Application of Kohlrausch's Law

1. **Determination of Limiting equivalent conductance of weak electrolytes.**

Suppose we want to determine λ_∞ value of CH_3COOH from Kohlrausch's Law.

$$(\lambda_\infty)_{CH_3COOH} = \lambda_\infty CH_3COONa + \lambda_\infty HCl - \lambda_\infty NaCl$$

$$= \lambda_\infty Na^+ + \lambda_\infty CH_3COO^- + \lambda_\infty H^+ + \lambda_\infty Cl^- - \lambda_\infty Na^+ - \lambda_\infty Cl^-$$

$$= \lambda_\infty CH_3COO^- + \lambda_\infty H^+$$

Thus from the conductances of completely dissociated sodium acetate, HCl and NaCl in H_2O solution, the equivalent conductance of weakly dissociated acetic acid in water solution at infinite dilution can be obtained.

Numerical 1 The equivalent conductance of sodium propionate, hydrochloric acid and NaCl at infinite dilution are 85.9, 426.1 and 126.4 $S\,cm^2\,eq^{-1}$ respectively at 298K. Calculate the equivalent conductance at infinite dilution for propionic acid.

Solution According to Kohlrausch Law:

i) $\lambda_\infty C_2H_5COONa = \lambda_\infty C_2H_5COO^- + \lambda_\infty (H^+)$

ii) $\lambda_\infty HCl = \lambda_\infty H^+ + \lambda_\infty Cl^-$

iii) $\lambda_\infty NaCl = \lambda_\infty Na^+ + \lambda_\infty Cl^-$

To obtain

$$\lambda_\infty C_2H_5COOH = \lambda_\infty C_2H_5COONa + \lambda_\infty HCl - \lambda_\infty NaCl$$

$$= 85.9 + 426.1 - 126.4$$

$$= 385.6\ S\,cm^2\,eq^{-1}$$

2. Calculation of solubility of sparingly soluble salts. Conductance offers a very simple and convenient means for determining the solubility of sparingly soluble salts such as barium sulphate, lead sulphate, silver chloride etc. in water. The procedure involved is as follows :

A saturated solution of the salt in water of known specific conductance, k_{H_2O} is prepared. Next the specific conductance of the saturated solution $k_{solution}$ is measured. This specific conductance is due to both the salt and the water.

The specific conductance of the salt alone $= k_{salt} = k_{solution} - K_{H_2O}$. The equivalent conductance of the salt is

$$\lambda = \frac{1000\, k_{salt}}{C} \qquad ...(20.33)$$

where C is the concentration in equivalent dm^{-3}, and hence the solubility.

Since the solubility is very low, the salt is supposed to be completely ionised and the equivalent conductivity may be taken as the equivalent conductivity at infinite dilution *i.e.*, λ_∞.

Making this substitution in the equation (20.33)

$$\lambda_\infty = \frac{1000\, k_{salt}}{C} \qquad ...(20.34)$$

Now.

$$(\lambda_\infty)\ \text{salt} = \lambda^+ + \lambda^-$$

From the value of λ_∞ obtained from the Table of ionic conductances, C can be calculated from equation (20.34).

Example 20.10. *The molar conductivity at infinite dilution of $AgNO_3$ $NaCl$ and $NaNO_3$ is 116·5, 110·3 and 105·2 $S\ cm^2\ mol^{-1}$ respectively. The conductivity of AgCl in water is $2·4\times10^{-6}\ S\ cm^{-1}$ and of water used in experiment is $1·16\times10^{-6}\ S\ cm^{-1}$. Find out the solubility of AgCl in $g\ dm^{-3}$.*

Solution. From the equation,

$$\lambda_\infty = \frac{1000\, k_{salt}}{C}$$

Now,

$$(\lambda_\infty)_{AgCl} = (\lambda_\infty)_{AgNO_3} + (\lambda_\infty)_{NaCl} - (\lambda_\infty)_{NaNO_3}$$
$$= 116·5 + 110·3 - 105·2$$
$$= 121·6$$

