is the time (in second) during which current was passed.

$$\text{Or} \quad m = z \times I \times t \quad (14.3)$$

where *z* is a constant of proportionality, and is known as the *electrochemical equivalent* of the substance. If *I* = 1 A and *t* = 1 second then, *m* = *z*. Thus,

The electrochemical equivalent is the amount of substance liberated when 1 A current is passed through the electrolyte for 1 second or when one Coulomb of electricity is passed.

Second Law of Electrolysis: *When the same quantity of electricity is passed through different electrolyte solutions of different substances, 'equivalent masses' of the elements are liberated at the electrodes.*

The meaning of the term 'equivalent masses' as used by Faraday needs explanation in the context of present ideas and is described in Section 14.6.

These laws have been found to hold under all conditions, provided the current is carried entirely by the ions.

14.5.1 Verification of the First Law of Faraday

Faraday's first law may be verified by measuring the quantity of electricity flowing through an electrical circuit. The apparatus used for the purpose is known as a *voltameter*, or better a *coulometer* (Figure 14.1) because the same apparatus can be used to measure the quantity of electricity passed. In this apparatus the amount of a metal deposited on a clean electrode by passing a known current for a definite time through a solution of a salt of the metal is determined. If AgNO_3 solution is used as the electrolyte metallic Ag will be deposited on the cathode, generally a platinum basin containing the silver nitrate solution. The deposit is washed with water, dried and weighed. The mass of the metal deposited can be accurately determined by weighing the electrode before and after

14.6 Faraday and Significance of the Faraday's Laws

Using the first law it was found that the quantity of electricity required to deposit one mole of silver, was 96,500 Coulombs. Now one ion of silver is deposited at the cathode as an atom of silver as follows:



That is to say that one electron deposits one atom of silver. To deposit one mole of silver one mole of electrons will be required. Hence *one mole of electrons carries 96,500 Coulombs of electricity*. In honour of Michael Faraday 96,500 Coulombs of electricity was named as one *Faraday* of electricity. So we write

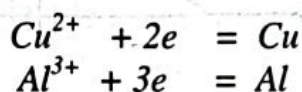
$$1 F = 96,500 \text{ Coulombs} = 96,500 C \quad (C \text{ stands for Coulomb})$$

and we say that to deposit one mole of silver $1F$ of electricity are required.

Now according to the First Law of Faraday $1F$ will deposit one mole of silver, $2 F$ will deposit 2 moles of Ag and $3 F$ will deposit 3 moles of silver.

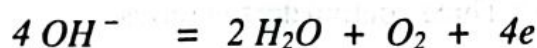
Since one mole of electrons carry 96,500 Coulombs of electricity the charge carried by one electron = $\frac{96,500}{6.02 \times 10^{23}} C = 1.60 \times 10^{-19} C$

Copper and aluminum are deposited as follows:



It follows that to deposit one mole of copper two moles of electrons are required, i.e. $2 F$ of electricity are required and to deposit one mole of aluminium $3 F$ are required. When 96,500 C or $1 F$ of electricity is passed through separate electrolytic cells containing Ag^+ , Cu^{2+} and Al^{3+} ions respectively the amount of metal deposited at the cathodes in the different cells were found to be Ag, 1 mol; Cu, $\frac{1}{2}$ mol; Al, $\frac{1}{3}$ mol, i.e. in each case the amount of metal deposited = $\frac{1.0 \text{ mol}}{\text{number of charges on the ion}}$. As mentioned earlier these amounts are what Faraday referred to as the *equivalent masses* of the metals in the second law.

We will see later that to discharge one mole of oxygen at the anode the reaction is



and $4F$ of electricity will be required.

The Second Law of Faraday may now be stated as follows:

The number of Faradays required to liberate one mole of a metal or discharge one mole of a gas is equal to the number of electrons showed in a balanced equation for the electrode reaction.

