25

CHAPTER

Theory of Electrolytic Dissociation

ARRHENIUS THEORY OF IONISATION

Savante Arrhenius studied the conduction of current through water solutions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions. In 1884, Arrhenius put forward his theory of ionisation. **Arrhenius theory of ionisation** may be stated as :

(1) When dissolved in water, **neutral electrolyte molecules are split up into two types of charged particles.** These particles were called ions and the process was termed **ionisation.** The positively charged particles were called **cations** and those having negative charge were called **anions.**

In its modern form, the theory assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic force. When placed in water, these neutral molecules *dissociate* to form separate anions and cations. Thus,

$$AB \longrightarrow A^+ + B^- \qquad \qquad (\textit{Old view})$$
$$A^+ B^- \longrightarrow A^+ + B^- \qquad \qquad (\textit{Modern view})$$

For that reason, this theory may be referred to as the theory of electrolytic dissociations.

(2) The **ions present in solution constantly reunite to form neutral molecules.** Thus there is a state of equilibrium between the undissociated molecules and the ions.

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

Applying the Law of Mass Action to the ionic equilibrium we have,

$$\frac{[A^+] [B^-]}{[AB]} = K$$

where K is called the **Dissociation constant.**

(3) The **charged ions are free to move through the solution to the oppositely charged electrode.** This movement of the ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

(4) The **electrical conductivity of an electrolyte solution depends on the number of ions present in solution.** Thus the degree of dissociation of an electrolyte determines whether it is a strong electrolyte or a weak electrolyte.

MIGRATION OF IONS

We know that electrolytes dissociate in solution to form positive ions (cations) and negative ions (anions).

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$
$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$
$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$
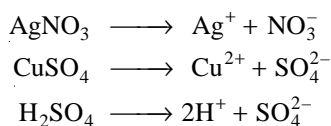
As the current is passed between the electrodes of the electrolytic cell, the ions migrate to the opposite electrodes. Thus in the electrolytic solution of $AgNO_3$, the cations (Ag^+) will move to the cathode and anions (NO_3^-) will move to the anode. Usually different ions move with different rates. The migration of ions through the electrolytic solution can be demonstrated by the following experiments.
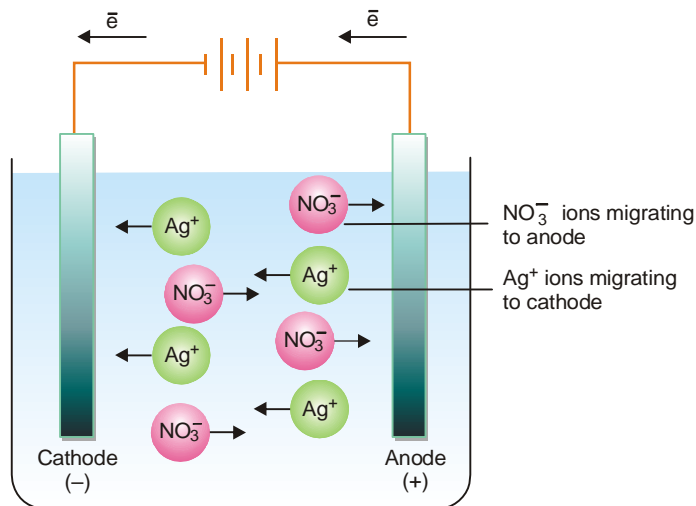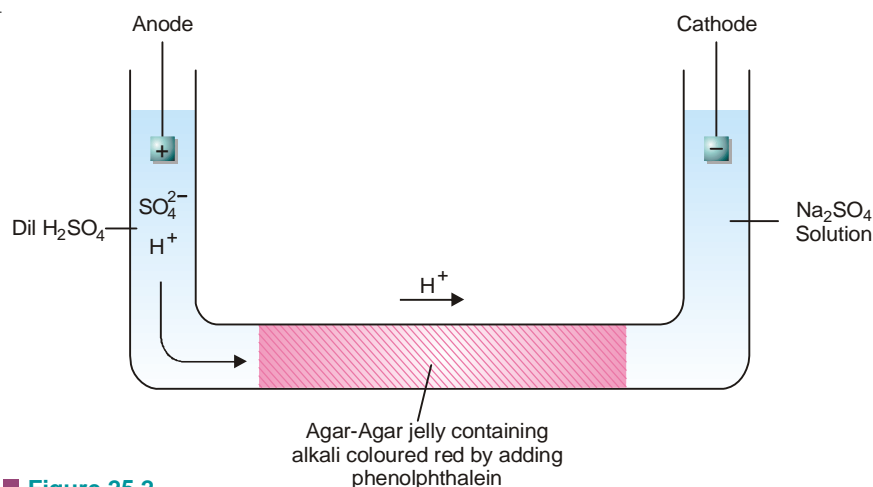

■ Figure 25.1
Migration of ions through electrolytic solution to opposite electrodes.

**(1) Lodge's moving boundary experiment**

The apparatus used consists of a U-tube which has a long horizontal portion. It is fitted with

electrodes in the side limbs. The horizontal portion is filled with a jelly of agar-agar treated with a trace of alkali. This is then made red by addition of a few drops of phenolphthalein. When the jelly is set, dilute sulphuric acid is added in the anodic limb of the tube. Sodium sulphate solution is added in the cathodic limb. On passing the current, H^+ ions in the left limb solution eventually move into the agar-agar jelly. Their passage is marked by the gradual discharge of the red colour due to the neutralisation of the alkali by H^+ ions. The movement of the red boundary through the agar-agar jelly shows that H^+ ions migrate to the cathode limb.

Figure 25.2
Experiment showing the migration of H^+ ions as indicated by the movement of the red boundary through the agar-agar jelly.
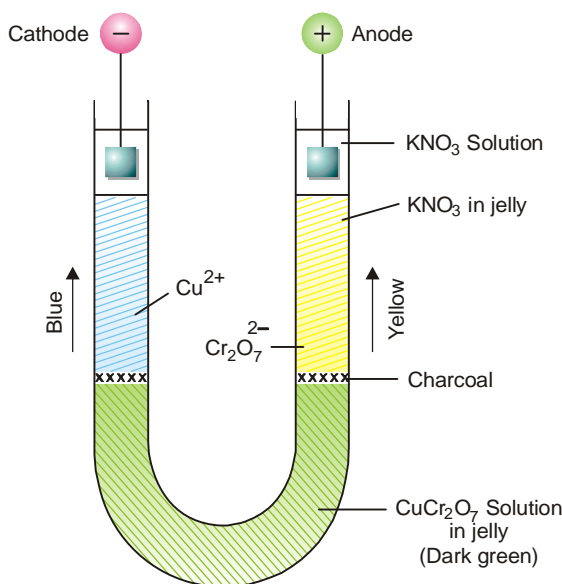
Figure 25.3
Apparatus for demonstrating the migration Cu^{2+} and $Cr_2O_7^{2-}$ ions.

(2) Movement of coloured ions

The lower part of a U-tube is filled with a 5 percent water-solution of agar-agar with a small amount of copper dichromate ($CuSO_4 + K_2Cr_2O_7$). The dark green colour sets to a jelly. The surface

of the green solution in the two limbs of the U-tube is marked by a small amount of charcoal. In both the limbs is then placed a layer of solution of potassium nitrate and agar-agar. This is also allowed to set. Over this second layer is placed some solution of pot. nitrate in pure water and the two electrodes are inserted in it. As the current is turned on, the blue colour of Cu^{2+} ions rises into the jelly under the cathode. The reddish yellow dichromate ions ($Cr_2 O_7^{2-}$) move up under the anode. After some time the two types of ions are seen rising with well-defined boundaries. The use of jelly in this experiment prevents the mixing of the solutions by diffusion.

RELATIVE SPEED OF IONS

We have already considered that ions move to the oppositely charged electrodes under the influence of the electric current. But the speeds of cations migrating towards the cathode and those of anions migrating towards the anode are not necessarily the same. However, the speed of a cation moving away from the anode will be proportional to the fall of concentration of these ions at the anode. Similarly, the speed of an anion moving away from the cathode will be proportional to the fall of concentration of anions around the cathode. Hittorf studied such changes experimentally and gave a general rule known as the **Hittorf's Rule**. It states that : **the loss of concentration around any electrode is proportional to the speed of the ion moving away from it.** Hittorf's Rule may be illustrated by the following scheme.