K_{salt} = [illegible]

$= 2{\cdot}4 \times 10^{-6} - 1{\cdot}16 \times 10^{-6}$ S cm^{-1}

$= 1{\cdot}24 \times 10^{-6}$ S cm^{-1}

Substituting these values in the above equation

$$121{\cdot}6 = \frac{1000 \times 1{\cdot}24 \times 10^{-6}}{C}$$

or $$C = \frac{1000 \times 1{\cdot}24 \times 10^{-6}}{121{\cdot}6}$$

$= 1{\cdot}019 \times 10^{-5}$ equivalent per dm^3

$(1{\cdot}019 \times 10^{-5} \times 143{\cdot}5)$

$= 1{\cdot}4620 \times 10^{-3}$ g dm^{-3}

3. **Calculation of degree of dissociation of weak electrolyte.** The degree of dissociation of weak electrolytes such as NH_4OH, CH_3COOH etc. at any dilution can be calculated by measuring the equivalent conductivity of solution, λ_c and by λ_∞ of the electrolyte by the relationship.

$$\alpha = \frac{\lambda_c}{\lambda_\infty}$$

Example 20.11. *Calculate the degree of dissociation of sodium chloride in 0·1N solution. The equivalent conductivity at this dilution is 98·4 S cm² equivalent⁻¹ and ionic conductances of sodium and chloride ions are 43·4 and 65·5 S cm² respectively.* (*Nagpur B.Sc. 1962*)

Solution. λ_c for NaCl $= 98{\cdot}4$ S cm² equivalent^{-1}

λ_∞ for NaCl $= \lambda_{Na^+} + \lambda_{Cl^-}$

$= 43{\cdot}4 + 65{\cdot}5$

$= 108{\cdot}9$

$$\alpha = \frac{\lambda_c}{\lambda_\infty} = \frac{98{\cdot}4}{108{\cdot}9}$$

4. **Calculation of ionic conductances.** By combining Kohlrausch's law and the results of transport number measurements, it is possible to calculate the value of ionic conductances from the equations (20.31), and (20.32) *i.e.*

$$\lambda_c^\circ = n_c \lambda_\infty$$

$$\lambda_a^\circ = n_a \lambda_\infty$$

The knowledge of ionic conductances (Table 20.8) is very useful. It helps in

(1) calculating the equivalent conductivity at infinite dilution of weak electrolytes and

(2) calculating the absolute velocities of the ions.

Absolute ionic mobility is related with ionic conductance numerically as

$$\text{Absolute ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

TABLE 20.8. Equivalent conductivities of aqueous ions at 298 K.

Cation	Equivalent Conductivity ($cm^2\ equiv^{-1}\ ohm^{-1}$)	Anion	Equivalent Conductivity ($cm^2\ equiv.^{-1}\ ohm^{-1}$)
H^+	349·7	OH^-	198
Li^+	38·7	F^-	55
Na^+	50·1	Cl^-	76·3
K^+	73.5	Br^-	78·4
Rb^+	76·4	I^-	76·8
Cs^+	76·8	NO_3^-	71·44
Ag^+	61·9	HSO_3^-	50
NH_4^+	73·7	SO_3^{2-}	72
Be^{2+}	45	HCO_3^-	44·5
Mg^{2+}	53·06	CO_3^{2-}	72
Ca^{2+}	59·50	SO_4^{2-}	79·8
Ba^{2+}	63·7	$HCOO^-$	56
La^{3+}	69·6	$HC_2O_4^-$	40·2
$CO(NH_3)_6^{3+}$	102	$C_2O_4^{2-}$	74
Tl^+	74·7	CH_3COO^-	40·9
Sr^+	59·46	ClO_4	68
		$Fe(CN)_6^{3-}$	101·0
		$Fe(CN)_6^{4-}$	110·5

