

17.

ELECTROCHEMISTRY

1. INTRODUCTION

Electrochemistry is a branch of chemistry which deals with inter-conversion of chemical energies and electrical energy. We'll discuss electrolytic reactions (reactions that occur when electricity passes through solutions) as well as electromagnetic reaction (reactions that produce electric energy). Some examples of electrolytic reactions are electrolysis, electroplating, electro refining of metals, etc. Some examples of electro genetic reactions are reactions occurring in cells or batteries.

2. TERMINOLOGIES IN ELECTROCHEMISTRY

Some important terms used in Electrochemistry are as follows:

- (a) **Electrical Conductors:** Materials that allow flow of electrons are known as conductors. There are broadly two types of conductors-Electronic/Metallic and Electrolytic/Solution.

Table 17.1: Difference between Electronic Conductor and Electrolytic Conductors

	Electronic Conductors or Metallic Conductors	Electrolytic Conductors or Solution Conductors
1.	Passage of current by movement of electrons in the metallic lattice, e.g., Cu, Ag, etc.	Passage of current by ions in molten state or in aqueous solution of electrolytes, e.g., NaCl (aq) or NaCl (fused).
2.	Passage of current brings in only physical changes.	Passage of current brings in physical as well as chemical changes.
3.	It generally shows no transfer of matter.	It involves transfer of matter in the form of ions.
4.	It generally shows an increase in resistance during the passage of current due to increase in temperature. Thermal motion of metal ions hindering the flow of electrons increases with increase in temperature.	It generally shows a decrease in resistance due to decrease in viscosity of the medium and degree of hydration of ions with increase in temperature.
5.	The conducting power of metals is usually high.	The conducting power of electrolytic conductors is relatively low.

- (b) **Insulators:** Those materials which don't allow the passage of electrons are known as Insulators. For e.g. wood, wool, plastic, silk, etc.
- (c) **Electrolytes:** The substance that in solution or in the molten state, conducts electric current and is simultaneously decomposed is called an electrolyte. The extent or degree of dissociation of different electrolytes in solution is different. Electrolytes can be broadly categorized into two: Strong and Weak Electrolytes.
- (d) **Strong Electrolytes:** Substances which are largely dissociated and form a highly conducting liquid in water are strong electrolytes, e.g., **All salts (except CdBr_2 , HgCl_2), mineral acids like HCl, H_2SO_4 , HNO_3 , etc. and bases like NaOH, KOH, etc. are strong electrolytes.** The strong electrolytes are almost 100% ionized at normal dilution.

- (e) **Weak Electrolytes:** Substances which dissociate only to a small extent in aqueous solution forming low conducting liquid are weak electrolytes, e.g., **All organic acids (except sulphonic acids), inorganic acids like HCN, H_3BO_3 , etc. and bases like NH_3 , amines, etc. are weak electrolytes.**
- (f) **Electrodes:** In order to pass the current through an electrolytic conductor, two rods or plates are always needed which are connected with the terminals of a battery. These rods/plates are called Electrodes. The electrode where oxidation reaction takes place is anode and electrode where reduction takes place is cathode.

3. ELECTROLYSIS

The phenomenon in which passage of current through an electrolyte (molten or solution) brings in chemical changes involving electronation (reduction) as well as de-electronation (oxidation) of ions is known as **electrolysis**.

3.1 Preferential Discharge Theory

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged from the electrodes simultaneously but certain ions are liberated from the electrodes in preference to others. This is explained by **preferential discharge theory**. It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge potential or deposition potential. The values of discharge potential are different for different ions.

Table 17.2: Examples of preferential discharge theory

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified CuCl_2 solution	Pt	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	$2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$
Molten PbBr_2	Pt	$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	$2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{e}^-$
Sodium chloride solution	Hg	$2\text{Na}^+ + 2\text{e}^- \longrightarrow 2\text{Na}$	$2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$
Silver nitrate solution	Pt	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	$2\text{OH}^- \longrightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$
Sodium nitrate solution	Pt	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	$2\text{OH}^- \longrightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$

Illustration 1: Find the charge in coulomb on 1 g-ion of N^{3-} .

(JEE MAIN)

Sol: First determine charge on one ions of this can be calculated as product of number of electron and charge of electron. According to Avogadro's law one g of ion contains 6.02×10^{23} ions. So, charge on one g-ion of N^{3-} can be calculated by multiplying charge.

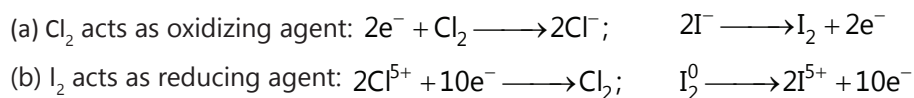
Charge on one ions of N^{3-} into Avogadro number.

Charge on one ions of $\text{N}^{3-} = 3 \times 1.6 \times 10^{-19}$ coulomb One g-ion = 6.02×10^{23} ions

Thus, charge on one g-ion of $\text{N}^{3-} = 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23} = 2.89 \times 10^5$ coulomb

Illustration 2: Explain the reaction: (a) $2\text{KI} + \text{Cl}_2 \longrightarrow 2\text{KCl} + \text{I}_2$, (b) $2\text{KClO}_3 + \text{I}_2 \longrightarrow 2\text{KIO}_3 + \text{Cl}_2$

Sol: Compound which undergoes oxidation acts as a reducing agent and compound which undergoes reduction acts as an oxidizing agent.