In Fig. 25.4, A is anode and C is cathode. AA′ and BB′ are two imaginary planes which divide the cell into three compartments, **the anode compartment, the middle compartment and the cathode compartment.** The sign (+) represents a cation while the sign (–) represents an anion.
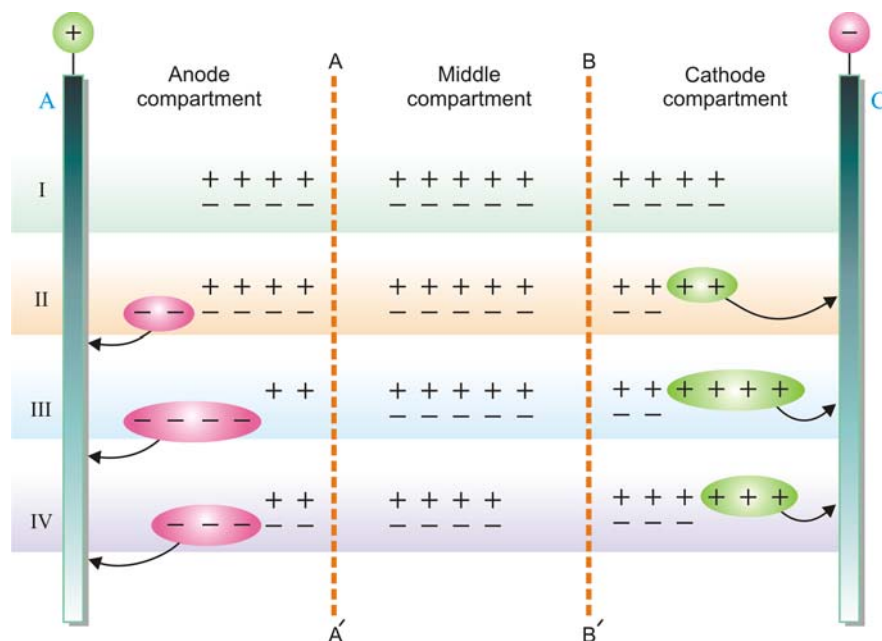
■ **Figure 25.4**
Scheme showing that the loss of concentration around any electrode is proportional to the speed of the ion moving away from it.

Before electrolysis, let there be 13 ion-pairs in the cell. The number of ion-pairs in the two outer compartments is 4 each and there are 5 ion-pairs in the middle compartment (Position I). Now let us consider the following cases:

(*i*) Let the anions alone be capable of movement

When, say, two anions have moved towards the anode, we get the position as shown in II. The cations have not moved at all. But inspite of that the number of discharged anions and cations is the same *viz.*, 2. *The concentration in the anode compartment*, *however*, *has not altered while in the cathode compartment it has fallen by two ion-pairs.*

(*ii*) Let the anions and cations move at the same rate

When two ions of each type have crossed over towards the opposite electrodes, we get the condition as shown in III. The number of discharged anions and cations is the same *viz.*, 4. *The concentration of both the anode compartment and the cathode compartment has fallen to the same extent viz, by two ion-pairs.*

(*iii*) Let the cations move at twice the speed of the anions

In this case, when cations have moved to the cathode compartment, one anion passes into the anode compartment. The state of affairs is shown in IV. The total number of discharged anions and cations is again the same *viz.*, 3. Although the concentration in the cathode compartment has fallen by one ion-pair, the concentration in the anode compartment decreases by two ion-pairs.

It is evident from the above considerations that ions are always discharged in equivalent amounts on the opposite electrodes. It is really due to the difference in the speeds of anions and cations that the changes in concentration around electrodes are caused. We also conclude that the **loss in concentration around any electrode is proportional to the speed of the ion moving away from it.**

This is **Hittorf's Rule**. We can write the expression :

$$\frac{\text{Fall around anode}}{\text{Fall around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{v_+}{v_-}$$

where v_+ and v_- is the speed of cations and anions respectively.

In deriving the above relation, an important assumption has been made, namely, the discharged ions do not react with the material of the electrodes. However, in many cases they combine with the material of the electrodes rather than depositing on it. This results in an increase in concentration around such an electrode instead of a decrease.

Migration Speed of Ag^+ and NO_3^- ions

Let us study the electrolysis of a solution of silver nitrate in a cell of the type described above but using silver electrodes. We find that instead of a fall in concentration of silver nitrate around the anode, it increases. This is due to the fact that every NO_3^- ion that arrives at the anode dissolves from it one Ag^+ ion to form $AgNO_3$. If the electrodes were of platinum, the state of affairs would be as shown in Fig. 25.4 III when ions moved at the same rate. That is, there should have taken place a fall in concentration by 2 ion-pairs in each compartment. With silver electrodes, however, we have the condition shown in Fig. 25.5.
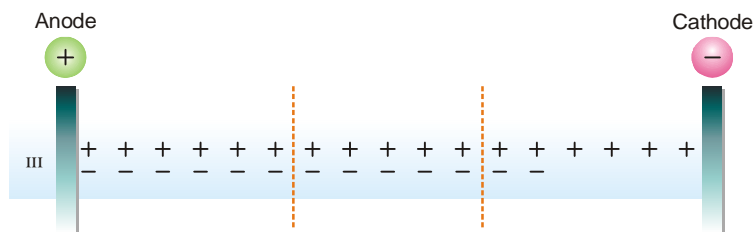
■ Figure 25.5
With silver electrodes, concentration around the cathode falls while it increases around the anode.

It is clear that the concentration around the cathode has fallen from 4 to 2 ion-pairs but around the anode it has increased from 4 to 6 ion-pairs. It is very easy to calculate the speed ratio of ions in this case as well by putting a silver coulometer in the circuit. This would give us the total current passed or increase in concentration around the anode as if no silver ions had migrated towards the cathode. The difference of the total increase and the actual increase around the anode would give the fall in concentration around the anode due to the migration of silver ions.

SOLVED PROBLEM. In an experiment, the increase in concentration of $AgNO_3$ around the silver anode was 5.6 mg of silver. 10.73 mg of silver were deposited by the same current in the silver coulometer placed in series. Find the speed ratio of Ag^+ and NO_3^- ions.

SOLUTION

Fall of concentration around cathode (= rise of concentration around anode) = 5.6 mg

If no Ag^+ ions had migrated from the anode, the increase in concentration around the anode would have been 10.73 mg silver. But the actual increase is 5.6 mg.

∴Fall around the anode due to migration of $Ag^+ = (10.73 - 5.6) = 5.13$

$$\frac{\text{Speed of Ag}^+}{\text{Speed of NO}_3^-} = \frac{\text{Fall around anode}}{\text{Fall around cathode}} = \frac{5.13}{5.6} = \textbf{0.916}$$

WHAT IS TRANSPORT NUMBER ?

During electrolysis the current is carried by the anions and the cations. **The fraction of the total current carried by the cation or the anion is termed its Transport number or Hittorf's number.** If v_+ represents the speed of migration of the cation and v_- that of the anion,

$$\text{the transport number of cation} = \frac{v_+}{v_+ + v_-}$$

$$\text{the transport number of anion} = \frac{v_-}{v_+ + v_-}$$

The transport number of the cation is represented by t_+ and that of the anion by t_-.

Thus $$t_+ = \frac{v_+}{v_+ + v_-} \quad \text{and} \quad t_- = \frac{v_-}{v_+ + v_-}$$

or $$\frac{t_+}{t_-} = \frac{v_+}{v_-} \quad \text{and} \quad t_+ + t_- = 1$$

If the speed ratio v_+/v_- be denoted by r, we have,

$$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$$

and $$t_- = \frac{1}{1 + r}$$

SOLVED PROBLEM. The speed ratio of silver and nitrate ions in a solution of silver nitrate electrolysed between silver electrodes is 0.916. Find the transport number of the two ion.

SOLUTION

We know that $$t_- = \frac{1}{1 + r}$$

where t_- is the transport number of the anion and r is the speed ratio of the anion and the cation.

$$\therefore \qquad t_{NO_3^-} = \frac{1}{1 + 0.916} = 0.521$$

and
$$t_{Ag^+} = 1 - t_{NO_3^-} = 1 - 0.521 = \mathbf{0.479}$$

DETERMINATION OF TRANSPORT NUMBER

There are two methods for determination of the transport number of an ion :

(1) Hittorf's method

(2) Moving Boundary method

Hittorf's Method

This method of determining transport number is based on **Hittorf's Rule.** According to this rule, **the loss of concentration around any electrode is proportional to the speed of the ion moving away from that electrode.** The transport number of an ion is calculated from the changes in concentration found experimentally around the electrodes. The apparatus used in this method consists of two vertical glass tubes joined together through a U-tube in the middle. All the three tubes are provided with stopcocks at the bottom. The U-tube is also provided with stopcocks at the tops of the two limbs. By closing these stopcocks, the communication between the solutions in the cathode and anode limbs can be stopped. The silver anode is sealed in a glass-tube and the cathode is a piece of freshly silvered foil. The apparatus is filled with a solution of silver nitrate and a steady current of about 0.01 ampere is passed for two to three hours. It is an **important precaution** that the current is passed only for a short time so that too large a change in concentrating does not take place. The apparatus is connected with a silver or copper coulometer as shown in Fig. 25.6, which shows the circuit for the experiment.
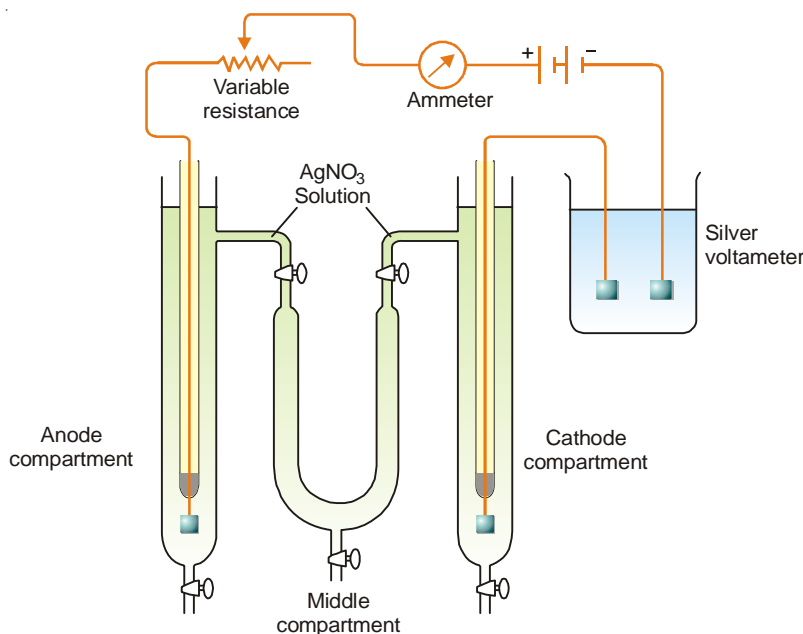
■ **Figure 25.6**
Hittorf's apparatus for determining Transport numbers.