Example 20.12. *At 291 K the ionic velocities of Ag^+ is 0·00057 cm sec^{-1} and that of NO_3^- 0·00063 cm sec^{-1}. What is the value of λ_∞ for $AgNO_3$ at 291 K? If the specific conductivity of 0·1N $AgNO_3$ is 0·00947 S cm^{-1}. Find the degree of dissociation at this dilution.*

(Gwalior B.Sc. 1966 ; Aligarh, B.Sc. 1958)

Solution. $\text{Absolute ionic mobility} = \frac{\text{Ionic conductance}}{96500}$

$$\therefore \quad \lambda_{Ag^+} = 0{\cdot}00057 \times 96500$$

$$\lambda_{NO_3^-} = 0\ 00063 \times 96500$$

$$\therefore \quad \lambda_{Ag^+} + \lambda_{NO_3} = 96500\ (0{\cdot}00057 + 0{\cdot}00063)$$

$$= 96500 \times 0{\cdot}0012$$

$$= 115{\cdot}1$$

$$\lambda_c = \frac{1000 \times k}{C}$$

$$= \frac{1000 \times 0{\cdot}00947}{0{\cdot}1} = 94{\cdot}7$$

$$\therefore \quad \alpha = \frac{\lambda_c}{\lambda_\infty} = \frac{94{\cdot}7}{115{\cdot}1} = 0{\cdot}822$$

Example 20.13. *The transport number of Ag^+ ion in $AgNO_3$ is 0·48. The equivalent conductivity of $AgNO_3$ solution at infinite dilution is 120. Calculate the ionic conductance and ionic velocity of NO_3^- ions.*

(Lucknow B.Sc. 1965)

Solution.

$$\lambda = n_c \lambda_\infty$$

$$\lambda_{Ag^+} = n_{Ag^+} + \lambda_\infty$$

$$= 0{\cdot}48 \times 120$$

$$= 57{\cdot}6$$

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

$$120 = \lambda_{NO_3^-} + 57{\cdot}6$$

$$\lambda_{NO_3^-} = 120 - 57{\cdot}6$$

$$= 62{\cdot}4$$

Absolute velocity of $NO_3^- = \frac{62{\cdot}4}{96500} = 0{\cdot}000646$ cm sec^{-1}

5. Ionic product of water. Conductance measurements and other evidences support that water ionizes according to the equation

$$H_2O \rightleftharpoons H^+ + OH^-$$

For this ionization the equilibrium constant K is $= \frac{[H^+][OH^-]}{[H_2O]}$

Since water dissociates very slightly the concentration of undisso-

ciated water may be taken constant

$$\therefore \quad [H^+]\,[OH^-] = \text{constant}$$

This constant is represented by K_w which is called ionic product of water. Thus

$$K_w = [H^+]\,[OH]$$

The product of concentration of H^+ and OH^- ions in water is constant at constant temperature. This can be determined by a number of methods. Conductivity is one of them. This method can be clearly understood by the following examples.

Example 20 14. *At 298 K the specific conductivity of pure water is* $5{\cdot}51 \times 10^{-8}$ *S cm*$^{-1}$. *The ionic conductance of* H^+ *and* OH^- *ions at the same temperature are 349·8 and 198·5 respectively. Calculate the value of ionization constant of water.*

Solution.

$$\lambda_c = \frac{1000 \times k}{C}$$

$$= \frac{1000 \times 5{\cdot}51 \times 10^{-8}}{C}$$

$$\lambda_\infty = \lambda_{H^+} + \lambda_{OH^-} = 349{\cdot}8 + 198{\cdot}5$$

$$= 548{\cdot}3$$

Water may be considered to be the dilute solution of H^+ and OH^- ions in undissociated molecule of H_2O. Therefore, λ_c will be taken as λ_∞

$$\therefore \quad 548{\cdot}3 = \frac{1000 \times 5{\cdot}51 \times 10^{-8}}{C}$$

$$C = \frac{1000 \times 5{\cdot}51 \times 10^{-8}}{548{\cdot}3}$$

$$= 1{\cdot}005 \times 10^{-7}$$

$$\therefore \quad K_w = [H^+]\,[OH^-]$$

$$= 1{\cdot}005 \times 10^{-7} \times 1{\cdot}005 \times 10^{-7}$$

$$= 1{\cdot}01 \times 10^{-14}$$

Ionic product of water depends on temperature. In Table 20·9 the best values of K_w at different temperatures are given.