Example 14.1: 2.0 ampere current is passed through a Ag coulometer for 1 hour 10 minute. Calculate the mass of Ag deposited in the coulometer. (R.A.M. of Ag = 107.88)

Solution: Time = (60 + 10) × 60 seconds = 4200 seconds

Electricity passed = 2.0 × 4200 = 8400 C

$$= \frac{8400}{96500} F = 0.087 F$$

Ag is deposited as shown: $\text{Ag}^+ + e = \text{Ag}$

i.e. One F deposits one mole of Ag

Hence moles of Ag deposited = 0.087

Mass of Ag deposited = 0.087 × 107.88 g
= 9.39 g

Example 14.2: Calculate the time required to discharge 200 cm³ of oxygen (measured at r.t.p.) by electrolysing dilute sulphuric acid solution with a current of 4 A.

Solution: Oxygen is discharged as shown: $4 \text{OH}^- = 2\text{H}_2\text{O} + \text{O}_2 + 4e$

It shows that for the discharge of one mole oxygen 4 F of electricity will be required.

$$\text{Now } 200 \text{ cm}^3 = \frac{200}{24000} \text{ mol} = 0.008333 \text{ mol}$$

$$\text{Quantity of electricity required} = 0.008333 \times 4 F = 0.03333 F = 3217 C$$

$$\text{Hence the time required} = \frac{3217}{4} = 804 \text{ seconds}$$

14.7 The Conductance of Electrolytic Solutions

The power of conducting electricity by any conductor is described in terms of its conductivity or conductance. Conductance is reciprocal of resistance. If the electrical resistance of a conductor is measured the conductance may be calculated as

$$\text{Conductance} = \frac{1}{\text{Resistance}}$$

Resistance of an electrical conductor may be measured by using Ohm's law written as:

$$R = \frac{E}{I} \quad (14.4)$$

where R is the resistance measured in ohms (Ω), I is the current in ampere and E is the potential difference (volts) between the two ends. This law can be applied in case of solutions except at very high voltages or with very high frequency alternating current.

In order to be able to compare the resistances of different substances the term *specific resistance* has been introduced. The resistance, R , of a conductor is directly proportional to its length, l , and inversely proportional to its area of cross-section, a ; i.e.,

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

$$\text{Or} \quad R = \rho \times \frac{l}{a} \quad (14.5)$$

where ρ (rho) is a constant for the conducting material and is called its *specific resistance or resistivity*. When $l = 1$ cm and $a = 1$ sq cm, $R = \rho$. The specific resistance is then defined as follows:

The specific resistance of a substance is the resistance in ohms between the opposite faces of a cube of the material having an edge one centimeter long.

The unit of specific resistance can be found from equation (14.5)

$$\rho = \frac{R \times a}{l} = \frac{\text{ohm} \times \text{cm}^2}{\text{cm}} = \text{ohm} - \text{cm} \quad (\Omega - \text{cm})$$

The reciprocal of resistance is called *conductance*, Λ (lambda).

$$\Lambda = \frac{1}{R} = \frac{1}{\text{ohm}} = \text{ohm}^{-1} \quad (\Omega^{-1}) \quad (14.6)$$

The reciprocal of specific resistance is known as the *specific conductance*, κ (kappa). By definition

$$\text{specific conductance } (\kappa) = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a} \quad (14.7)$$

The unit of specific conductance can be derived as follows:

$$\text{specific conductance } (\kappa) = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a} = \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1} \text{cm}^{-1} \quad (14.7a)$$

The specific conductance of a solution is dependent on its concentration. In order to compare the conductance of different electrolytic solutions, molar conductance (Λ_m) is used. The molar conductance is defined as,

"The conductance of all the ions produced when 1 mole of an electrolyte is dissociated into its ions in a volume V mL."

This is obtained by multiplying *specific conductance* (κ) by the volume V in mL that contains 1 mole of the electrolyte. In other words,

$$\Lambda_m = \kappa \times V \quad (14.8)$$

where V is the volume of the solution in mL containing 1 mole of the electrolyte.

The unit of Λ_m may be derived as follows:

$$\begin{aligned}\Lambda_m &= \kappa \times V \\ &= \frac{1}{R} \times \frac{l}{a} \times V \\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{mol}}\end{aligned}\quad (14.9)$$

The unit of Λ_m is then

$$\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

Example 14.3: A metal rod of length 3.2 cm and area of cross-section 0.45 sq. cm offers a resistance of 1.8 ohms. Calculate its specific conductance.

