Electrochemistry

Electrochemistry :

Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy to chemical change and vice versa .

Conductors: substance that allows electric current to pass through them

1→ Metallic or electronic conductor

2→ electrolytic conductor

Electronic conductor	**Electrolytic**
- Remains unchanged with the passage of electric current.	- Changed with the passage of electric current
- Electrons are the charge carriers	- Ions are the charge carriers
- Conduction decrease with increase temperature	- Conduction increase with increase temperature
Example: Metals, alloys, solid salts.	**Example:** (1) Conduct in pure state acid – base – salt in water. (2) Solution of one or more substance.

Electrolysis: The decomposition of solution by electric currents result in liberation of metals and gases (oxygen).

Electrolyte:

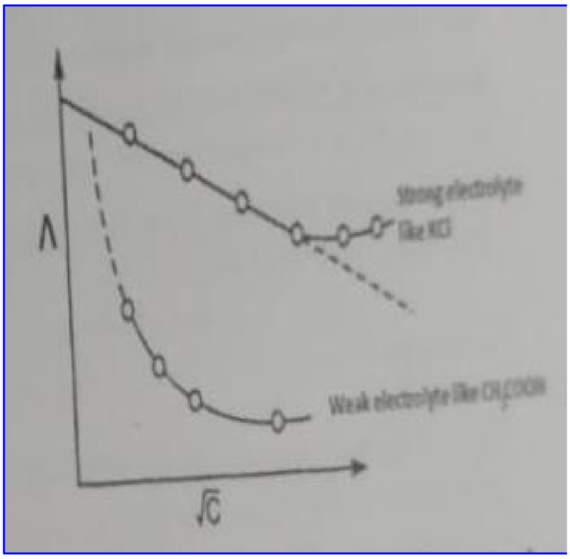
Solutes giving conducting solution in a suitable solvent.

They are divided in two categories on the basis of degree of ionization.

(1) Strong electrolyte **(2) Weak electrolyte**

- Completely ionized in water
- No of ions doesn't increase by dilution
- The molar conductance increase very slowly.
- As it is completely ionized / HCl – H_2SO_4 (N_aOH, KOH)

- Partially ionized in water.
- No of ions increase by dilution
- Molar conduction increase rapidly by dilution as more molecule ionized on dilution
- Amine – phonol – carboxy –



$$\lambda = K.\frac{1000}{N}$$

- Strong electrolytes (e.g., KCl) molar conductance increase with dilution until reaching limiting value called (Λ∞) conductance at infinite dilution

- Upon dilution, interionic attractions decrease, ion mobility increases, and hence equivalent and molar conductance increase.

- Weak electrolytes (e.g., CH_3COOH) molar conductance increase with dilution and cannot have Λ∞ determined experimentally since they are not completely ionized.

- Upon dilution, the degree of ionization increases and large number of ions are produced and hence conductance increases with dilution

Ions: Carrying positive charge and moving in the direction of current towards the cathode and called cations

Metalic conductor:

The resistance is directly proportional to the distance between the electrodes and inversely proportional to the cross – section area of the solution between the electrodes.

مقاومة المحلول تتناسب طرديًا مع المسافة بين الإلكترود يين وعكسيًا مع المادة السطحية الموجودة بينالإلكترود يين.

$$\left(R\ x\ \frac{1}{a}\right) \qquad R = Q\left(\frac{1}{a}\right)$$

L → distance between the electrodes.

a → cross section area of solution between two electrode

if $L = 1$ cm $a = 1\ cm^2$

$R = \rho$

ρ → specific resistance

→ = ohom cm

$$R = \rho\ \frac{L}{a}$$

Specific resistance: → ρ المقاومة النوعية

Resistance of a wire of 1 cm in length (L) and 1 cm^2 in cross section area.

$$G = \frac{1}{R} = \frac{1}{\rho} . \frac{a}{L}$$

Conductance

$$\frac{1}{R} = K . \frac{a}{L}$$

specific conductance التوصيل النوعي

$$K = \frac{1}{R} . \frac{L}{a} = ohm^{-1}\ cm^{-1}$$

$$\frac{L}{a} = \text{cell constant}$$

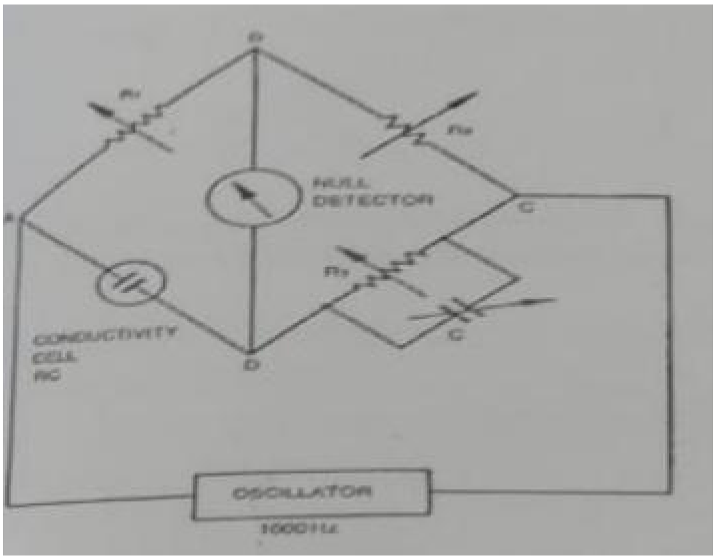
$$K = \frac{1}{\rho}$$

Electrolytic conduction:

