$= 0.1/1000$ g eqvt/ml

We know 108 g silver $= 1$ Faraday

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

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

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

$$= 0.852$$

$\therefore$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,

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

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

$\therefore$ $$\frac{\lambda_a}{\lambda_\infty} = \frac{kv_-}{k(v_- + v_+)} = \frac{v_-}{v_- + v_+} = t_- \qquad ...(1)$$

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

Dividing (1) by (2), we have

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

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 $= \lambda_a + \lambda_c$

$= 42.77 + 345.06$

$=$ **387.83 mhos**

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

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

SOLUTION

Applying Kohlrausch's law,

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

$$= 130 + 174 - 66$$

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

(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 $$\lambda_{\neq} = FU_{\neq}$$

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, $\lambda_a = \lambda_\infty \times t_-$

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

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

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

$= 130.1 \times 0.495$

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

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

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

$\therefore$ $$V = \frac{119.1}{1.24 \times 10^{-6}}\ \text{ml}$$

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

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

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

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

(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

Specific conductivity (κ) in N/10 solution = 0.00947 mhos

Volume containing 1 g equivalent = 10,000 ml

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

= 94.7 mhos

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 $\dfrac{\lambda_v}{\lambda_\infty} = a$

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

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

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*,