Solution: Using equation (14.6) specific conductance $\kappa = \frac{1}{1.8} \times \frac{3.2}{0.45}$
 $= 8.0 \text{ ohm}^{-1} \text{cm}^{-1}$

Example 14.4: An electrolyte solution of concentration 0.1 mol L^{-1} has a specific conductance of $0.01289 \text{ ohm}^{-1} \text{cm}^{-1}$. Calculate its molar conductance.

Solution: The volume in mL (V) containing one mol of the electrolyte

$$= \frac{1000}{0.1} = 10000 \text{ mL}$$

$$\text{The molar conductance} = 0.01289 \times 10000 = 128.9 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

14.8 Experimental Determination of Conductance

The basic principle of the experimental determination of electrolytic conductance is that of the *Wheatstone's bridge*. A simplified circuit diagram of a conductance bridge is shown in Figure 14.3. This conductance bridge was originally devised by Kohlrausch, and is known as Kohlrausch's conductance bridge. For measuring conductance of solutions direct current cannot be used because electrolysis will take place and polarisation of the electrodes occurs; further complication will be caused by evolution of gases in many cases. Also secondary reactions at the electrodes will spoil the experiments. This difficulty has been eliminated by use of high frequency alternating current from a small induction coil called a 'buzzer' or better from an oscillator. The a-c source generates usually 1-3 kilo cycles/sec. Due to rapid change of polarity at the electrodes polarisation is reduced considerably and electrolysis is stopped. The galvanometer in the Wheatstone's bridge circuit is generally replaced by a small sensitive telephone.

14.11 Conductance and Electrolyte Concentration

It has been mentioned that the specific conductance of solutions depends on the concentration of the electrolyte. A look at Table 14.1 will reveal it clearly. As the current is carried by ions the specific conductance will depend on the actual number of ions per unit volume of the solution. Hence the specific conductance progressively decreases with increasing dilution (i.e. decreasing concentration). However, the molar conductance, Λ_m , increases with dilution and tends to attain a limiting constant value for strong electrolytes; but for weak electrolytes, like ethanoic acid, NH_4OH etc., the molar conductance rises rapidly at low concentrations. The behaviour of both strong and weak electrolytes are shown in Figure 14.6

The plots for Λ_m vs $\sqrt{\text{molarity}}$ for strong electrolytes like KCl , Na_2SO_4 , CH_3COONa follow almost a linear relation at low concentration and the straight lines can be extrapolated to zero concentration to give Λ_m^0 , the molar conductance at infinite dilution*. But the curve for ethanoic acid shows a rapid upward trend for \sqrt{c} values approximately below 0.05. Extrapolation of such a curve to zero concentration is neither feasible nor at all reliable.

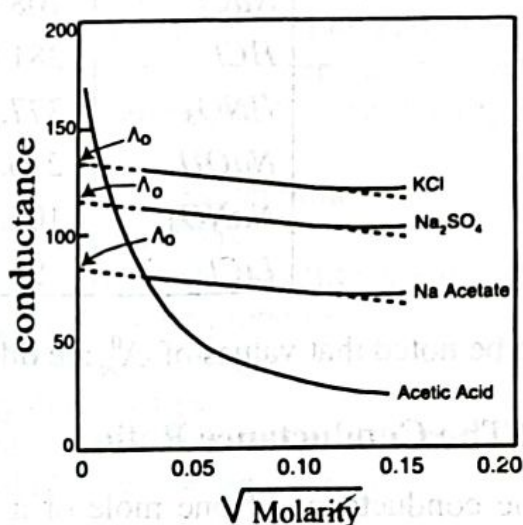


Figure 14.6 Molar conductance vs square root of concentration

Table 14.3 Molar conductance ($ohm^{-1} cm^2 mol^{-1}$) of different electrolytes in aqueous solutions at $25^\circ C$

C $mol L^{-1}$	$NaCl$	KCl	HCl	$AgNO_3$	HAc
0.0000	126.45	149.86	426.16	133.4	(390.7)
0.0005	124.50	147.81	422.74	131.4	67.7
0.001	123.74	146.95	421.36	130.5	49.2
0.01	118.51	141.27	412.00	124.8	16.3
0.10	106.74	128.96	391.32	109.1	5.2

* At very low concentrations the line shows an upward trend even in case of strong electrolytes like KCl , $NaCl$ etc.

