

Electrochemistry

C1 Conductance :

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a).

$$R \propto \frac{l}{a}$$

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

where ρ is a constant depending upon the nature of the material and is called specific resistance or resistivity of the material.

Specific resistance is the resistance of one centimetre cube of a material.

The reciprocal of the specific resistance, $\left(\frac{1}{\rho}\right)$ is called specific conductance or conductivity.

Conductivity is the conductance of one cm cube of a material.

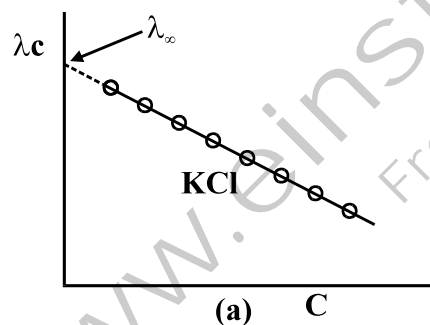
taking $\frac{1}{\rho} = K$ (specific conductance), $\frac{1}{R} = C$ (conductance) $K = C \times \left(\frac{l}{a}\right) \dots \left(\frac{l}{a}\right)$ is called cell constant, l = distance between two electrodes, a = cross-sectional area of electrodes

C2A Equivalent Conductance :

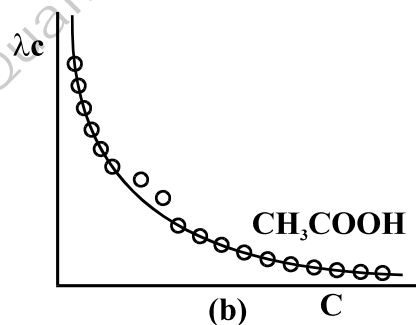
It is defined as the conducting power of all the ions present in one gram equivalent of an electrolyte in a given solution. At concentration N (in gm equivalent L^{-1}) equivalent conductance is denoted by λ_{eq}

(equivalent conductance at concentration c) $\lambda_c = \frac{k \times 1000}{N}$; units: $ohm^{-1} cm^2, eq^{-1}$

Equivalent conductance increases with dilution. When the solution is infinitely diluted the equivalent conductance is denoted as λ_{∞} . The λ_{∞} can be determined by extrapolation method, in which graph between λ_c and C is extended to zero concentration.



for strong electrolyte extrapolation is possible



for weak electrolyte graph is not linear in low concentration range. Thus extrapolation is not possible

C2B Molar Conductance :

It is defined as the conducting power of all the ions present in one mol of an electrolyte in a given solution.

$$\lambda_m = \frac{k \times 1000}{M} \text{ unit : } ohm^{-1} cm^2 mol^{-1}$$

λ_{eq} and λ_m both increases with decrease in concentration.

C2C Kohlrausch's Law :

At infinite dilution, when ionisation is complete, each ion makes its contribution towards equivalent conductance of the electrolyte and at infinite dilution equivalent conductance is given by the sum of the equivalent conductances of the contributing ions.

Thus for $A_x B_y$, $\lambda_m^\infty = x\lambda_a^\infty + y\lambda_b^\infty$

where, λ_a^∞ is the molar conductance of A (say cation) and λ_b^∞ that of B (say anion) at infinite dilution.

(degree of dissociation of weak electrolyte) $\alpha = \frac{\lambda_m^c}{\lambda_m^\infty}$

Practice Problems :

1. Molar conductance at infinite dilution of $BaCl_2$, H_2SO_4 and HCl aq. solution are x_1 , x_2 and x_3 respectively. Molar conductance of $BaSO_4$ solution is :

(a) $x_1 + x_2 - x_3$ (b) $x_1 - x_2 - x_3$ (c) $x_1 + x_2 - 2x_3$ (d) $x_1 - 2x_2 + x_3$

[Answers : (1) c]

C3A Electrical Conductors :

All substances which can allow the flow of electricity are known as electrical conductors. Mainly we have two types of electrical conductors which are given below :

1. **Electronic Conductor :** They are those conductors in which the flow of electricity is due to the movement of loosely bonded electrons in their own standard state. In this case, the movement of matter does not take place during the flow of electricity. For example :

(a) all metals in their elemental state (b) graphite and (c) alloys

2. **Electrolytical Conductors :**

In this case of electrolytic conductors, the flow of electricity is due to the movement of ions i.e., here actual transport of matter takes place.

C3B Electrolytes :

Electrolytes may be pure substances (e.g., salts, acids or bases) in their fused states or more commonly they are aqueous solutions of these compounds or they are sometimes pure liquid.