When the current has been passed for about three hours, the stopcocks at the top of the U-tube are closed. The whole of the liquid in the anode compartment is carefully drained into a weighed flask

and its weight determined. Its silver content is determined by titrating against a standard solution of potassium thiocyanate. The weight of silver deposited in the silver coulometer is also noted. If a copper coulometer is used in place of silver coulometer, the weight of silver equivalent to the copper deposited is calculated by multiplying it with 108/31.5. There should be no change in the concentration of the solution in the U-tube if the experiment has been successfully performed.

If the above experiment has been performed by using silver electrodes, in this case nitrate ions attack the silver anode. Consequently, there is an increase in concentration of Ag^+ ions rather than decrease. The same experiment can also be performed by using platinum electrodes to avoid the attack of anions on the anode.

Calculations :

Two different cases may arise :

Case 1. When electrodes are unattackable (Pt electrodes are used).

After passing electric current :

Let the weight of anodic solution taken out $= a\ g$

weight of $AgNO_3$ present in it by titration $= b\ g$

weight of water $= (a - b)\ g$

Before passing electric current :

Let weight of $AgNO_3$ in $(a - b)\ g$ of water before passing electric current be $= c\ g$

∴Fall in concentration

$$= (c - b)\ g \text{ of } AgNO_3 = \frac{(c - b)}{170}\ g \text{ eqvt of } AgNO_3$$

$$= \frac{(c - b)}{170}\ g \text{ eqvt of } Ag = d \text{ (say)}$$

Let the weight of silver deposited in silver coulometer be

$$= w_1 g$$

$$= \frac{w_1}{108}\ g \text{ eqvt of } Ag$$

$$= W \text{ (say) } g \text{ eqvt of } Ag$$

Transport number of $Ag^+ \left(t_{Ag^+} \right) = \dfrac{\text{Fall in concentration around anode in g eqvt}}{\text{Amt. of Ag deposited in g eqvt}} = \dfrac{d}{W}$

and Transport number of NO_3^- ion $\left(t_{NO_3^-} \right) = 1 - \dfrac{d}{W}$

Case 2. When electrodes are attackable (Ag electrodes are used).

Increase in conc. of anodic solution $= (b - c)$ g of $AgNO_3$

$$= \frac{(b - c)}{170} \times 108\ g \text{ of } Ag$$

$$= \frac{(b - c)}{170}\ g \text{ eqvt of } Ag$$

$$= e \text{ (say)}$$

If no Ag^+ ions had migrated from the anode, the increase in concentration of Ag^+ ions would have been equal to W.

∴Fall in concentration due to migration of Ag^+ ion $= W - e$

Hence, transport number of Ag^+ ion $\left(t_{Ag^+} \right) = \dfrac{W - e}{W}$

and transport number of NO_3^- ion $\left(t_{NO_3^-}\right) = 1 - \dfrac{W - e}{W}$

SOLVED PROBLEM 1. A solution of silver nitrate containing 12.14 g of silver in 50 ml of solution was electrolysed between platinum electrodes. After electrolysis, 50 ml of the anode solution was found to contain 11.55 g of silver, while 1.25 g of metallic silver was deposited on the cathode. Calculate the transport number of Ag^+ and NO_3^- ions.

SOLUTION

Weight of Ag in 50 ml of the solution before electrolysis $= 12.14$ g
Weight of Ag in 50 ml of the solution after electrolysis $= 11.55$ g
∴ Fall in concentration of Ag $= 12.14 - 11.55$
$\qquad\qquad = 0.59$ g
$\qquad\qquad = 0.0055$ g eq

Weight of Ag deposited in silver coulometer $= 1.25$ g

$$= \frac{1.25}{108} \ g \ eq$$
$$= 0.0116$$

Hence, transport number of $Ag^+ \left(t_{Ag^+}\right) = \dfrac{\text{Fall in conc. around anode}}{\text{No. of g eqvt deposited in silver coulometer}}$

$$= \frac{0.0055}{0.0116}$$
$$= 0.474$$

and $\qquad$ Transport number of NO_3^- ion $(t_{NO_3^-}) = 1 - 0.474$
$$= \mathbf{0.526}$$

SOLVED PROBLEM 2. In an electrolysis of copper sulphate between copper electrodes the total mass of copper deposited at the cathode was 0.153 g and the masses of copper per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 g respectively. Calculate the transport number of the Cu^{2+} and SO_4^{2-} ions.

SOLUTION

Wt. of copper in the anode liquid before electrolysis $= 0.79$ g
Wt. of copper in the anode liquid after electrolysis $= 0.91$ g
$\qquad\qquad$ Increase in weight $= 0.91 - 0.79$
$\qquad\qquad\qquad = 0.12$ g

Increase in weight of copper cathode in the coulometer $= 0.153$ g

This means that if no copper had migrated from the anode, increase in weight would have been 0.153 g.

$\qquad\qquad$ But actual increase $= 0.12$
$\qquad$ Fall in concentration due to migration of Cu^{2+} ions $= 0.153 - 0.12$
$\qquad\qquad\qquad = 0.033$

∴ $\qquad\qquad$ Transport number of Cu^{2+} ion $= \dfrac{0.033}{0.153}$
$\qquad\qquad\qquad = 0.215$

and Transport number of SO_4^{2-} ion $= (1 - 0.215)$
$\qquad\qquad\qquad = \mathbf{0.785}$
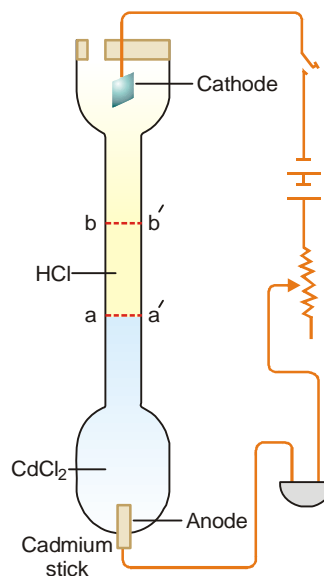
Moving Boundary Method

The moving boundary method is based on the direct observation of migration of ions under the influence of applied potential. This method is very accurate and has been used in recent years for precision measurements.

The apparatus used consists of a long vertical tube fitted with two electrodes at the two ends (Fig. 25.7). The tube is filled with a solution of cadmium chloride ($CdCl_2$) at the lower end and hydrochloric acid at the upper end in a way that there is a sharp boundary between the two (due to difference in their refractive indices).

The platinum cathode dipped in HCl solution is inserted at the top and the anode (cadmium stick) is introduced at the bottom.

On passing electric current through the apparatus, hydrogen gas is evolved at the cathode and H^+ ions move toward the anode. The H^+ ions are replaced by Cd^{2+} ions and hence the boundary line moves in the upward direction. By noting the length through which the boundary moves and the quantity of electricity passed through the cell, the transport number of H^+ ion can be calculated.

Figure 25.7
Determination of transport number by moving boundary method.

In general, if the transport number of a cation A^+ is to be determined, the electrolyte AX solution is taken in the upper part of the apparatus and a layer of another electrolyte *BX* having the common ion X^- is introduced in the lower part of the apparatus. The electrolyte *BX* is selected so that the velocity of B^+ ion is less than that of A^+ ion. In such a case, the situation is described in Fig. 25.8.

Figure 25.8
Moving boundary experiment for determining the transport number of A^+ ion.

Calculations :

Let c be the original concentration of A^+ ions in gram-equivalents per ml of the solution.

If the distance through which boundary moves $= l$ cm, and the area of cross-section of the tube $= s$ sq cm.

$$\text{Then the number of equivalents of } A^+ \text{ moving upward } = s \times l \times c$$

$$\text{Let the number of Faradays of current passed } = n$$

$$\text{The fraction of current carried by } A^+ \text{ ions } = n \times t_{A^+}$$

Hence $\qquad n \times t_{A^+} = s \times l \times c$

and $\qquad\qquad t_{A^+} = \dfrac{s \times l \times c}{n}$ ... (1)

where $n = Q/F$. Q being the quantity of current passed and F stands for Faraday ($= 96,500$ coulombs).