Λ'_m = molar conductance of the electrolyte solution of concentration $C \text{ mol L}^{-1}$

Λ_m^0 = molar conductance of the electrolyte solution at infinite dilution

A and B = constant terms for a particular solvent at a given temperature

On increasing the dilution the average distance between ions increases and, therefore, the retarding force decreases, and there is an increase in Λ_m with increase in dilution. The above explanation, which is only a fragmentary reflection of a more detailed picture, leads to a relation between molar conductance and concentration of the same form as Kohlrausch's equation. Debye, Huckel and Onsager were able to calculate the constant A and B for many electrolytes in dilute solution. The calculated values were found to be in agreement with the values found from the slopes of the experimental data plotted as Λ_m vs \sqrt{C} .

The theory which explains many other facts, however, fails when applied to solutions of moderate or higher concentration, i.e., 0.1 to 1 mol L^{-1} and above. Although no satisfactory theoretical treatment for such solutions is still available, mention may be made of the concept of the formation of *ion-pairs* or *ion triplets*, primarily by Fuoss, Bjerrum and others. Because of the proximity of the ions at high concentrations there may be specific attraction between the oppositely charged ions, so that two oppositely charged ions in an ion-pair will virtually behave like an undissociated molecule so far as conductance is concerned. The ion-pairs cannot be regarded as molecules as these can exchange partners. The concept of ion-pair is of importance particularly in solutions of low dielectric constant.

14.14 Independent Migration of Ions: Kohlrausch's Law

Kohlrausch examined the values of Λ_m^0 of a number of strong electrolytes with common anions or cations and found some regularity in the Λ_m^0 values of various electrolytes. He observed that when the electrolytes were considered in pairs having one common ion the difference between the Λ_m^0 values were constant (Table 14.5).

Table 14.5 Differences in values of Λ_m^0 for several pairs of electrolytes with a common ion

Electrolyte	Λ_m^0 at 298 K $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Difference	Electrolyte	Λ_m^0 at 298 K $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Difference
<i>KBr</i>	151.92	23.41	<i>KBr</i>	151.92	2.06
<i>NaBr</i>	128.51		<i>KCl</i>	149.86	
<i>KCl</i>	149.86	23.41	<i>NaBr</i>	128.51	2.06
<i>NaCl</i>	126.45		<i>NaCl</i>	126.45	
<i>KNO₃</i>	144.96	23.41	<i>LiBr</i>	117.09	2.06
<i>NaNO₃</i>	121.55		<i>LiCl</i>	115.03	

These observations led Kohlrausch (1875) to state that *the molar conductance at infinite dilution is different for different electrolytes and is equal to the sum of the conductance of the constituent ions of the electrolytes*. This is known as the *Kohlrausch's law of independent ionic migration*. The law may be expressed in the form

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0 \quad (14.16)$$

where λ_+^0 and λ_-^0 are called the ion conductance of the cation and anion respectively. The above equation means that each ion of an electrolyte contributes independently to the value of Λ_m^0 at infinite dilution. For example, the molar conductance of KCl at infinite dilution is $149.86 \Omega^{-1} cm^2 mol^{-1}$. The ion conductances of K^+ and Cl^- are 73.50 and $76.30 \Omega^{-1} cm^2 mol^{-1}$. According to *Kohlrausch's law of independent ionic migration*,

$$\begin{aligned} \Lambda_{m(KCl)}^0 &= \lambda_{K^+}^0 + \lambda_{Cl^-}^0 \\ &= 73.50 + 76.30 \Omega^{-1} cm^2 mol^{-1} \\ &= 149.80 \Omega^{-1} cm^2 mol^{-1} \end{aligned}$$

This is in agreement with the value measured directly. The *Kohlrausch's law of independent ionic migration* is useful for calculation of Λ^0 for weak electrolytes for which Λ_m^0 cannot be ascertained from the plot of Λ_m vs \sqrt{C} as shown in Figure 14.6.

