

ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-12) TOPIC-ELECTROCHEMISTRY PREPARED BY: MR. ARNAB PAUL CHOWDHURY SET NUMBER-02 DATE: 03.07.2020



WHAT IS ELECTROCHEMISTRY?

Electrochemistry is a branch of Physical Chemistry that deals with the interaction between electrical energy and chemical energy. It is broadly divided into two categories:

- 1. Production of chemical change by electrical energy i.e. the phenomenon of electrolysis
- 2. Conversion of chemical energy into electrical energy. i.e., the generation of electricity by spontaneous redox reactions.

To put it in simple terms, electrochemistry is the study of the relationship between electricity. Here, we study electricity as a quantitative and measurable phenomenon involving some chemical change. The outcome of this chemical change can be electricity or vice versa.

Therefore, to give you a better idea, electricity can be produced usually when electrons move from one element to another in a certain type of reaction. These can be either redox or oxidation-reduction reaction. We study all of these in electrochemistry.

In other words, electrochemistry is also concerned with chemical phenomena that basically involves charge separation as seen commonly in liquids such as solutions. The dissociation of charge often involves charge transfer that occurs homogeneously or heterogeneously between different chemical species.

ELECTROCHEMICAL CELL

A spontaneous chemical process is the one which can take place on its own and in such a process Gibbs free energy of a system decreases. In electrochemistry, spontaneous reaction (redox reaction) results in the conversion of chemical energy into electrical energy. The reverse process is also possible where a non-spontaneous chemical reaction occurs by supplying electricity. These interconversions are carried out in equipment called electrochemical cell.

TYPES OF ELECTROCHEMICAL CELL

Electrochemical cell are of two types: galvanic cells and electrolytic cells

GALVANIC CELL

The galvanic cell converts chemical energy into electrical energy i.e, electricity can be obtained with the help of redox reaction. The oxidation and reduction take place in two separate compartments. Each compartment consists of an electrolyte solution and metallic conductor which acts as an

electrode. The compartment containing the electrode and the solution of the electrolyte is called half cells.

For example- Daniell cell is a galvanic cell in which zinc and copper are used for a redox reaction to take place.

 $Zn(s) + Cu^{_{+2}}(aq) \rightarrow Zn^{_{+2}} + Cu(s)$

At anode (oxidation half)

 $Zn(s) \rightarrow Zn^{+2} + 2e^{-}$

At cathode(reduction half)

 $Cu^{+2}(aq) + 2e^{-} \rightarrow Cu(s)$



Salt bridge: Salt bridge is usually an inverted U- tube filled with a concentrated solution of inert electrolytes. It is used to maintain the charge balance and to complete the circuit by allowing the flow of ions through it. It contains a gel in which inert electrolytes like KNO_3 or K_2SO_4 are mixed. Through the salt bridge, negative ion flows towards the anode and positive ion flow to the cathode and the charge balance is maintained and cell keeps on functioning.

Electrode potential: In a galvanic cell, when two-electrode are dipped in their respective ion there is a tendency of one of the electrodes (anode) to undergo oxidation whereas the ion of the other electrode (cathode) has the tendency to gain an electron. This tendency of losing of electrons (oxidation) or gaining of electrons (reduction) is called electrode potential.

Standard electrode potential (E^o): Standard electrode potential is defined as the electrode potential of an electrode relative to standard hydrogen electrode under standard conditions. The standard conditions taken are:

- 1 molar concentration of each ion in the solution.
- A Temperature of 298 K.
- 1 bar pressure.



Electrochemical Series

A series of the standard electrode has been established by measuring the potential of various electrodes versus standard hydrogen electrode (SHE). When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potential or standard oxidation potentials, the resulting series is called the **electrochemical series**.