The above expression can now be written as

$$t_{A^+} = \frac{s \times l \times F \times c}{Q} \qquad\qquad ...(2)$$

With the help of the expressions (1) and (2), the value of t_{A^+} (transport number of A^+), can be found from the experimental values of s, l, c and n.

SOLVED PROBLEM 1. In a moving boundary experiment with 0.100 N KCl using 0.065 N LiCl as indicator solution, a constant current of 0.005893 amp was passed for 2130 seconds. The boundary was observed to move through 5.6 cm in a tube of 0.1142 sq cm cross-section. Calculate the transport number of K^+ and Cl^- ions.

SOLUTION

Here, $\qquad\qquad s = 0.1142$ sq cm $\qquad l = 5.6$ cm

$\qquad\qquad\qquad\quad Q = 0.005893 \times 2130$ coulombs

$\qquad\qquad\qquad\quad c = 0.1/1000$ g eqvt ml^{-1}

$\qquad\qquad\qquad\quad F = 96,500$ coulombs

Applying

$$t_k = \frac{s \times l \times F \times c}{Q}$$

$$= \frac{0.1142 \times 5.6 \times 96500 \times 0.1}{1000 \times 0.005893 \times 2130}$$

$$= 0.492$$

and $\qquad\qquad t_{cl^-} = 1 - t_{k^+} = 1 - 0.492 = \mathbf{0.508}$

SOLVED PROBLEM 2. Calculate the transport number of H^+ ion from the following data obtained by moving boundary method :

Concentration of HCl solution	$= 0.10$ N
Weight of silver deposited in the coulometer	$= 0.12$ g
Distance moved by the boundary	$= 7.5$ cm
Cross-section of the tube	$= 1.25$ sq cm
Equivalent weight of silver	$= 108$

SOLUTION

Here, $\qquad\qquad s = 1.25$ sq cm $\quad l = 7.5$ cm

$\qquad\qquad\qquad c = 0.1$ g eqvt/litre

$$= 0.1/1000 \text{ g eqvt/ml}$$

We know   108 g silver $= 1$ Faraday

$$0.12 \text{ g silver} = \frac{0.12}{108} = 0.00111$$

Applying $t_{H^+} = \dfrac{s \times l \times c}{n}$

We have $t_{H^+} = \dfrac{1.25 \times 7.5 \times 0.1}{1000 \times 0.0011}$

$$= 0.852$$

∴The transport number of H$^+$ is **0.852.**

KOHLRAUSCH'S LAW

From a study of the equivalent conductances of different electrolytes at infinite dilution (λ_∞), Kohlrausch discovered that each ion contributes to the conductance of the solution. In 1875, he enunciated a generalisation which is called the **Kohlrausch's Law.** It states that : **the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.**

The law may be expressed mathematically as :

$$\lambda_\infty = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cation.

For example, the equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45. The equivalent conductance of Na$^+$ and Cl$^-$ ion is 50.11 ohm^{-1} and 76.34 ohm^{-1} respectively. Thus,

$$\lambda_\infty(\text{NaCl}) = \lambda_{Cl^-} + \lambda_{Na^+}$$

or $126.45 = 50.11 + 76.34$

This is in conformity with the Kohlrausch's Law.

Applications of Kohlrausch's Law

Each ion has the same constant ionic conductance at a fixed temperature, no matter of which electrolyte it forms a part. It is expressed in ohm^{-1} cm^2 and is directly proportional to the speeds of the ions.

$$\lambda_a \propto v_- \quad \text{or} \quad \lambda_a = k \times v_-$$
$$\lambda_c \propto v_+ \quad \text{or} \quad \lambda_c = k \times v_+$$

where k is the proportionality constant.

Also $\lambda_\infty \propto (\lambda_a + \lambda_c) = k\,(v_- + v_+)$

∴ $\dfrac{\lambda_a}{\lambda_\infty} = \dfrac{kv_-}{k(v_- + v_+)} = \dfrac{v_-}{v_- + v_+} = t_-$ ...(1)

and $\dfrac{\lambda_c}{\lambda_\infty} = \dfrac{kv_+}{k(v_- + v_+)} = \dfrac{v_+}{v_- + v_+} = t_+ = 1 - t_-$ ...(2)

Dividing (1) by (2), we have

$$\frac{\lambda_a}{\lambda_c} = \frac{t_-}{1 - t_-}$$ ...(3)

With the help of the expression (3), we can determine ionic conductances from the experimental values of the transport number of the ions.

(1) Calculation of λ_∞ for Weak electrolytes

Weak electrolytes do not ionise to a sufficient extent in solution and are far from being completely ionised even at very great dilution. The practical determination of λ_∞ in such cases is, therefore, not possible. However, it can be calculated with the help of Kohlrausch's law.

$$\frac{\lambda_a}{\lambda_c} = \frac{t_-}{1 - t_-}$$

$$\lambda_a - t_- \lambda_a = t_- \lambda_c$$

$$\lambda_a = t_- (\lambda_a + \lambda_c)$$

$$= t_- \lambda_\infty$$

Thus the ionic conductance of an ion is obtained by multiplying the equivalent conductance at infinite dilution of any strong electrolyte containing that ion by its transport number.

In this manner, the ionic mobilities of the two ions present in the weak electrolyte can be calculated. Thus we can get the equivalent conductance of the electrolyte at infinite dilution by adding up these two values.

SOLVED PROBLEM 1. At 25°C the transport number of H^+ ion in HCl and CH_3COO^- ion in CH_3COONa are 0.81 and 0.47 respectively. The equivalent conductances at infinite dilution of HCl and CH_3COONa are 426 ohm^{-1} cm^2 eqvt^{-1} and 91.0 ohm^{-1} cm eqvt^{-1} respectively. Calculate the equivalent conductance of acetic acid at infinite dilution.

SOLUTION

Conductance of H^+ ion $= \lambda_\infty(HCl) \times t_{H^+}$

$$= 426 \times 0.81 = 345.06$$

Conductance of CH_3COO^- ion $= \lambda_\infty(CH_3COOH) \times t_{CH_3COO^-}$

$$= 91 \times 0.47 = 42.77$$

$\therefore$ Conductance of acetic acid at infinite dilution $= \lambda_a + \lambda_c$

$$= 42.77 + 345.06$$

$$= \textbf{387.83 mhos}$$

SOLVED PROBLEM 2. Calculate the equivalent conductance at 20°C of NH_4OH at infinite dilution.
Given :

$$\lambda_\infty(NH_4Cl) = 130 \qquad \lambda_\infty(OH^-) = 174 \qquad \lambda_\infty(Cl^-) = 66$$

SOLUTION

Applying Kohlrausch's law,

$$\lambda_\infty(NH_4OH) = \lambda_\infty(NH_4Cl) + \lambda_\infty(OH^-) - \lambda_\infty(Cl^-)$$

$$= 130 + 174 - 66$$

$$= \textbf{238 ohm}^{-1} \textbf{ cm}^2 \textbf{ eqvt}^{-1}$$

(2) Calculation of Absolute Ionic mobilities

The absolute ionic mobility of an ion is defined as **the velocity of an ion in centimetres per second under a potential gradient of one volt per centimetre.** (Potential gradient = applied EMF/distance between (the electrodes). It is expressed in cm sec^{-1}.

For example, let the velocity of the ion at infinite dilution be U cm per second when the distance between the electrodes is 20 cm and the voltage 100 V. Then the potential difference is 100/20 *i.e.*, 5 volts per cm and the ionic mobility is U/5 cm sec^{-1}.

It has been found that the ionic conductance is directly proportional to the ionic mobility *i.e.*,

$$\lambda_a \propto U_a \quad \text{and} \quad \lambda_c \propto U_c$$

or

$$\lambda_a = k\,U_a \quad \text{and} \quad \lambda_c = k\,U_c$$

where k is the proportionality constant. Its value is equal to the charge on one gram-equivalent of the ion under the potential gradient of 1 volt per cm *i.e.*, $k = 96{,}500$ coulomb (1 Faraday). Therefore, the ionic mobility is obtained by dividing the ionic conductance by 96,500 coulombs.

$$U_{\neq} = \frac{\lambda_{\neq}}{96{,}500}$$

or

$$\lambda_{\neq} = F U_{\neq}$$

SOLVED PROBLEM. The molecular conductance at infinite dilution of KCl is 130.1. The Hittorf number, t_- for the chloride ion in very dilute solution is 0.505. Calculate the mobilities in cm sec^{-1} of potassium and chloride ions.