There are two types of electrolytes :

- (a) **Strong Electrolyte :** The compounds which are 100% ionised at any dilution, are treated as strong electrolytes, for e.g., $HClO_4$, HI , HBr , HCl , H_2SO_4 , HNO_3 , $NaOH$, KOH , $NaCl$ etc.
- (b) **Weak Electrolyte :** The compounds which are less or feebly ionised (at lower dilution) are treated as weak electrolytes.

All weak acids, weak bases or the salts having less ionic character are treated as weak electrolytes e.g. CH_3COOH , $COOH$, H_2CO_3 , $Mg(OH)_2$, $Zn(OH)_2$ etc.

**C4A Electrolysis :**

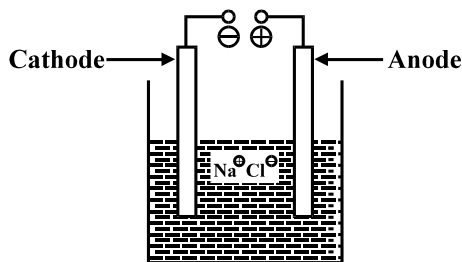
Electrolysis is a process which involves a chemical change at the electrodes when electricity is passed through an electrolyte.

“Electrolysis is a process which involves a chemical change at the electrodes when electricity is passed through an electrolyte”.

It was found experimentally that the positive ions from the electrolyte are attracted on the negative electrode (cathode) and get reduced. Similarly, the negative ions are attracted on the positive electrode (anode) and are oxidised.

Hence due to electrolysis, the species under consideration gets decomposed at cathode and anode.

Faraday has established a relationship between the amount of electricity passes through the electrolyte and the amount of chemical change occurring at an electrode. This relationship is known as Faraday's law of electrolysis.



Electrolytic Cell
(having aq. NaCl Sol.)

C4B Faraday's Laws of Electrolysis :

First Law of Electrolysis :

The amount of chemical change produced is proportional to the quantity of electric charge passing through an electrolysis cell.

Suppose after passing Q coulombs of electricity (amount of electricity), W amount of a substance has appeared (or disappeared).

Thus $W \propto Q$

$W = ZQ$ (Where Z is a constant, which is known as electrochemical equivalent)

$W = Z i t$ ($Q = i t$, where i is current passed for t seconds)

* Also $Q = nF$ (F is a faraday constant i.e., it is charged carried by one mole of electron, where n is no. of mole of electrons transfer takes place).

Second Law of Electrolysis :

When same amount of amount of electricity is passed through different electrolytes, the weight of the substance appeared or disappeared by any electrode is always directly proportional to the equivalent weight of the substance appeared or disappeared.

According to the second law of electrolysis $W \propto E$, in general, $\frac{W_1}{E_1} = \frac{W_2}{E_2}$

C4C Relation between Electrochemical Equivalent and Equivalent Weight :

By the use of above two laws $E \propto Z$

Thus, $E = FZ$ (where F is Faraday's constant, E is equivalent weight and Z is electrochemical equivalent).

If we combine first and second law of electrolysis then following expressions takes place :

$$n_{eq} = \frac{W}{E} = \frac{Q}{F} \text{ or } \text{mol} \times n.\text{factor} = \frac{W}{E} = \frac{It}{F}, (n_{eq, \text{oxidised}} = n_{eq, \text{reduced}})$$

Practice Problems :

- The density of Cu is 8.94 g cm^{-3} . The quantity of electricity needed to plate an area $10 \text{ cm} \times 10 \text{ cm}$ to a thickness of 10^{-2} cm using CuSO_4 solution is
 (a) 13586 C (b) 27172 C (c) 40758 C (d) 20348 C
- The same amount of electricity was passed through two cells containing molten Al_2O_3 and molten NaCl . If 1.8 g of Al were liberated in one cell, the amount of Na liberated in the other cell is
 (a) 4.6 g (b) 2.3 g (c) 6.4 g (d) 3.2 g
- Silver is removed electrolytically from 200 mL of a 0.1 N solution of AgNO_3 by a current of 0.1 ampere. How long will it take to remove half of the silver from the solution (At. wt. of $\text{Ag} = 108 \text{ g}$)
 (a) 10 sec (b) 16 sec (c) 100 sec (d) 9650 sec
- Consider the following electrolysis
 (1) CuSO_4 (2) $\text{Fe}_2(\text{SO}_4)_3$ (3) AlCl_3 (4) AgNO_3

The quantity of electricity needed to electrolyse completely 1 M solutions of these electrolytes will be

- (a) 2F, 6F, 3F and 1F respectively (b) 6F, 2F, 3F and 1F respectively
 (c) 2F, 6F, 1F and 3F respectively (d) 6F, 2F, 1F and 3F respectively