Table 14.6 Ion conductance at 25°C

Cation	λ_+^0 ($\Omega^{-1} cm^2 mol^{-1}$)	Anion	λ_-^0 ($\Omega^{-1} cm^2 mol^{-1}$)
H^+	350.0	OH^-	198.0
Li^+	38.7	Cl^-	76.3
Na^+	50.1	Br^-	78.4
K^+	73.5	I^-	76.8
Rb^+	77.8	NO_3^-	71.4
Cs^+	77.3	ClO_4^-	68.0
NH_4^+	73.4	SO_4^{2-}	160.0
Ag^+	61.9	CO_3^{2-}	140.0
Ba^{2+}	127.2	$C_2O_4^{2-}$	48.0
Fe^{3+}	204.0	CH_3COO^-	40.9

The computation is done by addition and subtraction of Λ_0 values for different strong electrolytes.

Example 14.6: The molar conductances at 25°C of HCl , $NaCl$ and CH_3COONa are 426.1, 126.4 and $91.00 \Omega^{-1} cm^2 mol^{-1}$ respectively at infinite dilution. Calculate the molar conductance of CH_3COOH at infinite dilution.

(d) Determination of solubility of sparingly soluble salts:

Conductance measurement can be used for measurements of solubility of slightly soluble substances like $BaSO_4$, $PbSO_4$, $AgCl$ etc. The method is based on the difference in the conductance of the ions of the salts. For the purpose a saturated solution of the salt is prepared in conductivity water and allowed to stand until almost all the insoluble fraction settles down. The clear solution from the top is taken and its conductance is measured in a conductance cell whose cell constant has been determined earlier. The cell is thoroughly washed and filled with the same conductivity water and the conductance of the water measured in the same cell. The observed conductance is then converted to specific conductance. The conductance of water is then subtracted from the conductance of the solution. The value so obtained is the conductance due to the salt. The molar conductance (Λ_m) of a saturated solution is given by equation (14.8)

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

where κ is the specific conductance and c is the concentration of the solution in mol L^{-1} . Since the salt is sparingly soluble, the solution is very dilute and Λ_m may be considered to be equal to Λ_m^0 i.e., the molar conductance at infinite dilution. The value of Λ_m^0 for $AgCl$ can be found by applying Kohlrausch's law of independent ionic migration. According to this law, $\Lambda_m^0(AgCl) = \lambda_{Ag^+}^0 + \lambda_{Cl^-}^0$. Substituting Λ_m^0 in above equation c can be calculated

provided κ is known. This will give the value of c in mol L^{-1} from which the solubility in g L^{-1} may be calculated.

Example 14.9: The specific conductance of a saturated solution of $BaSO_4$ at 25°C is $3.590 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and that of the conductivity water used is $0.618 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The limiting ion conductance at infinite dilution for Ba^{2+} and SO_4^{2-} ions are 127.2 and $160.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Calculate the solubility of $BaSO_4$ at this temperature (RFM of $BaSO_4 = 233$).

Solution: The specific conductance of the solute,

$$\kappa = 3.590 \times 10^{-6} - 0.618 \times 10^{-6} = 2.972 \times 10^{-6}$$

$$\begin{aligned} \text{Solubility in } \text{mol L}^{-1} \quad c &= \frac{1000 \kappa}{\Lambda_m^0} = \frac{1000 \kappa}{\lambda_{Ba^{2+}}^0 + \lambda_{SO_4^{2-}}^0} \\ &= \frac{1000 \times 2.972 \times 10^{-6}}{287.2} = 1.035 \times 10^{-5} \end{aligned}$$

$$\text{Solubility in } \text{g L}^{-1} = 1.035 \times 10^{-5} \times (233) = 2.41 \times 10^{-3}$$

14.17 Transport Number (or Transference Number)

In an electrolytic solution the current is carried by both cations and anions. In a solution of an electrolyte where the number of ions is fixed or does not vary much, the conductance would be mainly governed by ionic velocities. If u_+ represents the ionic

velocity of the cation and u_- that of the anion then the current carried by the cation will be proportional to u_+ and the current carried by anion will be proportional to u_- . The total current carried through the solution will be proportional to $(u_+ + u_-)$.