SOLUTION

Ionic conductance of Cl$^-$ ion, $\lambda_a = \lambda_\infty \times t_-$

∴Ionic mobility of Cl$^-$ ion, $U_a = \dfrac{130.1 \times 0.505}{96{,}500}$

$$= \textbf{0.000681 cm sec}^{-1}$$

Ionic conductance of K$^+$ ion, $\lambda_c = \lambda_\infty (1 - t_-)$

$$= 130.1 \times 0.495$$

∴Ionic mobility of K$^+$ ion, $U_c = \dfrac{130.1 \times 0.495}{96{,}500}$

$$= \textbf{0.000667 cm sec}^{-1}$$

(3) Calculation of the solubility of sparingly soluble salts

Substance like AgCl or PbSO$_4$ which are ordinarily called insoluble do possess a definite value of solubility in water. This can be determined from conductance measurements of their saturated solutions (*Chapter* 24). Since a very small amount of solute is present it must be completely dissociated into ions even in a saturated solution so that the equivalent conductance κV is equal to equivalent conductance at infinite dilution. This according to Kohlrausch's Law is the sum of the ionic mobilities.

i.e.,

$$\kappa V = \lambda_\infty = \lambda_a + \lambda_c$$

knowing κ and λ_∞, V can be found out which is the volume in ml containing 1 g-eqvt of the electrolyte.

SOLVED PROBLEM. The specific conductance of saturated solution of silver chloride at 18°C is 1.24×10^{-6} mhos after subtracting that of water. The mobilities of Ag$^+$ and Cl$^-$ ions at this temperature are 53.8 and 65.3 respectively. Calculate the solubility of silver chloride in grams per litre.

SOLUTION

Here $\kappa = 1.24 \times 10^{-6}$ mhos

and $\lambda_\infty = \lambda Ag + \lambda Cl = 53.8 + 65.3 = 119.1$

Now $\lambda_\infty = \kappa \times V$

or $119.1 = 1.24 \times 10^{-6} \times V$

∴ $V = \dfrac{119.1}{1.24 \times 10^{-6}}$ ml

$$i.e., \qquad \frac{119.1}{1.24 \times 10^{-6}} \text{ ml contains AgCl} = 1 \text{ g-eqvt} = 143.5$$

$$\therefore \qquad 1000 \text{ ml contain AgCl} = \frac{143.5 \times 1.24 \times 10^{-6}}{119.1} \times 1000$$

$$= \frac{143.5 \times 1.24}{119.1} \times 10^{-3}$$

$$= \mathbf{1.494 \times 10^{-3} \text{ g}}$$

(4) Calculation of the Degree of Dissociation or Conductance Ratio

The apparent degree of dissociation, α, of an electrolyte at the dilution V is given by $\alpha = \lambda_v / \lambda_\infty$ where λ_v is the equivalent conductance of the electrolyte at the dilution V and λ_∞ is its equivalent conductance at infinite dilution. This according to Kohlrausch's Law is the sum of λ_a and λ_c.

SOLVED PROBLEM 1. The conductance of silver ion at 18° is 55.7 and of the nitrate ion 60.8. If the specific conductance of $AgNO_3$ in a decinormal solution at 18° is 0.00947 mhos, what will be the percentage of dissociation of the salt at this concentration ?

SOLUTION

$$\text{Specific conductivity } (\kappa) \text{ in N/10 solution} = 0.00947 \text{ mhos}$$

$$\text{Volume containing 1 g equivalent} = 10,000 \text{ ml}$$

$$\therefore \qquad \text{Eqvt conductance at this dilution} = 0.00947 \times 10,000$$

$$= 94.7 \text{ mhos}$$

$$\text{Eqvt conductance at infinite dilution} = 55.7 + 60.8 = 116.5$$

$$\alpha = \frac{94.7}{116.5} = 0.8128$$

Hence the salt is **81.28%** dissociated.

SOLVED PROBLEM 2. The equivalent conductance at 18° of a normal solution of KCl is 98.2 and for infinite dilution at the same temperature 131. Calculate the degree of dissociation of KCl at this dilution.

SOLUTION

We know $$\frac{\lambda_v}{\lambda_\infty} = a$$

Here, $$\lambda_v = 98.2, \qquad \lambda_\infty = 131$$

$$\therefore \qquad \frac{\lambda_v}{\lambda_\infty} = \frac{98.2}{131} = 0.75$$

Hence the degree of dissociation of KCl in normal solution is **0.75**.

(5) Calculation of the Ionic product for Water

The observed specific conductance of the purest water at 25°C is 5.54×10^{-8} mhos. The conductance of one litre of water containing 1 gram eqvt of it would be :

$$\lambda_{H_2O} = 5.54 \times 10^{-8} \times 1000 = 5.54 \times 10^{-5} \text{ mhos}$$

At the same temperature the conductance of H^+ ions and OH^- ions are :

$$\lambda_{H^+} = 349.8 \text{ mhos}$$

$$\lambda_{OH^-} = 198.5 \text{ mhos}$$

According to Kohlrausch's Law

$$\lambda_{H_2O} = \lambda_{H^+} + \lambda_{OH^-}$$

$$= 349.8 + 198.5 = 548.3 \text{ mhos}$$

One molecule of water gives one H^+ ion and one OH^- ion

$$H_2O = H^+ + OH^-$$

Assuming that ionic concentration is proportional to conductance, we have

$$[H^+] = [OH^-] = \frac{5.5 \times 10^{-5}}{548.3} = 1.01 \times 10^{-7} \text{ g ion litre}^{-1}$$

The ionic product of water is then

$$K_w = [H^+][OH^-] = 1.02 \times 10^{-14} \text{ at } 25°C$$

For most purposes, the value of K_w is taken to be 10^{-14}

CONDUCTOMETRIC TITRATIONS

Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called **Conductometric titrations.** In these titrations, advantage is taken of the fact that the **conductance of a solution at a constant temperature depends upon the number of ions present in it and their mobility.** For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant. In this way two linear curves are obtained, the point of intersection of which is the **end-point.** Several phenomena like hydrolysis of reactants or products or partial solubility of a precipitated product give rise, however to a curvature in the curves. The shapes of curves obtained in certain types of titration are discussed below :

(1) Titration of a Strong acid against a Strong base

Consider the reaction in which hydrochloric acid solution is titrated against a solution of sodium hydroxide. Take 20 ml of the acid solution in the conductance cell placed in a thermostat and determine its conductance. Now add 1 ml sodium hydroxide solution from the burette at a time. After each addition, determine the conductance of the solution after through mixing and plot the conductance of the solution against the volume of the alkali added. It will be observed that the points lie on two lines which are almost straight. The point of intersection of the interpolated lines will be the end point and the volume of alkali corresponding to this point is the volume of alkali required to neutralise 20 ml of the acid (Fig. 25.9). The reason for this is that before the addition of alkali, the conductance of the solution is due to presence of H^+ and Cl^- ions. Since hydrogen ions possess the greatest mobility of any ion, the greater part of the conductance is due to it. As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions forming feebly ionised water molecules and their place is taken up by comparatively slow moving Na^+ ions.

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O \qquad \textit{(feebly ionised)}$$
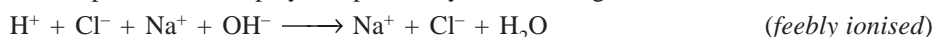
As a result of this, the conductance of the solution decreases and continues to fall with every subsequent addition of alkali till the end-point is reached. After the equivalence point, the further addition of sodium hydroxide solution results in an increase of conductance since the hydroxyl ions are no longer removed in the chemical reaction in the form of feebly ionised water. **The point of minimum conductance, therefore, coincides with the end-point of the titration.**

In order to get accurate results, the volume change during titration should be as little as possible. The titrant should, therefore, be about 10 times as strong as the acid solution in the conductance cell in order to keep the volume change small. If this is not so, a correction to the readings has to be applied *viz,*

$$\text{actual conductance} = \left(\frac{v + V}{V}\right) \times \text{observed conductance}$$

where v is the volume of the titrant and V is the original volume of the solution to be titrated.
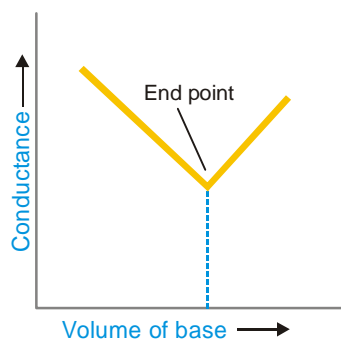
■ Figure 25.9
Conductometric titration curve
for strong acid and strong base.
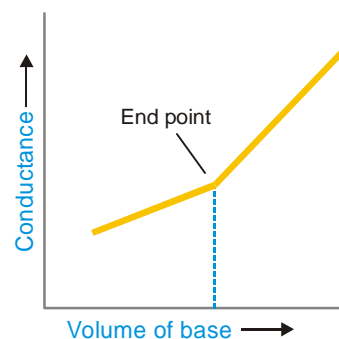
■ Figure 25.10
Curve for titration of a weak
acid against a strong base.