Elements reduction reaction

$F_2(g) + 2e$	\rightarrow	2F-(aq)	+2.87
$Au_{+}(aq) + e_{-}$	\rightarrow	Au(s)	+1.68
$Cl_2(g) + 2e$	\rightarrow	2Cl-(aq)	+1.36
$O_2(g) + 4H_+(aq) + 4e$	\rightarrow	2H2O(1)	+1.23
Ag+(aq) + e-	\rightarrow	Ag(s)	+0.80
Fe3+(aq) + e-	\rightarrow	Fe2+(aq)	+0.77
I2(s) + 2e-	\rightarrow	2I-(aq)	+0.54
$O_2(g) + 2H_2O(l) + 4e$	\rightarrow	40H-(aq)	+0.40
Cu2+(aq) + 2e-	\rightarrow	Cu(s)	+0.34
2H+(aq) + 2e-	\rightarrow	$H_2(g)$	0.00
Pb2+(aq) + 2e-	\rightarrow	Pb(s)	-0.13
Sn2+(aq) + 2e-	\rightarrow	Sn(s)	-0.14
Ni2+(aq) + 2e-	\rightarrow	Ni(s)	-0.23
Co2+(aq) + 2e-	\rightarrow	Co(s)	-0.28
Fe2+(aq) + 2e-	\rightarrow	Fe(s)	-0.44
Zn2+(aq) + 2e-	\rightarrow	Zn(s)	-0.76
2H2O(I) + 2e-	\rightarrow	H2(g) + 20H-(aq)	-0.83
Als+(aq) + 3e-	\rightarrow	Al(s)	-1.67
Mg2+(aq) + 2e-	\rightarrow	Mg(s)	-2.34
Na+(aq) + e-	\rightarrow	Na(s)	-2.71
Ca2+(aq) + 2e-	\rightarrow	Ca(s)	-2.87
K+(aq) + e-	\rightarrow	K(s)	-2.93

<u>Cell potential or emf of a cell</u>: In the galvanic cell there are two half cell, the oxidation half-cell(anode) and the reduction half -cell(cathode).Due to the difference in the potentials of these halfcells, the electric current moves from the electrode of higher potential (cathode) to the electrode of lower potential (anode). The difference between the electrode potential of the two half cell is called cell potential or emf of a cell.

 $\mathsf{E}^{\circ}_{\text{cell}} = \mathsf{E}_{\text{Cathode}} - \mathsf{E}_{\text{anode}}$

 $E_{Cathode}$ = standard reduction potential of the cathode.

 E_{anode} = standard reduction potential of the anode.

If E°_{cell} is positive then the reaction is feasible.

If E°_{cell} is negative then the reaction is not feasible.

Electrode and cell potentials- Nernst equation: The electrode potential and the emf of the cell depends upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution.

For the general electrochemical reaction of the type:

 $aA + bB \rightarrow cC + dD$

 $E_{\text{\tiny cell}} = E^{\circ}_{\text{\tiny cell}} - \text{RT/ nF In } [C]^{\circ} [D]^{\text{d}} / [A]^{\text{a}} [B]^{\text{b}}$

 $E_{\tiny cell} = E^{\circ}_{\tiny cell} - 2.0303 \text{ RT} / nF \text{ log } [C]^{\circ} [D]^{d} / [A]^{a} [B]^{b}$

 $E_{cell} = E^{\circ}_{cell} - 0.0591 / n log [C]^{c} [D]^{d} / [A]^{a} [B]^{b} at 298K$

ELECTROLÝTIC CELL

The electrolytic cell converts electrical energy to chemical energy. Here the electrodes are dipped in an electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation take place.

For example, in the electrolysis of molten sodium chloride, sodium chloride is melted (above 801°C), two electrodes are inserted into the melt, and an electric current is passed through the molten salt. The chemical reaction that takes place at the electrodes are:

• Sodium-ion migrates to the cathode, where sodium ion gains one electron and reduce to sodium metal.

 $Na^{+} + e^{-} \rightarrow Na$

• Chloride ions migrate towards the anode where it loses one electron and gets oxidised to chlorine gas.

 $CI^{-} \rightarrow 1/2 CI_2 + e^{-}$

The overall reaction is the breakdown of sodium chloride into its elements

 $2NaCl \rightarrow 2Na(s) + Cl_2(g)$



Preferential discharge of ions: When there are more than one cations or anion the process of discharge becomes competitive in nature. For example, in the electrolysis of NaCl solution, apart from Na⁺ and Cl⁻ions the solution of sodium chloride also contains H⁺ and OH⁻ ions due to ionisation of water. When the potential difference is applied between the two electrodes, Na⁺ and H⁺ ions move towards the cathode and Cl⁻ and OH⁻ ions move towards the anode. At cathode H⁺ ions get reduce in preference to giving hydrogen gas because hydrogen has a higher reduction potential than sodium. Similarly, at the anode, Cl⁻ ions are oxidised in preference to OH⁻ to give chlorine gas.