The fraction of the current carried by each ionic species is called the transport number of that ion

The transport numbers of anions and cations are given by

$$t_- = \frac{A.u_-}{A.u_+ + A.u_-} = \frac{u_-}{u_+ + u_-} \quad (14.20)$$

and
$$t_+ = \frac{A.u_+}{A.u_- + A.u_+} = \frac{u_+}{u_- + u_+} \quad (14.21)$$

where t_+ and t_- are the transport number of cation and anion respectively and A is the proportionality constant. It is evident that $t_+ + t_- = 1$ since

$$\frac{u_+}{u_- + u_+} + \frac{u_-}{u_+ + u_-} = 1$$

So $t_+ = 1 - t_-$
and $t_- = 1 - t_+$

Due to the unequal velocities of the cation and the anion there will be a change in the concentration of the ion around the cathode and the anode. To explain this let us consider an arrangement of electrolysis as shown in Figure 14.13. The whole cell is divided into three imaginary compartments by the dotted lines aa and bb , the left is the anode compartment, the right one is the cathode compartment and between aa and bb is the middle compartment.

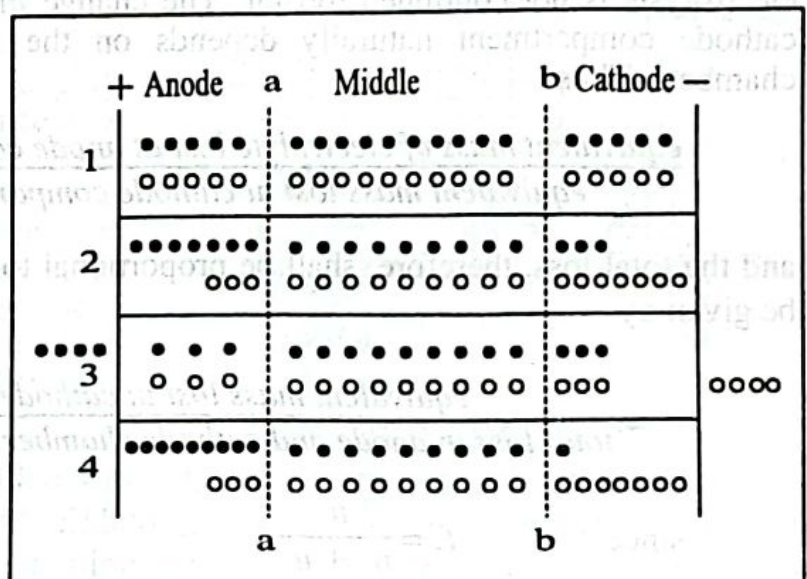


Figure 14.13 Mechanism of ionic transport

Let us assume that before electrolysis starts there are five anions (solid circles) and five cations (hollow circles) in each of the cathode and anode compartments and ten cations and ten anions in the middle compartment. The following cases may now be considered:

(I) *There is no electrolysis*

The number of anions and cations are the same in each compartment. This corresponds to the situation in line 1 in the diagram.

usually by titrating against standard NH_4SCN solution with ferric alum as indicator. Since the initial concentration of the $AgNO_3$ is known the fall in concentration in cathode and anode chambers are calculated.

Example 14.10: A dilute solution of $CuSO_4$ was electrolysed using two Pt electrodes. The amount of Cu per unit mass of the anodic solution was found to be 0.6350 and 0.6236 g after and before electrolysis respectively. The amount of Ag deposited in silver coulometer in the series was 0.1351 g. Calculate the transport numbers of Cu^{2+} and SO_4^{2-} ions. (RAM of $Cu = 63.5$ and $Ag = 107.88$)

Solution:

The mass of Cu^{2+} in anodic solution before electrolysis = 0.6350 g

And, the mass of Cu^{2+} in anodic solution after electrolysis = 0.6236 g

So, the loss in the mass of Cu in anodic solution = $(0.6350 - 0.6236) = 0.0114$ g

The mass of Ag deposited in the voltmeter = 0.1351 g

Now, this amount of Ag must be equivalent to $\frac{0.1351 \times (63.5/2)}{107.88} = 0.0397$ g of Cu deposited in voltmeter.