(2) Titration of a Weak acid against a Strong alkali

When a weak acid like acetic acid is titrated against a strong alkali like sodium hydroxide, we get a curve of the type shown in Fig. 25.10. The initial conductance of the solution is low because of the poor dissociation of the weak acid. On adding alkali, highly ionised sodium acetate is formed. The acetate ions at first tend to suppress the ionisation of acetic acid still further due to *Common Ion Effect* but after a while the conductance begins to increase because the conducting power of highly ionised salt exceeds that of the weak acid.

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O \qquad \textit{(feebly ionised)}$$

Immediately after the end point, further addition of sodium hydroxide introduces the fast moving hydroxyl ions. Thus, the *conductance value shows a sharp increase*. The point of intersection of the two curves, gives the end-point.

$$H^+ + Cl^- + NH_4OH \longrightarrow NH_4^+ + Cl^- + H_2O \qquad \textit{(feebly ionised)}$$

After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small compared with that of the acid or its salt. The shape of this part of the curve will, therefore, be as shown in the figure.

(3) Titration of a Strong acid against a Weak base

The curve obtained for the titration of a strong acid against a weak base is shown in Fig. 25.11. In this case, the conductance of the solution will first decrease due to the fixing up of the fast moving H^+ ions and their replacement by slow moving NH_4^+ ions.

(4) Titration of a Weak acid against a Weak base

The conductometric method is particularly suitable as such titrations do not give a sharp end-point with indicators. Consider the titration of acetic acid with ammonium hydroxide. The complete titration curve is shown in Fig. 25.12. The initial conductance of the solution in this case is also low due to the poor dissociation of the weak acid. But it starts increasing as the salt CH_3COONH_4 is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte. The end-point is quite sharp.
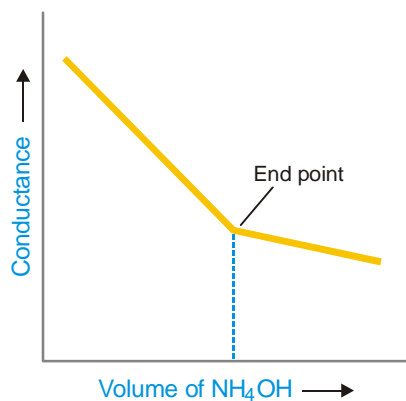
Figure 25.11
Curve for titration of a strong acid against a weak base.
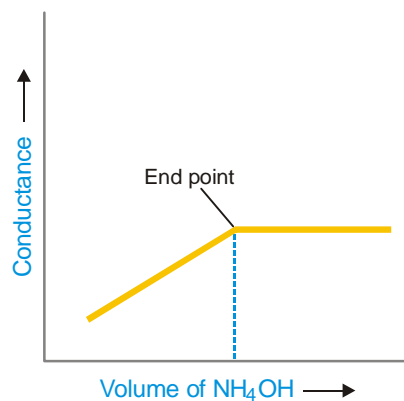
Figure 25.12
Curve for titration of acetic acid against ammonium hydroxide.

(5) Precipitation reactions

The end-point in precipitation reactions can be accurately determined by conductometric titration. The accuracy is further increased by working with fairly dilute solutions and addition of alcohol which reduces the solubility of the precipitate and prevents adsorption. In the titration of potassium chloride against silver nitrate, for example, the change in conductance on the addition of silver nitrate is not much since the mobility of the potassium ion and the silver ion is of the same order. Thus the curve is nearly horizontal.

$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow K^+ + NO_3^- + AgCl\,(ppt)$$
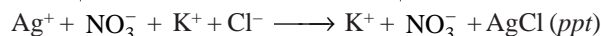
After the end-point, there is a sharp increase in conductance due to an increase in the number of free ions in solution.
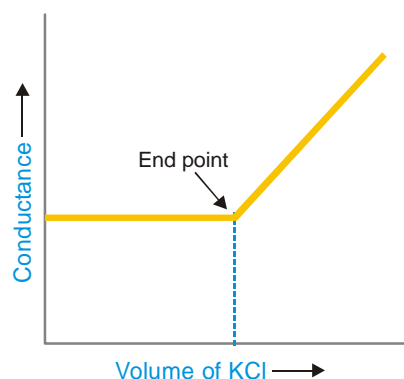
Figure 25.13
Titration of potassium chloride against silver nitrate.

Advantage of Conductometric Titrations

(1) Coloured solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.

(2) This method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indicators in ordinary volumetric analysis.

(3) More accurate results are obtained because the end -point is determined graphically.

Precautions. (*i*) It is necessary to keep the temperature constant throughout the experiment. (*ii*) In acid-alkali titrations, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

DIFFERENCES BETWEEN CONDUCTOMETRIC AND VOLUMETRIC TITRATIONS

Conductometric Titrations	Volumetric Titrations
1. Conductance measurements are done to check end points.	1. Volume measurements are done to check end points.
2. Titrations can be carried out even with coloured solution.	2. These titrations fail in coloured solutions as suitable indicators are not available some times.
3. Accurate results are obtained.	3. Results are not so accurate.
4. End point is determined graphically.	4. End point is determined by change in colour of indicator.
5. In case of polybasic acids conductometric titrations can be used.	5. In case of polybasic acids volumetric titrations do not give correct end points.
6. These are successful even in weak acids and strong bases.	6. These are not successful in weak acids and strong bases.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   - (*a*) Arrhenius theory
   - (*b*) Transport number
   - (*c*) Hittorf's method
   - (*d*) Moving boundary method
   - (*e*) Kohlrausch's law
   - (*f*) Degree of dissociation

2. (*a*) Explain ionic conductance, transport number of an ion, and absolute ionic velocity.
   (*b*) The absolute velocity of Ag^+ is 0.00057 cm sec^{-1} and of the NO_3^- is 0.00069 cm sec^{-1}. Assuming complete dissociation, calculate the specific conductivity of 0.01 M solution of silver nitrate.
   Answer. (*b*) 0.00012 mhos

3. Describe Hittorf's method for the experimental determination of the transference number. The speed ratio of silver and nitrate ions in $AgNO_3$ electrolysed between silver electrodes was found to be 0.89. Calculate the transference number of silver and nitrate ions.
   Answer. Ag^+ = 0.4708; NO_3^- = 0.5292

4. (*a*) What do you understand by the transport number of an ion? Does it vary?
   (*b*) In a moving boundary experiment with 0.1 N KCl using 0.65 N LiCl as indicator solution, a constant current of 0.006 amp was passed for 1900 secs and the boundary was observed to move through 5 cm in a tube of 0.1142 cm^2 cross-section. Calculate the transport number of K^+ and Cl^- ions.
   Answer. (*b*) K^+ = 0.4833; Cl^- = 0.5167

5. (*a*) What is meant by transport number of ions? Describe Hittorf's method for the determination of transport number of silver ions.
   (*b*) A dilute solution of silver nitrate was electrolysed using platinum electrodes. After passing small

current for three hours, a fall of 0.00064 g equivalent of electrolyte occurred in the anionic solution. The weight of copper deposited was found to be 0.05088 gm. Calculate transport number of silver ions.

Answer. (*b*) 0.40

6. (*a*) Explain Kohlrausch's law of ionic mobility. How does it help in determining the equivalent conductivity of infinite dilution of weak electrolyte?

   (*b*) Describe the Hittorf's method for determining the transport number of Ag^+ and NO_3^- ions in solution of silver nitrate.

7. The specific conductance of a saturated solution of AgCl is 1.55×10^{-6} ohm^{-1} cm^{-1} at 25°C. The ion conductance of Ag^+ Cl^{-1} are 61.94 and 76.34 ohm^{-1} cm^2 respectively. Calculate the solubility of AgCl in gram equivalent per litre at 25°C. Neglect the specific conductance of water.

   Answer. 1.6148×10^{-3} g lit^{-1}

8. In a moving boundary experiment with 0.1 N KCl solution, the boundary moved 4.94 cm during 67 minutes when a current of 5.21 A was used. The cross-sectional area of the tube was 0.230 cm^2. Calculate the transport number of K^+ ions.

   Answer. 0.523

9. What do you understand by the terms: transport number and ionic mobility of an ion? How are these related to each other? Write their units. (*Punjabi BSc, 2000*)

10. What do you understand by transport number? Give one method for the determination of it.
    (*Punjabi BSc, 2000*)

11. Describe Hittorf's method for determining the transport number of Ag^+ and NO_3^- ions in a solution of $AgNO_3$ when the electrodes are made up of silver. (*Jiwaji BSc, 2000*)

12. Give the applications of transport number. (*Himachal Pradesh BSc, 2000*)

13. State Kohlrausch's law. (*Madurai BSc, 2000*)

14. Write short notes on :

    (*a*) Transport number

    (*b*) Kohlrausch law of independent migration of ions (*Delhi BSc, 2000*)

15. (*a*) How is solubility of sparingly soluble salt is determined by conductance measurement?

    (*b*) Discuss the application of Kohlrausch's law. (*Lucknow BSc, 2001*)

16. If the conductance at infinite dilution of NaCl, HCl and CH_3COONa are 125.45×10^{-4}, 426.1×10^{-4} and 91.0×10^{-4} cm^2 $eqvt^{-1}$ respectively, calculate equivalent conductance of acetic acid at infinite dilution.