Faraday's Law of Electrolysis

The relationship between the quantity of electric charge passed through an electrolyte and the amount of substance deposited at the electrodes was given by Faraday in 1834, in the form of the law of electrolysis.

Faraday's First Law

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W is the mass of the substance deposited by passing Q coulomb of charge then according to this law:

 $W \propto Q$

Now, $Q = I \times t$

 $W \propto I \times t$

 $W = z \times I \times t$

Where Z is a constant known as electrochemical equivalent and is characteristic of a substance deposited.

Faraday's constant(F) – It is the charge possessed by 1 mole of electrons and it is equal to 96500 coulombs(approx.). In terms of Faraday's constant the number of gram equivalent of electrolyte discharged at an electrode is equal to the Faraday's passed

W = E X Q / 96500

Faraday's Second Law

When the same quantity of charge is passed through different electrolytes, then the mass of different substance deposited at the respective electrodes will be in the ratio of their equivalent masses.

Mathematically it is represented as;

 $W_1 / W_2 = Z_1 / Z_2$

Where W_1 and W_2 are the weight of two substances which are deposited at their respective electrodes and Z_1 and Z_2 are their respective equivalent weight.

SOLVED PROBLEMS:

1. Given that,

Fe²⁺/ Fe = -0.44 v, Ni⁺²/ Ni = 0.25 v

 $Ag^{+}/Ag = 0.80 v, Cu^{+2}/Cu = 0.34 v$

Which of the following reactions under standard condition will not take place in the specified direction.

 $Ni^{2}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2}(aq)$

 $Cu(s) + 2 \operatorname{Ag}^{\scriptscriptstyle +}(aq) \rightarrow Cu^{\scriptscriptstyle +2}(aq) + 2 \operatorname{Ag}(s)$

 $Cu(s) + 2H^{*}(aq) \rightarrow Cu^{*2} + H_{2}(g)$

 $Fe(s) + 2H^{*}(aq) \rightarrow Fe^{+2}(aq) + 3H_{2}$

Solution:

Option a and c

 $Ni^{+2}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{+2}(aq)$

 $E^{\circ}_{cell} = 0.25 - 0.34$

= -0.11v

Reaction is not feasible (negative E[°]_{cell})

 $Cu(s) + 2 \operatorname{Ag}^{+}(aq) \rightarrow Cu^{+2}(aq) + 2 \operatorname{Ag}(s)$

 E°_{cell} =0.80 - 0.34 = 0.46 v

Reaction is feasible(positiveE°_{cell})

 $Cu(s) + 2H^{+}(aq) \rightarrow Cu^{+2} + H_{2}(g)$

 $E^{\circ}_{cell} = 0 - 0.34 = -0.34 v$

Reaction is not feasible (negativeE°_{cell})

 $Fe(s) + 2H^{+}(aq) \rightarrow Fe^{+2}(aq) + 3H_{2}$

 $E^{\circ}_{cell} = 0 - (-0.44) = 0.44 \text{ v}$

Reaction is feasible(positive E°_{cell})

2. The emf of a cell corresponding to the reaction, $Zn + 2H^{+}(aq) \rightarrow Zn^{+2}(0.1M) + H_{2}(g)$ 1 atm is 0.30 v at 25 ° C. Write the half cell reactions and calculate the pH of the solution at the hydrogen electrode. ($E^{0}_{cell} = -0.76 v$)

Solution :

 $E_{cell}^{\circ} = 0 - (-0.76) = 0.76 \text{ v}$

Applying the Nernst equation,

 $E_{cell} = E_{cell}^{\circ} - 0.0591 / 2 \log [zN^{+2}][H2] / [H]^{+}$ $0.30 = 0.76 - 0.0591 / 2 \log 0.1 \times 1 / [H^{+}]^{2}$ $\log 0.1 / [H^{+}]^{2} = 2 \times 0.46 / 0.0591$ $\log 0.1 - \log [H^{+}]^{2} = 15.56$ $2 \text{ pH} = 15.56 - \log 0.1$ pH = 16.56 / 2 = 8.28

3. The solution of metal of atomic mass X was electrolyzed for 1 hour with a current of 0.25 ampere. The mass of metal deposited was 0.295g. Find the metal X if its valency is 2.