Electrolytes are also conductors of electricity due to ions it contains. The greater the conc. Of ions, the higher conductance.

المحلول الإلكتروليتي أيضًا موصل للكهرباء.
بسبب الأيونات التي تحتويها وكلما زاد تركيز الأيونات كلما زاد التوصيل.

Conductance is the reciprocal of resistance and the resistance can be determined by a Wheatstone bridge circuit in which the conductivity cell forms one arm of the bridge. This method is known as Null Method (Kohlrausch Conductance Bridge).



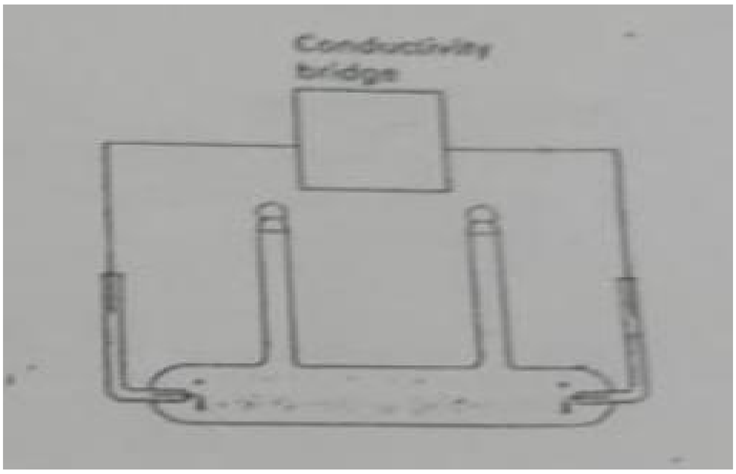


Fig. 2: (A) Wheatstone bridge circuit for measurement of conductivity. (B) Conductivity cell with one arm of a resistance bridge for measurement of conductivity of an electrolyte.

The arms AB and BC represented by resistance R1 and R2 are usually in the form of a single calibrated slide wire resistor with a sliding contact connected to the null detector. The solution whose conductance is to be determined is placed in conductivity cell. When the bridge is balanced, assuming that the conductivity cell behaves as a pure resistance, then the voltage between 'B' and 'D' is equal to zero.

Measurement of Resistance

$R = (R1 / R2) \times R3$

The ratio R1 / R2 can be varied to cover a wide range of resistances.

A variable capacitor is used with R3 to compensate for the cell capacitance.

The device is adjusted to give a definite null point.

The detector is not a galvanometer because a galvanometer does not respond to alternating current used in the bridge.

2. Problem of Electrolysis:

When direct current is passed through an electrolytic solution, two difficulties arise:

(a) Polarization of electrodes — resistance changes.

(b) Change in concentration of the solution.

To avoid these, alternating current of about 1000 Hz frequency is used.

example :1

Calculate the specific conductance of a solution (0.01 N) cupric sulphate $CuSO_4$ if you known the conductance of cupric sulphate equal [2884 x 10^{-5} ohm^{-1}] and conductance of KCl = 9612 x 10^{-5} ohm^{-1} and specific conductance Kd = 0.003499 ohm^{-1}. cm^{-1}.

For KCl

$$K = \frac{1}{R} \cdot \frac{L}{a}$$

$$0.003499 = 9612 \text{ x } 10^{-5} \text{ x } \frac{L}{a}$$

$$\frac{L}{a} = 0.2447\ cm^{-1}$$

For $CuSO_4$

$$K = \frac{1}{R} \cdot \frac{1}{a}$$

$$= 2884 \text{ x } 10^{-5} \text{ x } 0.2497$$

$$= 0.0007188\ ohm^{-1}cm^{-1}.$$

Equivalent conductance:

Conductance of volume of solution containing one gram equivalent of dissolved substance.

$$\lambda = K.V$$

λ = equivalent conductance.

K = specific conductance.

