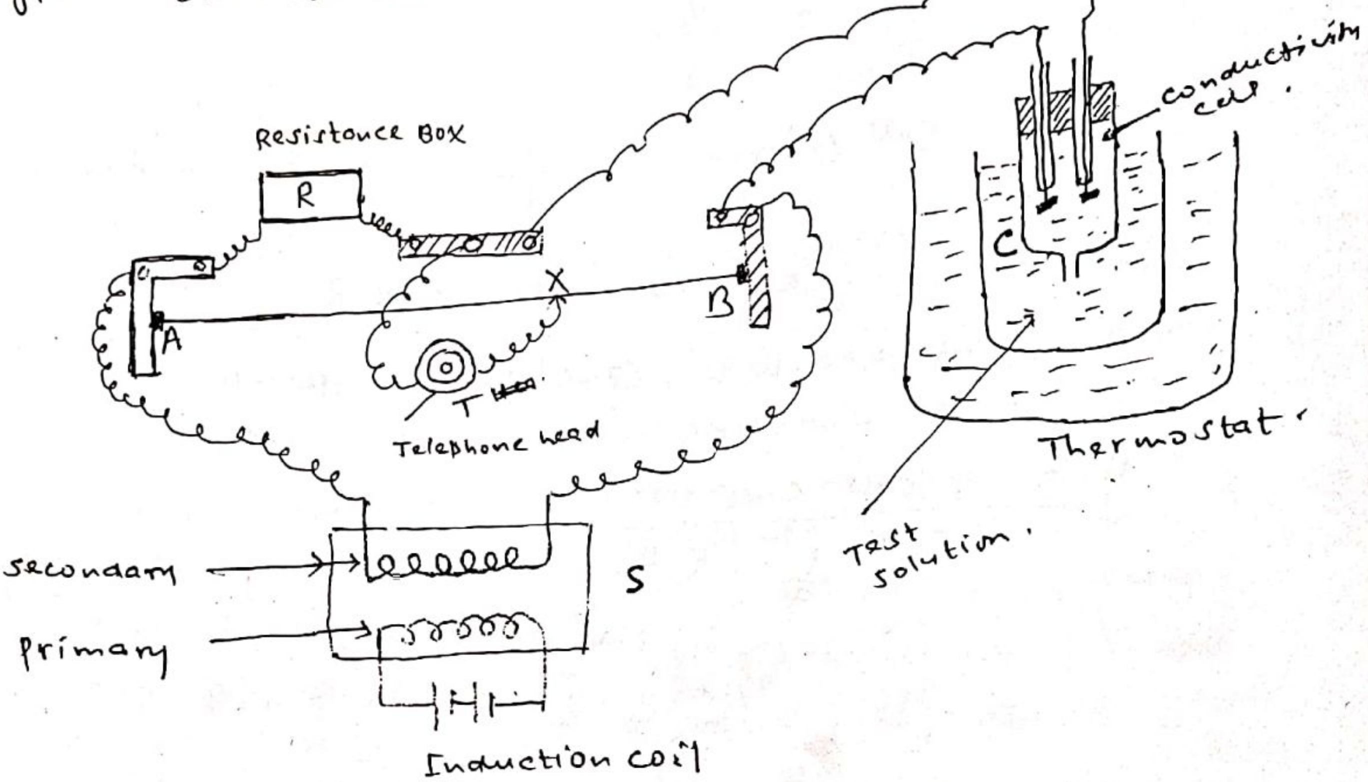
wheatstone bridge method

Determination of conductance

Resistance of solution can be determined by wheat stone Bridge method. The reciprocal of this resistance of solution gives conductance.



AB is a uniform wire and a sliding contact moves over it. S represents the source of alternating current, fed into the circuit. C is the conductivity cell containing solution, whose resistance is to be determined. R is the resistance box and T is a telephone-head to detect the current.

When current is flowing, a known resistance is introduced through the resistance box. The resistance should be the same order as that of the solution under examination in the cell. The sliding contact X is then moved along the wire AB until a point of minimum sound in the telephone is detected.

At this stage

$$\frac{\text{Resistance of the Solution}}{\text{Resistance } R} = \frac{\text{Length } XB}{\text{Length } XA}$$

Since R is known and lengths XB and XA can be read from the scale fixed below the wire, AB, the resistance of the solution can be calculated. Reciprocal of this ~~conductance~~ resistance gives the conductance of solution.

Important point

(i) Direct current can not be used because this leads to polarisation effect.

(ii) Alternating current is produced by induction coil.

(iii) Telephone head is used to obtain null point (position of minimum sound).

(iv) For accurate work, solution should be prepared in absolutely pure water which has no conductance. Kohlrausch prepared absolutely pure water is known as conductivity water. It is prepared by distilling 40 times the ordinary distilled water under reduced pressure. The conductance of this water is very low 4.3×10^{-8} ohm^{-1}

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Kohlrausch's law

This law states that, at infinite dilution when the dissociation is complete, each ion of the electrolyte makes a definite contribution of its own towards the molar conductivity of the electrolyte and it is quite independent of the presence of the other ion of the electrolyte.