Solution:

Given, I = 0.25 ampere, t= 1 hr = 60 x 60 = 3600s

 $Q = I \times t$

 $Q = 0.25 \times 3600$

= 900 coulombs

Therefore, 900 coulombs of electricity deposit = 0.295

96500 coulomb of electricity deposit = 0.295 X 96500 / 900 = 31.63g

Valency of metal = atomic mass / equivalent mass

Atomic mass of metal $X = 31.63 \times 2 = 63.26g$

Therefore, the metal X is copper.

ELECTRICAL RESISTANCE & CONDUCTANCE

<u>**Resistance** (R)</u>: The tendency of a material to stop the flow of current is known as resistance. It is measured in ohms (Ω).

According to Ohm's law, the resistance offered by a substance is directly proportional to its length (/), but inversely proportional to its cross sectional area (A).



In case of electrolytic solutions, 'I' represents the distance between two electrodes and the 'A' is the cross sectional area of the electrodes.

The above equation can also be written as:

$$R = \rho \frac{l}{A}$$
 Equation (1)

Where ρ is the proportionality constant and is known as specific resistance or resistivity.

If $A = 1 \text{ cm}^2$ and I = 1 cm, then $R = \rho$.

Therefore, the specific resistance can be defined as follows:

<u>Specific resistance or resistivity (ρ)</u>: It is the resistance offered by a material or solution occupying one cm³ volume.

It is measured in:

ohm. cm (in C.G.S system)

or

ohm. m (in S.I system)

Its unit can be derived as follows:

$$\rho = \mathrm{R}.\frac{\mathrm{A}}{l} = ohm.\frac{cm^2}{cm} = ohm.cm$$

<u>Conductance (G)</u>: It is the tendency of a material to allow the flow of current through it. It is the reciprocal of resistance.

It is measured in $ohm^{-1} = mho = Siemens$.

Conductance (G) =
$$\frac{1}{\text{Resistance (R)}}$$

By substituting, R from equation (1):

$$G = \frac{1}{\rho} \cdot \frac{A}{l} = \kappa \cdot \frac{A}{l}$$
 equation (2)

Where

$$\kappa = \frac{1}{\rho} = \text{ specific conductance (or) conductivity}$$

From the equation (2),

$$\kappa = G_{\cdot} \frac{l}{A}$$

If A = 1 cm² and I = 1 cm, then κ = G.

Therefore the specific conductance can be defined as:

<u>Specific conductance or conductivity (κ)</u>: It is the conductance of a material or solution between two electrodes of cross sectional area 1 cm² and separated by 1 cm distance.

Note that above solution is occupying one cm³ volume.

It is measured in:

 ohm^{-1} . cm⁻¹ = mho. cm⁻¹ (C.G.S system)

or

Siemens. m⁻¹ (S.I system)

* The specific conductance depends on the nature of substance or the electrolyte.

* It increases with increase in concentration of the electrolytic solution since the number of ions per unit area increases.

<u>Cell constant (G*)</u>: The ratio of the distance between the electrodes, *I* to the cross sectional area, A of the electrodes is known as cell constant.

cell constant (G*) =
$$\frac{l}{A}$$

The cell constant can be determined by using following relations which can be derived easily from expressions discussed above.

$$\mathbf{G}^* = \frac{l}{\mathbf{A}} = \frac{R}{\rho} = \frac{\kappa}{\mathbf{G}} = R\kappa = \frac{1}{\mathbf{G}.\rho}$$

Based on electrical conductivity, the materials are divided into two types as follows:

1) <u>Insulators</u>: The substances which resist the flow of electric current through them are called insulators. They do not have free electrons or freely moving charged particles.

E.g. Organic polymers (like plastics), glass, diamond, quartz etc.,

2) <u>Conductors</u>: The substances which allow the flow of electricity through them with little resistance are known as conductors.