    Answer. 390.7×10^{-4} ohm^{-1} cm^2 $eqvt^{-1}$ (*Guru Nanak Dev BSc, 2002*)

17. Define Transport number. Describe briefly the principle of experimental determination of Transport number by Hittorf's method. (*Panjab BSc, 2002*)

18. (*a*) State the principle of conductometric titrations. Draw the titration curves for

    (*i*) Weak acid with a strong base

    (*ii*) Na_2SO_4 solution with $BaCl_2$ solution

    (*b*) Calculate the ionisation constant of water if the specific conductivity of water is 5.51×10^{-8} ohm^{-1} cm^{-1} and ionic conductance of H^+ and OH^- ions at the same temperature are 349.8 and 196.5 respectively.

    Answer. 1.013×10^{-14} (*Arunachal BSc, 2002*)

19. How does Kohlrausch's law helps in determining the dissociation constants of a weak acid by conductance measurements? (*Vidyasagar BSc, 2002*)

20. Derive the expression for the determination of Transport number by Hittorf's method when electrodes are not attacked? (*Arunachal BSc, 2002*)

21. Explain the factors on which the transport number depends. (*MD Rohtak BSc, 2002*)

22. Explain why the transport number of cadmium ion in cadmium iodide solution at high concentration may become zero or negative also. (*Arunachal BSc, 2002*)

23. Explain how is Kohlrausch's law helpful in determining the equivalent conductance of weak electrolyte at infinite dilution. (*Jammu BSc, 2002*)

24. Write short notes on :
    (*i*) Activity and mean ionic activity of an electrolyte.
    (*ii*) Ionic atmosphere   (*Aligarh BSc, 2002*)
25. Discuss the effect of concentration on transference number.   (*Kalyani BSc, 2003*)
26. During the electrolysis of a solution of potassium chloride between platinum electrodes, 0.0137 g of chloride was lost from the anodic compartment and 0.0857 g of silver was deposited in a silver coulometer connected in series with the cell. Find at the transport number of K^+ and Cl^- ions.
    Answer. 0.4854; 0.5146   (*Delhi BSc, 2003*)
27. (*a*) Explain the term 'ionic mobility'. Describe Hittorf's theoretical device to show that although most of the ions differ largely in their mobilities, but their equivalent amounts are discharged on electrolysis at appropriate electrodes.
    (*b*) In moving boundary experiment with 0.100 N KCl using 0.065 N LiCl as indicator solution, a constant current of 0.005893 amp was passed for 2130 seconds. The boundary was observed to move through 5.6 cm in a tube of 0.1142 sq cm cross-section. Calculate the transport number of K^+ and Cl^- ions.
    Answer. 0.492; 0.508   (*Rajasthan BSc, 2003*)
28. What is meant by limiting equivalent conductance of weak electrolyte? How do you determine it by the help of Kohlrausch's law?   (*Sambalpur BSc, 2003*)
29. Explain the use of Kohlrausch's law to determine the solubility of a sparingly soluble salt.
                                                                                (*Nagpur BSc, 2003*)
30. (*a*) Define transport number.
    (*b*) A solution of silver nitrate containing 0.51 gm of the salt in 60.40 gm of the solution was electrolysed under similar electrodes. After electrolysis 64 gm of the anode solution was found to contain 0.56 gm of silver nitrate. A current of 0.04 amp was passed for 2950 seconds. Calculate the transference number of nitrate ion.
    Answer. (*b*) 0.520   (*Delhi BSc, 2004*)
31. (*a*) How is Kohlrausch's law helpful in determining the solubility of a sparingly soluble salt in water?
    (*b*) How can you find the transference number of an ion by Hittorf's method?
                                                                                (*Madurai BSc, 2004*)
32. A solution of HCl was electrolysed in a cell between two platinum electrodes. The cathode compartment contained 0.354 g of chloride ions before electrolysis and 0.32 g after electrolysis. A silver coulometer in series had a deposit of 0.532 g of silver after passing the same amount of current. Calculate the transport number of H^+ and Cl^- ions.
    Answer. 0.84 ; 0.160   (*Rajasthan BSc, 2005*)
33. In the Hittorf cell using silver electrodes and $AgNO_3$ as an electrolyte, a certain amount of current was passing which deposited 9.886×10^{-4} g equivalent of silver in the coulometer. The anode compartment had the composition 28.235 g of H_2O and 0.099 g of $AgNO_3$ before electrolysis and 28.435 g of water and 0.1874 g of $AgNO_3$ after electrolysis. Calculate the transport number of Ag^+ and NO_3^- ions.
    Answer. 0.48 and 0.52   (*Kalyani BSc, 2005*)
34. In a moving boundary experiment with 1 N KCl solution using $CaCl_2$ as indicator, a current of 0.0115 A was passed for half an hour and the boundary moved through a volume of 0.106 ml. Calculate the transport number of K^+ ion.
    Answer. 0.494   (*Vikram BSc, 2006*)
35. A conductivity cell whose cell constant is 2 cm^{-1}, is filled with 0.1 M acetic acid solution. Its resistance is found to be 3765 ohm^{-1}. Calculate the degree of dissociation of acetic acid.
    Answer. 0.0136   (*Delhi BSc, 2006*)
36. In a moving boundary method, a current of 30 m A was passed for 80 seconds. During this time the boundary of a solution of HCl containing 0.01 mol dm^{-3} moved 17.0 cm towards the cathode. Calculate the transport number of H^+ and Cl^- ions. (The cross-sectional area of the glass tube is $1.0 \times 10^{-5} m^2$).
    Answer. 0.68 ; 0.32   (*Mysore BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. According to Arrhenius theory an electrolyte when dissolved in water gives two types of
   - (a) charged particles
   - (b) molecules
   - (c) ion pairs
   - (d) fundamental particles

   Answer. (a)

2. For an electrolyte AB, the ionisation constant is given by the expression
   - (a) $K = \dfrac{[A][B]}{[AB]}$
   - (b) $K = \dfrac{[A^+]+[B^+]}{[AB]}$
   - (c) $K = \dfrac{[A^+]-[B^+]}{[AB]}$
   - (d) $K = \dfrac{[A^+][B^-]}{[AB]}$

   Answer. (d)

3. The conductivity of an electrolyte is due to the
   - (a) presence of ions in the electrolyte
   - (b) free movement of ions in the solution
   - (c) reunion of ions in the solution
   - (d) release of heat energy due to ionisation

   Answer. (b)

4. The electrical conductivity of an electrolyte depends upon
   - (a) the number of molecules in the electrolyte
   - (b) the number of ions present in the electrolyte
   - (c) the number of ions present in the solution
   - (d) the number of molecules of the solvent

   Answer. (c)

5. On passing electrical current through an electrolyte solution
   - (a) cations move towards anode
   - (b) anions move towards cathode
   - (c) cations move towards cathode and anions towards anode
   - (d) both cations and anions move in same direction

   Answer. (c)

6. On passing electrical current through an electrolyte solution, the cations
   - (a) move towards cathode with the speed equal to that of anions towards anode
   - (b) move with faster speed than that of anions
   - (c) move with different speed as compared to that of anions
   - (d) move with slower speed than that of anions

   Answer. (c)

7. The Hittorf's rule states that
   - (a) the loss of concentration around any electrode is proportional to the speed of the ions moving towards it
   - (b) the loss of concentration around any electrode is proportional to the speed of the ions moving away from it
   - (c) the loss of concentrations around both the electrodes is proportional to the sum of speed of cations and anions
   - (d) none of the above

   Answer. (b)

8. The Hittorf's rule can be represented by the expression

(a) $\dfrac{\text{Fall around anode}}{\text{Rise around cathode}} = \dfrac{\text{speed of cation}}{\text{speed of anion}}$

(b) $\dfrac{\text{Fall around anode}}{\text{Fall around cathode}} = \dfrac{\text{speed of anion}}{\text{speed of cation}}$

(c) $\dfrac{\text{Fall around anode}}{\text{Fall around cathode}} = \dfrac{\text{speed of cation}}{\text{speed of anion}}$

(d) $\dfrac{\text{Rise around cathode}}{\text{Fall around anode}} = \dfrac{\text{speed of anion}}{\text{speed of cation}}$

Answer. (*c*)

9. The fraction of the total current carried by the cation or anion is termed as

(*a*)   fractional number
(*b*)   speed number
(*c*)   carrier number
(*d*)   transport number

Answer. (*d*)

10. If v_+ is the speed of cation and v_- that of anion, the transport number of cation is given by

(*a*) $\dfrac{v_+}{v_+ - v_-}$

(*b*) $\dfrac{v_+}{v_- - v_+}$

(*c*) $\dfrac{v_+}{v_+ + v_-}$

(*d*) $\dfrac{v_-}{v_+ + v_-}$

Answer. (*c*)

11. If v_+ is the speed of cation and v_- that of anion, then the speed ratio is given by

(*a*) $r = \dfrac{t_\pm}{t_-}$

(*b*) $r = \dfrac{t_+}{1 + t_+}$

(*c*) $r = \dfrac{t_-}{1 - t_+}$

(*d*) $r = \dfrac{t_+}{1 - t_-}$

Answer. (*d*)