5. Assume that during electrolysis of AgNO_3 , only H_2O is electrolysed and O_2 is formed as :



O_2 formed at N.T.P. due to passage of 2 amperes of current for 965 s :

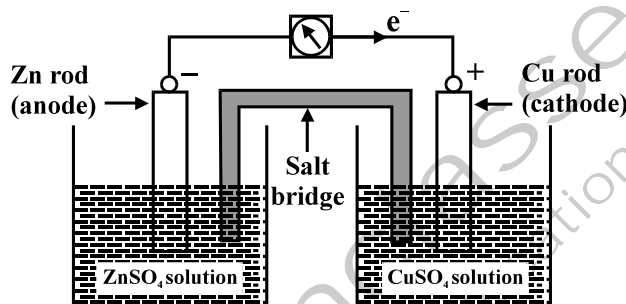
- (a) 0.112 L (b) 0.224 L (c) 11.2 L (d) 22.4 L

[Answers : (1) b (2) a (3) d (4) a (5) a]

C5A Electrochemical Cell :

A device that converts chemical energy into electrical energy. The cell is based on the principle of indirect redox reactions, i.e., the oxidation and reduction reactions takes place in different container.

The electrochemical cells (galvanic or voltaic) consists of two half cells connected with each other by means of an electric wire to allow an indirect redox reaction. Although the solutions of two half cells are in different containers, but for the continuous flow of electricity, transfer of ions from one solution to another solution are always allowed. Oxidation at anode and is a -ve electrode, reduction at cathode and is a +ve electrode. For e.g., Zn-Cu galvanic cell is represented as follows :



C5B Electrode Potential :

It is the potential difference established between the electrode and its electrolyte. It is of two types i.e., Reduction Potential and Oxidation Potential.

Reduction Potential is tendency of an electrode to receive electrons for the deposition of the solvated positive ions from its own solution. Whereas oxidation potential is the tendency of an electron to get oxidised in its own solution.

C5C E.M.F. (Electromotive Force) or Cell Potential of a Cell :

The difference between the reduction potentials of two half cells constituting the Galvanic cell is known as its cell potential (or e.m.f.) i.e.,

$$E_{\text{cell}} (\text{e.m.f.}) = (\text{Reduction Potential})_{\text{Cathode}} - (\text{Reduction Potential})_{\text{Anode}}$$

$$\text{or, } E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

For the spontaneous flow of electricity from the Galvanic cell, the e.m.f. of the cell must be positive.

C5D Concentration Effect in Voltaic Cell – Nernst Equation

Nerst equation gives a quantitative relationship between the concentration of ions and electrode potential.

For a general electrode reaction : $\text{M}^{n+} + \text{L}(\text{s}) \rightleftharpoons \text{L}^{n+} + \text{M}(\text{s})$.

$$\text{Emf}(E) = E^0 - 2.303 \frac{RT}{nF} \log \frac{[\text{L}^{n+}]}{[\text{M}^{n+}]}$$

Practice Problems :

- By how much will the potential of half-cell $\text{Cu}^{2+} | \text{Cu}$ change if the solution is diluted to 100 times at 298 K ?
 - Increase by 59 mV
 - Decreases by 59 mV
 - Increase by 29.5 mV
 - Decreases by 29.5 mV
 - Which of the following changes will increase the EMF of the cell :
 $\text{Co(s)} | \text{CoCl}_2(\text{M}_1) || \text{HCl}(\text{M}_2) | \text{Pt}(\text{H}_2, \text{g})$
 - increase in the volume of CoCl_2 solution from 100 mL to 200 mL
 - increase M_2 from 0.01 M to 0.50 M
 - increase the pressure of the $\text{H}_2(\text{g})$ from 1.00 to 2.00 atm
 - increase M_1 from 0.01 M to 0.50 M
 - The measured voltage of the following cell is 0.9 V at 25°C. $\text{Pt}, \text{H}_2(1 \text{ atm}) | \text{H}^+(\text{aq}) || \text{Ag}^+(1.0 \text{ M}) | \text{Ag}$
 If $E_{\text{Ag}^+ / \text{Ag}}^0 = 0.80 \text{ V}$. The pH of the aqueous solution of H^+ ion is
 - 1.69
 - 2.50
 - 5.20
 - 9.69
- [Answers : (1) b (2) b (3) a]

C6 Application of Nernst Equation

- Electrical work :

$$\Delta G = -nFE \text{ (in a given state), } \Delta G^0 = -nFE^0 \text{ (in a standard state), } \Delta G^0 = -RT \ln K \text{ aq}$$

$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$ (when different no. of element are involved, if equal no of electrons are involved)
 $E_1^0 + E_2^0 = E_3^0$.