They are again divided into:

i) Metallic or electronic conductors: The conductors which conduct the electricity through the electrons.

E.g. All metals, Graphite etc.

In case of metallic conductors;

* No chemical reaction occurs during the conduction of electricity.

* Conductivity decreases with increase in temperature due to vibrational disturbances.

ii) <u>Electrolytes</u>: The substances which furnish oppositely charged ions for the conduction of electricity.

E.g :- NaCl, KCl, CH₃COOH, HCl etc.

In case of electrolytes;

* There is flow of ions towards the oppositely charged electrodes.

* During conduction of electricity through electrolytes, oxidation occurs at anode whereas reduction occurs at cathode i.e., a chemical reaction occurs.

* The conductivity increases with increase in temperature as the extent of ionization increases.

The electrolytes undergo dissociation to furnish ions either in molten state or in aqueous solutions. Depending on the extent of ionization (or dissociation) in water, the electrolytes are further divided into:

a) <u>Strong electrolytes</u>: Undergo complete ionization in water.

E.g. NaCl, KCl, K₂SO₄, HCl, H₂SO₄, NaOH, NaNO₃ etc.

b) Weak electrolytes: Undergo partial ionization in water.

E.g. HF, CH₃COOH, NH₄OH, HCOOH etc.

<u>Non-electrolytes</u>: The substances which do not furnish ions for electrical conduction are called nonelectrolytes.

E.g : urea, glucose, sucrose etc.

Equivalent conductivity (Λ): The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity. It is denoted by Λ .

Let us consider, the V cm³ of solution containing one equivalent of an electrolyte. Its conductance is equal to equivalent conductance, Λ .

Also we know that the conductance shown by 1 cm³ solution (between two electrodes of cross sectional area 1 cm² and separated by a distance of 1 cm) containing this electrolyte is called specific conductance, κ .

i.e.,

The conductance of V cm³ ----- Λ

The conductance of 1 cm³ ------ κ

Therefore:

Λ = κ.V ------ equation (3)

We know that the normality (N) of a solution is given by the equation:

$$N=\frac{n_e}{V(in \ cc)} \ x \ 1000$$

For above electrolytic solution, no. of equivalents, $n_e = 1$.

Hence

$$V(in cc) = \frac{1000}{N}$$

By substituting the above value in the equation (3), we can now write:

$$\triangle = \kappa . \frac{1000}{N}$$

Units of Λ :



= cm^2 .ohm⁻¹. equiv⁻¹ = cm^2 . mho. equiv⁻¹ or m^2 . Siemens. equiv⁻¹

<u>Molar conductivity</u> $(\Lambda_m \text{ or } \mu)$: The conductance of that volume of solution containing one mole of an electrolyte is known as molar conductivity. It is denoted by Λ_m or μ .

It is related to specific conductance, κ as:

μ = к.V

or

$$\mu = \kappa . \frac{1000}{M}$$

Where

M = molarity of the electrolytic solution.

Units of μ :

= cm² .ohm⁻¹. mol⁻¹ = cm² . mho. mol⁻¹ or m² . Siemens. mol⁻¹

The relation between equivalent conductance, Λ and molar conductance, μ can be given by:

$\mu = \Lambda x$ equivalent factor of the electrolyte

The equivalent factor of the electrolyte is usually the total charge on either anions or cations present in one formula unit of it. It may be equal to basicity in case of acids or equal to acidity in case of bases.

<u>**Temperature:**</u> The conductance of an electrolyte solution increases with increase in the temperature due to increase in the extent of inonization.

Nature of electrolyte:

* The strong electrolytes undergo complete ionization and hence show higher conductivities since they furnish more number of ions.

* Whereas weak electrolytes undergo partial ionization and hence show comparatively low conductivities in their solutions.

Ionic size & mobility:

* The ionic mobility decreases with increase in its size and hence conductivity also decreases.

E.g. In molten state, the conductivities of lithium salts are greater than those of cesium salts since the size of Li^+ ion is smaller than that of Cs^+ ion.



* However, in aqueous solutions the extent of hydration affects the mobility of the ion, which in turn affect the conductivity. Heavily hydrated ions show low conductance values due to larger size.