Thus molar conductivity of an electrolyte at infinite dilution is the sum of ionic conductivities of the cations and anions each multiplied with the number of ions present in one formula unit of electrolyte.

Let an electrolyte A_xB_y

$$\Lambda_m^{\infty}(A_xB_y) = x\lambda_m^{\infty}(A^{y+}) + y\lambda_m^{\infty}(B^{x-}).$$

$$\Lambda_m^{\infty}(Al_2(SO_4)_3) = 2\lambda_m^{\infty}(Al^{3+}) + 3\lambda_m^{\infty}(SO_4^{2-})$$

$$\Lambda_m^{\infty}(CH_3COOH) = \Lambda_m^{\infty}(CH_3COO^-) + \Lambda_m^{\infty}(H^+).$$

Application of Kohlrausch's law

① calculation of molar conductance at infinite dilution for a week electrolytes

Let an example of week electrolyte CH_3COOH

From Kohlrausch's law

$$\Lambda_m^{\infty}(CH_3COOH) = \Lambda_m^{\infty}(CH_3COO^-) + \lambda_m^{\infty} H^+$$

The molar conductivity at infinite dilution of CH_3COOH can be determined from the knowledge of molar conductivities at infinite dilution for strong electrolytes such as CH_3COONa, HCl and $NaCl$

$$\Lambda_m^\infty (CH_3COONa) = \lambda_m^\infty (CH_3COO^-) + \lambda_m^\infty (Na^+) \quad \text{--- (i)}$$

$$\Lambda_m^\infty (HCl) = \lambda_m^\infty (H^+) + \lambda_m^\infty (Cl^-) \quad \text{--- (ii)}$$

$$\Lambda_m^\infty (NaCl) = \lambda_m^\infty (Na^+) + \lambda_m^\infty (Cl^-) \quad \text{--- (iii)}$$

By eqⁿ (i) + eqⁿ (ii) − eqⁿ (iii)

$$\Lambda_m^\infty (CH_3COONa) + \Lambda_m^\infty (HCl) - \Lambda_m^\infty (NaCl)$$
$$= \lambda_m^\infty (CH_3COO^-) + \lambda_m^\infty (Na^+) + \lambda_m^\infty (H^+) + \lambda_m^\infty (Cl^-) - \lambda_m^\infty (Na^+) - \lambda_m^\infty (Cl^-)$$

or, $$\Lambda_m^\infty (CH_3COONa) + \Lambda_m^\infty (HCl) - \Lambda_m^\infty (NaCl) = \lambda_m^\infty (CH_3COO^-) + \lambda_m^\infty (H^+)$$

$$\therefore \boxed{\Lambda_m^\infty (CH_3COONa) + \Lambda_m^\infty (HCl) - \Lambda_m^\infty (NaCl) = \Lambda_m^\infty CH_3COOH}$$

② Calculation of Degree of dissociation (α) of weak electrolyte

Molar conductance of an electrolyte depends upon the degree of dissociation. Higher the degree of dissociation, higher will be molar conductance. With increase in dilution the molar conductance increases and at infinite dilution the electrolyte is completely dissociated because degree of dissociation approaches to unity.

$$\text{Degree of dissociation}(\alpha) = \frac{\text{molar conductance at given concentration}}{\text{molar concentration at infinite dilution.}}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

Thus, degree of dissociation at given concentration C can be determined by measuring molar conductance at the dilution.

(3) calculation of molar solubility of sparingly soluble salts

Salts like $BaSO_4$, $PbSO_4$, $AgCl$, $AgBr$, AgI etc which do not dissolve to a large extent in water are called sparingly soluble salt. As they dissolve in very small extent, their solutions are considered as saturated solutions at infinite dilution. As such, their molar concentration in solution is equal to their solubility and their molar conductivity can be taken to be molar conductance at infinite dilution. Thus, by finding their specific conductivity (K) and molar conductance at infinite dilution Λ_m^∞ by Kohlrausch law, the molar solubility can be determined.

$$\Lambda_m^\infty = \frac{K \times 1000\ cm^3\ L^{-1}}{molarity} = \frac{K \times 1000\ cm^3\ L^{-1}}{solubility\ (\frac{mol}{Lit})}$$

$$solubility\ (\frac{mol}{Lit}) = \frac{K \times 1000\ cm^3\ L^{-1}}{\Lambda_m^\infty}$$

(4) Calculation of ionic product of water:

It has been found that ionic conductance of H^+ and OH^- at infinite dilution are

$\lambda^\circ_{H^+} = 349.8\ S\ cm^2\ mol^{-1}$ and $\lambda^\circ_{OH^-} = 198.5\ S\ cm^2\ mol^{-1}$

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