V = Volume of solution containing 1gm equivalent of an electrolyte $\left(\frac{1000}{N}\right)$

$$\lambda = K.\frac{1000}{N} \longrightarrow \text{Normality}$$

N = $\frac{no\ of\ gm\ equivalent\ of\ solute}{V(L)\ solution}$

No of gm eq = $\frac{wt}{eq.wt}$

eq.wt = $\frac{Mwt}{valency}$

$\boxed{\lambda = ohm^{-1}\ Cm^{2}\ equiv^{-1}}$

Molar conductance:

Conductance of volume of solution containing one mole of dissolved substance.

$$\lambda = \frac{1000K}{M}$$

$$M = \frac{no\ of\ mole\ of\ solute}{V(L)\ solution}$$

λ = ohm^{-1} Cm^{2} mol^{-1}

Factors influencing the magnitude of conductance of an electrolyte solution

1. Nature of electrolyte: A strong electrolyte which ionizes completely shows large conductance while a weak electrolyte which partially ionizes has low conductance.

2. Concentration of electrolyte: conductance increases with dilution.

3. Temperature: Conductance increases with increase in temperature. At higher temperature the mobility of ions is increased and hence the conductivity increases

4. Size of ions: Increase in the size of ions increases ionic interaction due to solvation and decreases the conductance.

$Li^{+} < Na^{+} < k^{+}$ order in size

$Li^{+} > Na^{+} > k^{+}$ order in conductivity

5. Inter-ionic forces: Increase in interionic forces will inhibit the movement of ions and the conductance of the electrolyte decreases.

6. Nature of solvent: Viscous medium restricts the movement of ions and hence the conductivity is reduced.

Example2

The resistance of a conductivity cell with 1.64 cm^2 in area of 0.85 L and filled with 1N solution KBr equal 5.03Ω. Calculate the equivalent conductance.

$K = \frac{1}{R} . \frac{L}{a}$ a = 1.64 cm^2

$= \frac{1}{5.03} \times \frac{0.85}{1.64}$ L = 0.85 cm

K = $ohm^{-1}cm^{-1}$ R = 5.03 ohm

$$\lambda = K . \frac{1000}{N} = K . \frac{1000}{1} \ ohm - 2cm^2 mol^2$$

Example3

The resistance of a conductivity cell filled with 0.02N KCl solution at 18°C equal 17.6 ohm, if the same cell filled with 0.1 N acetic acid. The resistance equal 14.8 ohm. If the specific conductance, of KCl is 2.399 x 10^{-3} $ohm^{-1}cm^{-1}$. Calculate the equivalent conductance of acetic acid.

KCl	**Acetic**
$N_{KCl} \rightarrow 0.02$ N	N = 0.1
$R_{KCl} \rightarrow 17.6\ \Omega$	Ω = 14.8
$K = 2.399 \times 10^{-3}$	

$$\lambda = K \frac{1000}{N}$$

$Kd \quad K = \frac{1}{R} . \frac{L}{a}$ cell constant

$$2.399 \times 10^{-3} = \frac{1}{17.6} \times \left(\frac{L}{a}\right)$$

$$\frac{L}{a} = \qquad Cm^{-1}$$

acetic $$K = \frac{1}{14.8} \times \left(\frac{L}{a}\right)$$

$$\lambda = K - \frac{1000}{0.1}$$

Determination the solubility of springly soluble salts:

$$\lambda_{\infty} = \frac{1000\ K}{S}$$

Solubility $$S = \frac{1000\,K}{\lambda\infty}$$

S = Solubility of salt in gram equivalent per litre.

K = Specific conductance.

Kohlrausch's law

The molar conductivity at infinite dilution of an electrolyte is equal to sum of the ionic conductance's of the ions composing it, provided the solvent and temperature are the same.

$$\lambda\infty = \underset{\substack{\swarrow \\ \text{no of cations}}}{r} + h^{\infty} + \underset{\substack{\searrow \\ \text{no of anions}}}{r^{-}}\ \lambda\infty$$

$$\lambda\infty = \lambda\infty^{+} + \lambda\infty^{-}$$

Example4: The equivalent conductance at infinite dilution for $[H^+]$ equal 314 and for acetate ion $[CH_3CO_0^-]$ equal 66 but the equivalent conductivity equal 38 for acetic acid.

Calculate:

(1) The equivalent conductance at infinite dilution of CH_3COOH.