E.g. In aqueous solutions Li⁺ ion with high charge density is heavily hydrated than Cs⁺ ion with low charge density. Hence hydrated Li⁺ bigger than hydrated Cs⁺. As a result, lithium salts show lower conductivities compared to those of cesium salts in water.



The nature of solvent and its viscosity:

* The ionic mobility is reduced in more viscous solvents. Hence the conductivity decreases.

Concentration:

* The specific conductance (κ) increases with increase in concentration of solution as the number of ions per unit volume increases.

* Whereas, both the equivalent conductivity and molar conductance increase with **decrease** in concentration (i.e. upon dilution) since the extent of ionization increases.

Explanation: Since the concentration decreases, one can expect decrease in equivalent conductivity due to decrease in available number of ions per unit volume. However the increase in volume (V) factor more than compensates this effect. The volume must be increased in order to get one equivalent of electrolyte since the concentration is decreased. Hence the net effect is increase in equivalent conductivity.

Limiting equivalent conductivity (Λ_o):

The equivalent conductivity reaches a maximum value at certain dilution and does not change upon further dilution (i.e., by adding solvent further). This concentration is also termed as infinite dilution.

The equivalent conductivity at infinite dilution is known as the limiting equivalent conductivity (Λ_o). At this dilution, the ionization of even the weak electrolyte is complete.

However at infinite dilution (i.e., when concentration approaches zero) the conductivity of the solution is so low that it cannot be measured accurately. Therefore the limiting equivalent conductivity of an electrolyte is calculated by using Debye-Huckel-Onsagar equation as explained below.

<u>Conductance ratio (α)</u> : The ratio of the equivalent conductance at given concentration, Λ_c to that at infinite dilution, Λ_o is called conductance ratio, α .

$$\alpha = \frac{\Lambda_c}{\Lambda_o}$$

For weak electrolytes, the ' α ' is also called as degree of ionization.

It is possible to determine the equivalent conductivities of electrolytes in water at given concentration by using Debye-Huckel-Onsagar equation.

$$\Lambda_{\rm c} = \Lambda_{\rm o} - A\sqrt{\rm c}$$

Where

 Λ_c = equivalent conductivity at given concentration.

 Λ_o = equivalent conductivity at infinite dilution.

c = concentration

A = a constant =
$$\frac{82.4}{(DT)^{\frac{1}{2}}} + \frac{8.2 \times 10^{5}}{(DT)^{\frac{3}{2}}} \Lambda_{o}$$

D = Dipole moment of water

T = Absolute temperature

A straight line with negative slope is obtained when the equivalent conductivity values (Λ_c) of strong electrolytes are plotted against square roots of different concentrations (Vc). The equivalent conductivity at infinite dilution (Λ_o) can be determined by extending this straight line to zero concentration.



However the equivalent conductivity of weak electrolytes increases steeply at very low concentrations (see the above graph) and hence their limiting values (Λ_o) cannot be determined by extrapolating the Λ_c to zero concentration.

Kohlrausch's Law States that



"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations. Thus,

$$\lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

Where,

 $\lambda_{eq}^{\infty} = Equivalence \ Conductivity \ at \ Infinite \ Dilution$ $\lambda_{c}^{\infty} = Conductivity \ of \ Cation$ $\lambda_{a}^{\infty} = Equivalence \ Conductivity \ of \ Anion$

According to Kohlrausch'slaw. "Conductivity of ions is constant at infinite dilution and it does not depend on nature of co-ions."

For A_xB_y type electrolyte,

$$A_x B_y \xrightarrow{H_2 O} x A^{+y} + Y B^{-x}$$
$$\lambda_{eq}^{\infty} = \frac{1}{z} \lambda_B^{\infty} + \frac{1}{z^-} \lambda_A^{\infty}$$

Here Z^{+} and Z^{-} are the charges present on cation and anion.

$$\lambda_m^\infty = m\lambda_c^\infty + n\lambda_a^\infty$$

Here m and n are the number of moles of cations and anions.





• Calculation of Molar Conductivity at Infinite Dilution For Weak Electrolytes

As already mentioned, the molar conductivity of weak electrolytes at infinite dilution cannot be determined experimentally, firstly because the conductance of such a solution is low and secondly because dissociation of such an electrolytes is not completed even at high dilutions.