Therefore, the $t_{Cu^{2+}} = \frac{\text{Loss of } Cu \text{ at the anode}}{\text{Total loss of } Cu} = \frac{0.0114}{0.0397} = 0.287$

And $t_{SO_4^{2-}} = 1 - 0.287 = 0.713$

(b) **Moving boundary method:** From the very definition of transport numbers as shown in equations (14.20) and (14.21), it can be seen that transport number may be directly calculated if cationic and anionic velocities or any parameter proportional to the ionic velocities can be determined. The moving boundary method utilizes this principle. The arrangement is shown in Figure 14.15. The solution of an electrolyte MA , which is to be studied, is placed between the solutions of two other salts MA' and $M'A$ such that $M'A$ has the anion A common with MA and MA' and MA have the common cation M . The salts are to be so chosen that the densities increase downwards. Also, the speed of the ion M' should be less than that of M while the speed of A' should be less than that of A ion.



Figure 14.15 Moving boundary method

This is essential to maintain sharp boundaries between the three solutions of electrolytes. The initial sharp boundary between the solutions of $M'A$ and MA is shown by the

horizontal line P whereas the initial sharp boundary between MA' and MA is shown by R . In passing current from the source B ionic migration starts and the boundary P moves downwards, say to P' , while the boundary R moves to R' . The distance travelled by the two boundaries in time t are PP' and RR' , which are directly proportional to the cationic and anionic velocities respectively. Therefore,

$$t_+ = \frac{u_+}{u_- + u_+} = \frac{PP'}{PP' + RR'} \quad (14.23)$$

$$t_- = \frac{u_-}{u_+ + u_-} = \frac{RR'}{PP' + RR'} \quad (14.24)$$

The transport numbers are thus measured. It should be noted that electrolytes MA , MA' and $M'A$ should be carefully chosen to get good results. In practice it is necessary to form one boundary and observe the rate of its movement to measure the transference number of one ion; that of the other ion may then be calculated as $t_+ + t_- = 1$.

Under this condition the transference number is calculated as follows: Suppose that the boundary of the moving cation is swept through a distance l in a tube of cross section a , so that the volume swept out by the passage of Q coulombs of electricity is $l \times a$. If 1F of electricity flows through the solution t_+ equivalent mass of cation must pass through any given point. Let c , be the concentration of the solution in equivalent mass L^{-1} ; then the volume of solution containing 1 equivalent mass of electrolyte is $1000/c$. Hence during the passage of 1 F of electricity the cation boundary will sweep through a volume $\frac{1000}{c}$. For the passage of Q coulombs, therefore, the same boundary will sweep out a volume of

$$\text{Hence } l \times a = \frac{1000 \times t_+ \times Q}{c \times F}$$

$$\text{or, } t_+ = \frac{l \times a \times c \times F}{1000 Q}$$

Example 14.11: A moving boundary experiment was carried out with $0.100 \text{ mol L}^{-1} \text{ HCl}$ solution with CdCl_2 as the indicator electrolyte. The boundary moved through a distance of 6.50 cm in a tube of cross section 0.11 cm^2 . If a constant current of 0.0056 A was passed for 2100 seconds, calculate the transport numbers of H^+ and Cl^- ions.

Solution: Here $a = 0.11 \text{ cm}^2$, $l = 6.50 \text{ cm}$, $c = 0.100 \text{ mol L}^{-1}$

$$\text{Or, } t_{\text{H}^+} = \frac{l \times a \times c \times F}{1000 Q} = \frac{0.11 \times 6.5 \times 0.1 \times 96500}{1000 \times 0.0056 \times 2100} = 0.5867$$

$$t_{\text{Cl}^-} = 1 - 0.5867 = 0.4133$$