(2) The degree of dissociation of CH_3COOH [α]

$$\lambda_\infty CH_3COOH = \lambda_\infty (H^+) + \lambda_\infty (CH_3COO^-)$$

$\lambda_\infty[H^+] = 314$

$\lambda_\infty [CH_3COO^-] = 66$

$\lambda_{eq} [CH_3COO] = 38$

$$\lambda \infty CH_3COOH = 314 + 66 = 380$$

$$\alpha = \frac{\lambda_{ea}}{\lambda_\infty} = \frac{38}{380} = \frac{1}{10}$$

- To calculate the $\lambda\infty$ for weak electrolyte

Example:5 calculate $\lambda\infty$ for NH_4OH

$\lambda\infty$ NaOH = 123

$\lambda\infty$ NaCl = 90

$\lambda\infty$ NH_4Cl = 340

$\lambda\infty NaOH = \lambda\infty Na^+ + \lambda\infty OH^-$ (1) = 123

$\lambda\infty NaCl = \lambda\infty Na+ + \lambda\infty Cl-$ (2) = 90

$\lambda\infty\ NH_4Cl = \lambda\infty NH_4^+ + \lambda\infty OH^- (\lambda\infty Na^+ + \lambda\infty Cl^-) - (\lambda\infty Na^+ + \lambda\infty Cl^-)$

$= 340 + 123 - 90$ $ohm^{-1}cm^2mol^{-1}$.

Degree of ionization or dissociation:

$$\alpha = \frac{\lambda_C}{\lambda \infty}$$ at infinite dilution

Degree of dissociation:

The ratio of equivalent conductivity at given conc to the equivalent conductivity at infinite dilution.

EXAMPLE:6

If the degree of dissociation of but uric acid at 25°C is 3.89×10^{-2} and the molar conductivity at infinite dilution 382.45×10^{-4} $ohm^{-1}cm^2mol^{-1}$ calculate the specific conductance of the acid at 0.01 μ of solution.

CALCULATE THE DISSOCIATION CONSTANT (Ka) OF WEAK ELECTROLYTE

Ostwald dilution law:

$\mathbf{AB \longleftrightarrow A^+ + B^-}$

$1\text{-}\alpha \qquad\qquad\qquad \alpha \quad \alpha$

$C(1\text{-}\alpha) \qquad\qquad C\alpha \;\; C\alpha$

$Ka = C^2\alpha^2 / C\,({}^{1\text{-}\alpha}\ )$

$Ka = C\alpha^2 / {}^{1\text{-}\alpha}$ $\qquad\qquad$ $1\text{-}\alpha = 1$ AS α is very small

$Ka = \alpha^2\ C$

$\alpha = \sqrt{\boldsymbol{Ka/c}}$

Calculation of Specific Conductance of n-Butyric Acid

Example:7: If the dissociation constant of n-butyric acid at 25°C is 1.515×10^{-5} and the molar conductance at infinite dilution = 382.42×10^{-4} ohm^{-1} cm^2 mol^{-1}.

Calculate the specific conductance of the acid at 0.01 M solution.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$Ka = \alpha^2 \times C$

$\alpha = \sqrt{\boldsymbol{Ka/c}} = \sqrt{(1.515 \times 10^{-5} / 0.01)} = 3.89 \times 10^{-2}$

$\alpha = \Lambda c / \Lambda\infty$

$\Lambda c = \alpha \times \Lambda\infty = 3.89 \times 10^{-2} \times 382.42 \times 10^{-4} = 1.488 \times 10^{-3}$

$\Lambda c = (K \times 1000) / C$

$1.488 \times 10^{-3} = (K \times 1000) / 0.01$

K=

Calculation of Dissociation Constant of Acetic Acid

Example8

The specific conductivity of 0.001 M acetic acid is 4.95×10^{-5} ohm^{-1} cm^{-1}. Calculate the dissociation constant of acetic acid. $\Lambda°$ for acetic acid is 390.5 ohm^{-1} cm^{2} mol^{-1}.

Solution

$\Lambda m = K \times (1000 / C)$

$\Lambda m = 4.95 \times 10^{-5} \times (10^{3} / 0.001) = 49.5$

$\alpha = 49.5 / 390.5$

$Ka = \alpha^{2} \times C = (49.5 / 390.5)^{2} \times 0.001$

$Ka = 1.6 \times 10^{-5}$

Solubility Product is the product of the concentration of its ions

For $Al(OH)_3$:

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^{-}$

$S \qquad 3S$

Let solubility = S

$Ksp = [Al^{3+}][OH^{-}]^{3} = S(3S)^{3} = 27S^{4}$

Example 9:

If the conductivity of a saturated solution of AgBr is $8.5 \times 10^{7}\ \Omega^{-1}\ cm^{-1}$ and $\Lambda^{0}(AgBr) = 140\ \Omega^{-1}\ cm^{2}\ mol^{-1}$, calculate the solubility and Ksp of AgBr.

$\Lambda^{0}m = \kappa \times 1000 / S$

$140 = 8.5 \times 10^{7} \times 1000 / S$

$S = (8.5 \times 10^{7} \times 1000) / 140 = 6.06 \times 10^{-4}$ mol/L

$Ksp = S^{2} = (6.06 \times 10^{-4})^{2} =$

Example 10

THE solubility of CaF_2 is 0.015 gm /litre calculate the solubility product

MWt =78

Solubility =0.015/78 = mole/litre

$Ksp=s(2s)^2 = 4s^3$