- At equilibrium $E = 0$ and $Q = K$ (equilibrium constant)

$$E^0 = \frac{RT}{nF} \ln K = \frac{0.059}{n} \log_{10} K$$

- For standard hydrogen electrodes (SHE)

$$E_{(\text{SHE})}^0 = 0.00 \text{ V.}$$



SHE, calomel-electrode and silver, silver-chloride electrodes are used as reference half cells.

$$E_{\text{H}_2/\text{H}^+} = 0.059 \text{ p}^{\text{H}}$$

- Concentration cells



$$E_{\text{cell}} = \frac{0.059}{n} \log \frac{\text{C}_2}{\text{C}_1} \dots\dots [\text{C}_1 > \text{C}_2]$$



$$E_{\text{cell}} = 0.059 \log \frac{\text{P}_1}{\text{P}_2} \dots\dots [\text{P}_1 > \text{P}_2]$$

Practice Problems :

- E^0 for the cell $\text{Zn} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$ is 1.10 V at 25°C. The equilibrium constant for the reaction $\text{Zn} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Cu} + \text{Zn}^{2+}(\text{aq})$ is of the order of
 - 10^{-37}
 - 10^{37}
 - 10^{+18}
 - 10^{17}

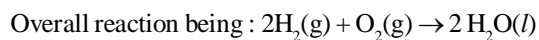
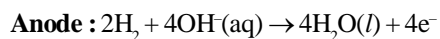
2. $\text{Pt}(\text{H}_2)_{p_1} | \text{H}^+(1\text{M}) | \text{Pt}(\text{H}_2)_{p_2}$ (where p_1 and p_2 are pressures) cell reaction will be spontaneous if :
- (a) $p_1 = p_2$ (b) $p_1 > p_2$
 (c) $p_2 > p_1$ (d) $p_1 = p_2 = 1\text{atm}$
3. The standard reduction potential of $\text{Cu}^{2+} | \text{Cu}$ and $\text{Cu}^{2+} | \text{Cu}^+$ are 0.337 and 0.153 V respectively. The standard electrode potential of $\text{Cu}^+ | \text{Cu}$ half cell is
- (a) 0.184 V (b) 0.827 V (c) 0.521 V (d) 0.490 V
- [Answers : (1) b (2) b (3) c]

C7A Batteries

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy.

1. **Primary Batteries :** In primary batteries, the reaction occurs only once and battery then becomes dead after use over a period of time and cannot be reused again, for e.g., :
- (a) **Dry cell :** Which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and ZnCl_2 . The electrode reactions are complex, but they can be written approximately as follows :
- Anode :** $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
Cathode : $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO}(\text{OH}) + \text{NH}_3$
 Ammonia produced in the reaction forms complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.
- (b) **Mercury cell :** Suitable for the low current devices like hearing aids and camera etc. consists of zinc-mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO . The electrode reactions for the cell are given below :
- Anode :** $\text{Zn}(\text{Hg}) + 2\text{OH}^- \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$
Cathode : $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg}(\text{l}) + 2\text{OH}^-$
2. **Secondary Batteries :** A secondary cell after use can be recharged by passing current through it in opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles, for e.g. :
- (a) **Lead storage battery :** commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.
- The cell reactions when the battery is in use are given below :
- Anode :** $\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
Cathode : $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
 i.e., overall cell reaction consisting of cathode and anode reaction is :
 $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
 On charging the battery the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.
- (b) **Nickel-cadmium cell :** Which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is :
- $\text{Cd}(\text{s}) + 2\text{Ni}(\text{OH})_3(\text{s}) \rightarrow \text{CdO}(\text{s}) + 2\text{Ni}(\text{OH})_2(\text{s}) + \text{H}_2\text{O}(\text{l})$
3. **Fuel Cells :** Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity.

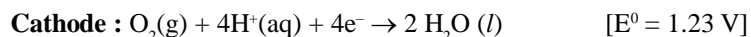
It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cell that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy are called **fuel cells**. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts.



C7B Corrosion

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as an anode and we can write the reaction :



The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as **rust in the form of hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)** and with further production of hydrogen ions.

Prevention of corrosion : one of the simplest method of preventing corrosion is to prevent the surface of the metallic object to come incontact with atmosphere. This can be done by covering the surface by paint or by some chemicals (e.g. bisphenol). Other simple method is to cover the surface by other metals (Sn, Zn etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn etc.) which corrodes itself but saves the object.