TABLE 20.9. Ionic product of water, K_w, at various temperatures.

Temperature (K)	K_w
273	$0{\cdot}114 \times 10^{-14}$
283	$0{\cdot}292 \times$
298	$1{\cdot}008 \times$
310	$2{\cdot}919 \times$
333	$9{\cdot}614 \times$

Conductometric titrations. Titrations followed conductometrically are often used in chemistry. The principle involved is that electrical conductance depends upon the number and mobility of ions. For practical purposes, it is not necessary to know the actual specific conductances of the solution. The conductance readings corresponding to various added amounts of titrants are plotted against the latter. The intersection of the lines gives the required end point. The method of conductometric titration is capable of considerable accuracy provided there is good temperature control and a correction is applied for the volume changes during the titration. The most common conductometric titrations are given here.

1. Titration of strong acid against strong base. When a strong alkali *i.e.*, NaOH, is added to a solution of a strong acid *i.e.*, HCl, the reaction is

$$(H^+ + Cl^-) + (Na^+ + OH)^- = Na^+ + Cl^- + H_2O$$

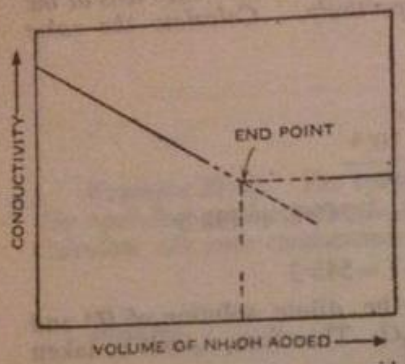

Fig. 20.12. Titration of strong acid against strong base.

As seen the fast moving hydrogen ions are replaced by slower moving sodium ions hence the conductance decreases with the addition of NaOH solution. After reaching the equivalence point, fast moving hydroxyl ion unneutralized will be present in excess which will increase the conductance of the solution. The equivalence point is determined from the break in the curve (Fig. 20.12).

(*ii*) **Titration of weak acid against strong base.** If a moderately weak acid such as acetic acid is titrated against strong base such as sodium hydroxide the form of conductance titration curve is as shown in Fig. 20.13. The neutralized reaction may be represented as

$$(CH_3COO^- + H^+) + (Na^+ + OH^-) \longrightarrow CH_3COO^- + Na^+ + H_2O$$

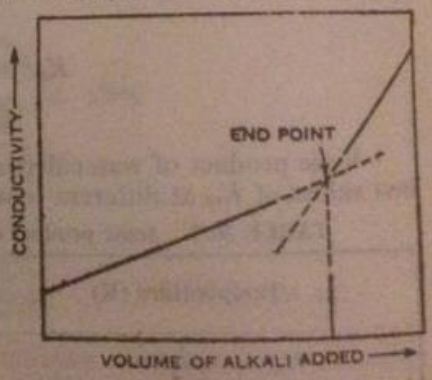

Fig. 20.13. Titration of a weak acid against a strong base.

The initial solution of the weak acid has a low conductance and the addition of alkali may first result in a further decrease inspite of the formation of a salt *i.e.*, sodium acetate with a high conducting power. The reason for this is that the common anion *i.e.*, CH_3COO^- suppresses the dissociation of the acetic acid. With further addition of NaOH, however, the conductance of the highly ionized salt soon exceeds that of the weak acid which it replaces, and so the specific conductance of the

solution increases. When the acid is completely neutralized, further addition of NaOH introduces excess of fast moving hydroxyl ion. The conductance, therefore, increases more rapidly after the equivalence point. The break in the conductance titration curve gives the equivalence point.