The molar conductivity of such an electrolyte at infinite dilution can be calculated using **Kohlrausch's law**

 $\begin{array}{l} \wedge_m^{\infty} \mbox{ or } \mu^{\infty} &= \mbox{ Molar conductance at infinite dilution} \\ &= m\lambda_+^{\infty} + n\lambda_-^{\infty} \end{array}$ Where m and n are number of ions formed. $\mu_{Al_2(SO_4)_5}^{\infty} = 2\lambda_{Al^{5+}}^{\infty} + 3\lambda_{SO_4^{2-}}^{\infty} = 6 \wedge_{Al_2(SO_4)_5}^{\infty} \\ \lambda_{BaCl_7} = \lambda_{Ba^{2+}}^{\infty} + 2\lambda_{Cl^{-}}^{\infty} = 2 \wedge_{BaCl_7}^{\infty} \end{array}$

• Calculation of Degree of Dissociation

According to Arrhenius theory of electrolytic dissociation, the increase in the molar conductivity with dilution is entirely due to the increase in the dissociation of the electrolyte; the molar conductivity at infinite dilution being maximum because the dissociation is almost complete.

Thus if λ_m^c is the molar conductivity of a solution at any concentration C and λ_m^∞ the molar conductivity at infinite dilution (i.e. zero concentration), we will have

$$\alpha = \frac{no.of \ dissociated \ ions}{no. \ of \ total \ ions \ present} = \frac{\lambda_m^c}{\lambda_m^{\infty}}$$

However, this relationship is found to hold good only for weak electrolytes. The value of λ_m^{∞} for the weak electrolytes can be calculated using **Kohlrausch's law**, as discussed already in the first application.

Calculation of Dissociation Constant For a Weak Electrolyte

Knowing the degree of dissociation (as calculated above) the dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated

Using the formula

$K_c =$	$C\alpha^2$	
	_	$1 - \alpha$

<u>Calculation of Solubility of Sparingly Soluble Salt</u>

Salts such as AgCl. BaSO₄, PbSO₄ etc which dissolve to a very small extent in water are called sparingly soluble salts.

A they dissolve very little, their solutions are considered as infinitely dilute. Further as their solutions are saturated, their concentration is equal to their solubility.

Thus by determining the specific conductivity (K) and the molar conductivity of such solutions, we have

$$\lambda_m^o = \kappa \times \frac{1000}{Molarity} = \kappa \times \frac{1000}{Solubility}$$
$$\Rightarrow Solubility = \frac{\kappa \times 1000}{\lambda_m^o}$$

SOME IMPORTANT QUESTIONS AND TOPICS:

1. Explain the function of a galvanic cell?

Answer:

A galvanic cell is an electrochemical cell, used to supply electrical current by making the transfer of electrons through a redox reaction. During redox reactions, the galvanic cell converts chemical energy into electrical energy by transferring energy between the electrons.

2. How does electrolytic cell works?

Answer:

An electrolytic cell converts electrical energy into chemical energy. In this cell redox reaction is not spontaneous, and electrical energy required to initiate the reaction.

3. What is a half-cell or electrode?

Answer:

It is a metal used to conduct electrons in a cell.

4. What is cell potential?

Answer:

In a cell, the potential difference between the two electrodes is called cell potential.

5. What is the electrochemical series? What is the potential of S.H.E?

Answer:

Electrochemical series: The various elements are arranged in the increasing order of standard reduction potential.

Potential of S.H.E: Standard hydrogen electrode potential is zero.

The tendency of an electrode to lose electrons is called oxidation potential, while tendency to gain electrons is called reduction potential.

EMF of a due cell is a measure of the free energy change which determines the tendency of the overall reaction to occur.

$$E^{\circ}_{cell} = \begin{bmatrix} Standard reduction \\ potential of cathode \end{bmatrix} \\ - \begin{bmatrix} Standard oxidation \\ potential of anode \end{bmatrix} \\ E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{right} - E^{\circ}_{left}$$

If the EMF comes out to be positive, the reaction takes place.

