KOLHRAUSCH'S LAW AND ITS APPLICATION

(FOR B.Sc.part-1I (Hons & Subs)

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KOHLRAUSCH'S LAW

FRIEDRICH KOHLRAUSCH in 1875 determined the equivalent conductivities of different electrolytes at infinite dilution and tabled them as given below:-

EQUIVALENT CONDUCTIVITY AT INFINITE DILUTION AT 298 K

Electrolytes	$\lambda\infty$ (mhos)	Difference	Electrolytes	$\lambda\infty$ (mhos)	Difference
KBr NaBr	151.92 128.51	23.41	NaBr NaCl	128.51 126.45	2.06
KCl NaCl	149.16 125.45	23.41	KBr KCl	151.92 149.86	2.06
KNO_3 $NaNO_3$	144.96 121.55	23.41	LiBr LiCl	117.06 115.03	2.06

He observed that the difference between the equivalent conductivity at infinite dilution of pairs of electrolytes having an ion in common is constant at constant temp.

From above table it is clear that when potassium ion is replaced by sodium ion in any of the electrolytes there will be a constant difference of 23.41 mhos in the values of equivalent conductivity irrespective of the nature of other ion with it is associated in the electrolyte .Similarly replacement of bromide ion by chloride ion gives 2.06 mhos difference irrespective of the nature of cation.

On the basis of above conclusion Kohlrausch put forwarded a law which is given below :-

"At infinite dilution where ionization is complete ,each ion makes a definite contribution towards equivalent conductivity of the electrolyte irrespective of the of the other ion with which it is attached and the value of equivalent conductivity at infinite dilution of an electrolyte is the sum of the contributions of the two ions"

Hence,

$\lambda\infty = \lambda_c + \lambda_a$

Where λ_c = ionic conductivity of cation at infinite dilution

And λ_a = ionic conductivity of anion at infinite dilution

Ionic conductivity is also known as ionic mobility

APPLICATION OF KOHLRAUSCH'S LAW

Calculation of equivalent conductivity of weak electrolytes

With the help of Kohlrausch law we can calculate equivalent conductivity of weak electrolytes at infinite dilution

Eg determination of equivalent conductivity of Acetic acid at infinite dilution

If we know ionic mobilities of acetate (CH_3COO^-) ION & H^+ ion then we can calculate EQUIVALENT CONDUCTIVITY of acetic acid by given below equation :-

$$\Lambda^{\infty}_{CH_3COOH} = \Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{H^+} \quad \text{——— (I)}$$

For determination of equivalent Conductivity of Acetic acid, we took HCl, CH_3COONa and NaCl and their equivalent Conductivities are determined by Conductivity Measurement process.

According to Kohrausch

$$\Lambda^{\infty}_{HCl} = \Lambda^{\infty}_{H^+} + \Lambda^{\infty}_{Cl^-} \quad \text{——— (II)}$$

$$\Lambda^{\infty}_{CH_3COONa} = \Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{Na^+} \quad \text{——— (III)}$$

$$\Lambda^{\infty}_{NaCl} = \Lambda^{\infty}_{Na^+} + \Lambda^{\infty}_{Cl^-} \quad \text{——— (IV)}$$

By adding eqn (II) & (III)

$$\Lambda^{\infty}_{HCl} + \Lambda^{\infty}_{CH_3COONa} = \Lambda^{\infty}_{H^+} + \Lambda^{\infty}_{Cl^-} + \Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{Na^+} \quad \text{——— (V)}$$

eqn (IV) is subtracting from eqn (V) we have

$$\Lambda^{\infty}_{HCl} + \Lambda^{\infty}_{CH_3COONa} - \Lambda^{\infty}_{NaCl} = \Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{H^+}$$

From eqn (I)

$$\Lambda^{\infty}_{CH_3COOH} = \Lambda^{\infty}_{HCl} + \Lambda^{\infty}_{CH_3COONa} - \Lambda^{\infty}_{NaCl}$$

##########################Thanks ######################