(*iii*) **Titration of strong acid against weak base.** If a strong acid is titrated with a weak base, *i.e.*, aqueous solution of HCl against NH_4OH the reaction occurs as

$$(H^+ + Cl^-) + (NH_4 + OH^-) \longrightarrow NH_4^+ + Cl^- + H_2O$$

The conductance will fall at first due to the replacement of fast moving H^+ by slow moving NH_4^+ ions. When the equilibrium point is passed however, the conductance will remain almost constant, since the free base is a weak electrolyte. The curves obtained are shown in the (Fig. 20.14).

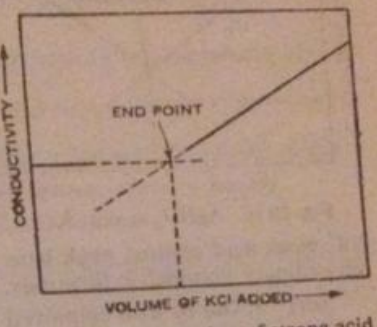

Fig. 20.14. Titration of strong acid against weak base.

(*iv*) **Titration of a mixture of strong and weak acids.** One of the valuable features of the conductance method of analysis is that it permits the analysis of a mixture of a strong and a weak acid in one titration. Suppose a mixture of HCl and CH_3COOH is to be titrated against an alkali, the curves are shown in the Fig. 20.15. The inital decrease is due to the neutralisation of strong acid first. The titration of acetic acid will start only after HCl has been completely neutralised. When the neutralisation is complete there is little further change in conductance due to the excess of strong base.

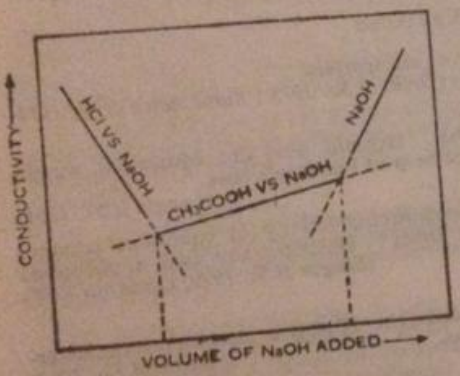

Fig. 20.15. Titration of a mixture of HCl and CH_3COOH against NaOH.

(*v*) **Titrations involving precipitation reactions.** In reactions of the type

$$(K^+ + Cl^-) + (Ag^+ + NO_3^-) \longrightarrow AgCl + K^+ + NO_3^-$$

When a precipitate is formed one salt is replaced by an equivalent amount of another *e.g.*, KCl by KNO_3 and show the conductance

remains almost constant in the initial stages. After the end point is passed however the excess of added salt causes a sharp rise in the conductance. The end point of the reaction can be determined from the plots (Fig. 20.16).

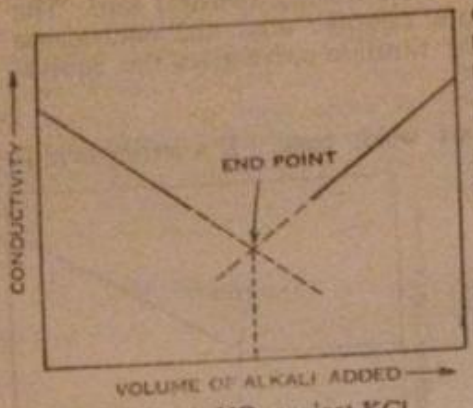

Fig. 20.16. $AgNO_3$ against KCl.

Advantages of conductometric reactions. Conductometric titrations have several advantages.

(*i*) Coloured solutions which cannot be titrated with the help of indicators can be successfully titrated conductometrically.

(*ii*) These titrations can be employed successfully for the titration of weak acid against weak base which do not give the sharp colour in ordinary volumetric titrations.

(*iii*) It can be also employed in case of very dilute solutions.

(*iv*) No special precaution is necessary near the end point as it is determined graphically.

(*v*) The conductometric titrations can be used to study the precipitation reactions.