NERNST EQUATION

Dependence of electrode potential and EMF on concentration and temperature.

For electrode potential;

$$M^{n+}_{(aq)} + ne^{-} \longrightarrow M_{(s)}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$
or
$$E = E^{\circ} - \frac{2 \cdot 303 RT}{nF} \log \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

For solids, liquids or gases at 1 atom.

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

GIBBS FREE ENERGY CHANGE:

Gibbs free energy change in an electrochemical reaction can be expressed as the equivalent of the potential difference.

$$-\Delta G = nFE$$
$$E = \frac{-\Delta G}{nF}$$

CONCENTRATION CELL

Concentration cells are electrochemical cells in which the emf arises from a transfer of material from one electrode to another due to a concentration difference between the two.

In general for concentration cells.

$$E_{\text{cell}} = -(0.059/2) \log (a_2/a_1)$$

 $E^0 = 0.$

ELECTROLYSIS

The process of decomposition of an electrolyte by passage of electricity through its aqueous solution or mole tn state.

Electrodes used in the electrolysis of different electrolytes are of twootypes, inert electrodes and active electrodes.

Faraday First Law of Electrolysis

The mass of primary products formed at an electrode by electrolysis is directly proportional to the quantity of electricity passed.

$$m \propto It \text{ or } m = ZIt$$

where

- I = current in amperes
- t = time in seconds
- m = mass of the primary product in grams
- Z = constant of proportionality (electrochemical equivalent). It is the mass of a substance liberated by 1 ampere-second of a current (1 coulomb).

Faraday Second Law of Electrolysis

The masses of different primary products formed by equal amounts of electricity are proportional to the ratio of molar mass to the number of electrons involved with a particular reaction.

$$m_1 \propto rac{M_1}{n_1} \propto Z_1$$

 $m_2 \propto rac{M_2}{n_2} \propto Z_2$

 $m_1, m_2 = \text{masses of primary product in grams}$ $M_1, M_2 = \text{molar masses (g.mol^{-1})}$

 n_1, n_2 = number of electrons

 Z_1, Z_2 = electrochemical equivalent.

Combining the first law and the second law, as in equation (3.1)

m = ZIt

Conductance

In relation to electrolytes, the term conductance (C) is used more frequently than resistance. Conductance implies the case with which electric current can flow through a conductor. It is defined as the reciprocal of resistance.

Conductance =
$$1/R$$
.

Specific Conductance

Specific conductance = Conductance x Cell constant

where

Molar Conductance

$$\mu = k \times V$$

Equivalent Conductance

Equivalent conductance = (Molar conductance) / n

Where n = (Molecular mass)/(Equivalent mass)

Kohlrausch Law

The molar conductivity of an electrolyte at infinite dilution can be expressed as the sum of the ionic conductivities of cations and anions each multiplied by the number of ions present in one formula unit of the electrolyte.

 $\Lambda^{\infty}_m \; = \; x \times \Lambda^{\infty}_{\text{cation}} + y \times \Lambda^{\infty}_{\text{anion}}$

Applications of Kohlrausch Law

1. In the calculation of molar conductivity at infinite dilution for weak electrolyte.

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

2. In the calculation of degree of dissociation.

$$\alpha = \frac{\text{Molar conductivity at conc. C}}{\text{Molar conductivity at infinite dilution}}$$
$$= \frac{\Lambda^{c}_{m}}{\Lambda^{\infty}_{m}}$$

3. In the calculation of solubility of a sparingly soluble salt. As the solution is saturated but infinitely dilute.

Molarity = solubility

Hence,

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}, \text{ we get}$$

Solubility (moles L⁻¹) = $\frac{\kappa \times 1000}{\Lambda_m^{\circ}}$
Also $\lambda_{\text{cation}}^{\circ} = u_{\text{cation}}^{\circ} \times \text{Faraday}$
 $\lambda_{\text{anion}}^{\circ} = u_{\text{anion}}^{\circ} \times \text{Faraday}$

Where 'u' are ionic mobilities at infinite dilution.

Electrochemistry is the study of chemical processes which lead to electrons moving. This movement of electrons is called electricity, which can be generated in a reaction known as an oxidation-reduction reaction by electrons from one element to another.

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