12. The sum of the transport number of cation and anion is equal to

(*a*)   1
(*b*)   0
(*c*)   0.5
(*d*) ∞

Answer. (*a*)

13. In Hittorf method for determination of transport numbers we make use of a

(*a*)   H-tube
(*b*)   V-tube
(*c*)   U-tube
(*d*)   L-tube

Answer. (*c*)

14. While determining transport number by Hittorf method, _____ electrodes are used when electrodes are attackable

(*a*)   silver
(*b*)   copper
(*c*)   mercury
(*d*)   platinum

Answer. (*d*)

15. In the moving boundary method for the determination of transport number, the formula used is (where *n* is the number of faradays of current passed)

(*a*) $t_{A^+} = \dfrac{s\,l\,c}{n}$

(*b*) $t_{A^+} = \dfrac{s\,l\,c}{n^2}$

(*c*) $t_{A^+} = \dfrac{s\,l\,c^2}{n}$

(*d*) $t_{A^+} = \dfrac{s\,l^2\,c}{n}$

Answer. (*a*)

16. One Faraday is equal to

(*a*)   96.500 coulombs
(*b*)   9650 coulombs

(*c*) 965.00 coulombs
(*d*) 96500 coulombs

Answer. (*d*)

17. The statement of Kohlrausch's law is

(*a*) the equivalent conductance of an electrolyte at infinite dilution is equal to the product of equivalent conductances of the component ions

(*b*) the equivalent conductance of an electrolyte at infinite dilution is equal to the difference of equivalent conductances of the component ions

(*c*) the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of equivalent conductances of the component ions

(*d*) none of the above

Answer. (*c*)

18. Kohlrausch's law can be expressed as

(*a*) $\lambda_\alpha = \lambda_a - \lambda_c$
(*b*) $\lambda_\alpha = \lambda_c - \lambda_a$
(*c*) $\lambda_\alpha = \lambda_a + \lambda_c$
(*d*) $\lambda_\alpha = \lambda_a \times \lambda_c$

Answer. (*c*)

19. Kohlrausch's law can be used to determine

(*a*) λ_α for weak electrolytes
(*b*) absolute ionic mobilities
(*c*) solubility of sparingly soluble salts
(*d*) all of these

Answer. (*d*)

20. If λ_α is the equivalent conductance at infinite dilution and λ_v the equivalent conductance of the electrolyte at the dilution *v*, the degree of dissociation is given by

(*a*) $\alpha = \dfrac{\lambda_\alpha}{\lambda_v}$
(*b*) $\alpha = \dfrac{\lambda_v}{\lambda_\alpha}$

(*c*) $\alpha = \lambda_\alpha - \lambda_v$
(*d*) $\alpha = \lambda_v - \lambda_\alpha$

Answer. (*b*)

21. When a strong acid is titrated against a strong base the end point is the point of

(*a*) zero conductance
(*b*) maximum conductance
(*c*) minimum conductance
(*d*) none of these

Answer. (*c*)

22. During titration of a weak acid against a weak base, there is a sharp increase in _____ at the end point

(*a*) conductivity
(*b*) equivalent conductance
(*c*) specific conductance
(*d*) none of these

Answer. (*a*)

23. If the equivalent conductance of a certain solution of acetic acid is 39.07 ohm^{-1} cm^2 eqvt^{-1}. If λ_α of CH_3COOH is 390.7, the degree of dissociation of acetic acid is

(*a*) 0.1
(*b*) 0.2
(*c*) 0.5
(*d*) 0.75

Answer. (*a*)

24. The equivalent conductance at infinite dilution of NaCl, HCl and CH_3COONa at 25°C are 126.0, 426.0 and 91.0 ohm^{-1} cm^2 respectively. The equivalent conductance of acetic acid at infinite dilution at 25°C will be

(*a*) 643.0
(*b*) 517.0
(*c*) 217.0
(*d*) 391.0

Answer. (*d*)

25. The equivalent conductance of decinormal solution of acetic acid at 298 K is 80 and at infinite dilution 400 ohm^{-1}. The percentage dissociation of acetic acid is

(a) 10%   (b) 20%

(c) 50%   (d) 100%

Answer. (b)

26. If the transport number of K^+ is 0.492 in KCl solution. The transport number of Cl^- ion will be

(a) 0.984   (b) 0.492

(c) 0.508   (d) 0.016

Answer. (c)

27. In a binary electrolyte AB of certain concentration, the transport number of cation is 0.4. The transport number of the anion will be

(a) 0.2   (b) 0.4

(c) 0.6   (d) 0.8

Answer. (c)

28. The equivalent conductance at 18°C of a normal solution of KCl is 98.2 and at infinite dilution at the same temperature is 131. The degree of dissociation of KCl will be

(a) 131/98.2   (b) 98.2/131

(c) 98.2/131 + 98.2   (d) 131/131 + 98.2

Answer. (b)

29. If the degree of dissociation of weak electrolyte at a certain temperature is 0.1, the percentage of the molecules undissociated will be

(a) 10%   (b) 20%

(c) 50%   (d) 90%

Answer. (d)

30. For strong electrolytes, the degree of dissociation is

(a) nearly equal to one   (b) nearly equal to zero

(c) nearly equal to infinity   (d) nearly equal to 0.5

Answer. (a)

31. The equivalent conductance at infinite dilution of NH_4Cl, NaOH and NaCl at 18°C are respectively, 129.8, 227.4 and 108.9 ohm^{-1} cm^2 g eqvt^{-1}. The equivalent conductance of NH_4OH at infinite dilution at 18°C will be

(a) 128.8   (b) 108.9

(c) 227.4   (d) 238.3

Answer. (d)

32. At infinite dilution the conductance of NH_4Br, KOH and KBr at 298 K are 151, 271 and 151 ohm^{-1} cm^2 g eqvt^{-1} respectively. If the equivalent conductance of NH_4OH at 0.01 N concentration at 298 K is 27.1 ohm^{-1} cm^2 g eqvt^{-1}, the degree of dissociation of NH_4OH would be

(a) 0.1   (b) 0.01

(c) 0.001   (d) 1.0

Answer. (a)

33. λ_o for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 228, 120 and 129 ohm^{-1} cm^2 g eqvt^{-1}. The value of λ_o for NH_4OH

(a) 108 ohm^{-1} cm^2 g eqvt^{-1} (b) 249 ohm^{-1} cm^2 g eqvt^{-1}

(c) 348 ohm^{-1} cm^2 g eqvt^{-1} (d) 183 ohm^{-1} cm^2 g eqvt^{-1}

Answer. (d)

34. The ionic mobility of an ion is given by the relation

(a) $\lambda_\alpha \div 96500$ (b) $\lambda_\alpha \times 96500$

(c) $\lambda_\alpha + 96500$ (d) $\lambda_\alpha - 96500$

Answer. (a)

35. If the velocity of an ion at infinite dilution be u cm per sec when the distance between the electrodes is 20 cm and the voltage 100 V, the ionic mobility is

(a) $u/5$ cm sec^{-1}

(b) $5\,u$ cm sec^{-1}

(c) $u + 5$ cm sec^{-1}

(d) $u - 5$ cm sec^{-1}

Answer. (a)

36. The ionic product of water is

(a) 1×10^{-7}

(b) 1×10^{-10}

(c) 1×10^{14}

(d) 1×10^{-14}

Answer. (d)

37. The solubility, s, of a sparingly soluble salt is related to its equivalent conductance at infinite dilution by the relation (K is specific conductance)

(a) $s = \dfrac{K \times 1000}{\lambda_\alpha}$

(b) $s = \dfrac{c \times 1000}{\lambda_\alpha - \lambda}$

(c) $s = \dfrac{K \times 1000}{\lambda_\alpha - \lambda}$

(d) $s = \dfrac{c \times 1000}{\lambda_\alpha}$

Answer. (a)

38. For an electrolyte of the type AB (sparingly soluble in water), the solubility is related to its solubility product by the relation

(a) $K_{sp} = \sqrt{s}$

(b) $K_{sp} = s^2$

(c) $K_{sp} = 4s^2$

(d) $K_{sp} = 4s^3$

Answer. (b)

39. The transport number of an ion depends on the mobility of that ion. It also depends upon the

(a) mobility of the solvent

(b) mobility of the electrolyte

(c) mobility of the other ion with which it is associated

(d) none of the above

Answer. (c)

40. The ionic mobility of Li$^+$ is small as compared to that of K$^+$ ion. It is because

(a) Li$^+$ ion is very small

(b) Li$^+$ ion is heavily hydrated

(c) Li$^+$ ion has only one principal quantum number

(d) none of the above

Answer. (b)

41. The λ_o for K$^+$ ion is 73.52 ohm^{-1} cm^{-1} g eqvt^{-1}. Its ionic mobility will be

(a) $73.52 \div 96500$

(b) 73.52×96500

(c) $73.52 + 96500$

(d) $73.52 - 96500$

Answer. (a)

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