MASTERJEE CONCEPTS

Misconception: Electrolysis does not mean breaking up of an ionic compound into ions. An ionic compound even on dissolution in water furnishes ions.

Note: During electrolysis, oxidation-reduction occurs simultaneously. Oxidation occurs at anode whereas reduction occurs at cathode.

Nikhil Khandelwal (JEE 2009 AIR 94)

3.2 Faraday's Law of Electrolysis

The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented as the 'laws of electrolysis' by Faraday in 1834.

3.2.1 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 be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation: $W \propto Q$

$$Q = \text{current in amperes} \times \text{time in seconds} = I \times t$$

$$\text{So, } W \propto I \times t \text{ or } W = Z \times I \times t$$

Where Z is a constant, known as **electrochemical equivalent** and is characteristic of the substance deposited. When a current of one ampere is passed for one second, i.e., one coulomb ($Q = 1$), then $W = Z$.

Definition of electrochemical equivalent: Mass of the substance deposited by one coulomb of charge or one ampere current for one second.

3.2.2 Faraday's Second Law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses. Again according to first law, $W = Z \times Q$

When, $Q = 96500$ coulomb, W becomes gram equivalent mass (E).

$$\text{Thus, } E = Z \times 96500 \text{ or } Z = \frac{E}{96500}; \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

3.2.3 Faraday's Law for Gaseous Electrolytic Product

$$\text{For the gases, we use } V = \frac{ItV_e}{96500}$$

Where, V = Volume of gas evolved at STP at an electrode

V_e = Equivalent volume = Volume of gas evolved at an electrode at STP by 1 faraday charge

Example: A 40.0 amp current flowed through molten iron (III) chloride for 10.0 hours (36,000 s). Determine the mass of iron and the volume of chlorine gas (measured at 25°C and 1 atm) that is produced during this time.

Sol:

- Write the half-reaction that take place at the anode and at the cathode.



- Calculate the number of moles of electrons.

$$40.0 \text{ amps} \times 36,000 \text{ s} = 1.44 \times 10^6 \text{ C}$$

$$1.44 \times 10^6 \text{ C} \times \frac{1\text{F}}{96,485 \text{ C}} = 14.9\text{F}; \quad 14.9\text{F} \times \frac{1 \text{ mole } \text{e}^-}{1\text{F}} = 14.9 \text{ mole } \text{e}^-$$

- Calculate the moles of iron and of chlorine produced using the number of moles of electrons calculated and the stoichiometry from the balanced half-reactions. According to the equations, three moles of electrons produce one mole of iron and 2 moles of electrons produce 1 mole of chlorine gas.

$$14.9 \text{ mole } \text{e}^- \times \frac{1 \text{ mole Fe}}{3 \text{ mole } \text{e}^-} = 4.97 \text{ mole Fe}; \quad 14.9 \text{ mole } \text{e}^- \times \frac{1 \text{ mole } \text{Cl}_2}{2 \text{ mole } \text{e}^-} = 7.45 \text{ mole } \text{Cl}_2$$

- Calculate the mass of iron using the molar mass and calculate the volume of chlorine gas using the ideal gas law ($PV = nRT$).

$$4.97 \text{ mole Fe} \times \frac{55.847 \text{ gFe}}{1 \text{ mole Fe}} = 278 \text{ gFe}; \quad \frac{(7.45 \text{ mole } \text{Cl}_2)(0.0821 \text{ atm L / mole K})(298\text{K})}{1 \text{ atm}} = 182 \text{ L } \text{Cl}_2$$

Calculating the Time required

To determine the quantity of time required to produce a known quantity of a substance given the amount of current that flowed:

- Find the quantity of substance produced/consumed in moles.
- Write the balanced half-reaction involved.
- Calculate the number of moles of electrons required.
- Convert the moles of electrons into coulombs.
- Calculate the time required.

Example: How long must a 20.0 amp current flow through a solution of ZnSO_4 in order to produce 25.00 g of Zn metal?

Sol:

- Convert the mass of Zn produced into moles using the molar mass of Zn.

$$25.00 \text{ g Zn} \times \frac{1 \text{ mole Zn}}{65.39 \text{ g Zn}} = 0.3823 \text{ mole Zn}$$

- Write the half-reaction for the production of Zn at the cathode. $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$

- Calculate the moles of e^- required to produce the moles of Zn using the stoichiometry of the balanced half-reaction. According to the equation, 2 moles of electrons will produce one mole of zinc.

$$0.3823 \text{ mole Zn} \times \frac{2 \text{ mole } \text{e}^-}{1 \text{ mole Zn}} = 0.7646 \text{ mole } \text{e}^-$$

(iv) Convert the moles of electrons into coulombs of charge using Faraday's constant.

$$0.76 \text{ mole } e^- \times \frac{1F}{1 \text{ mole } e^-} = 0.7646F; \quad 0.7646F \times \frac{96,485C}{1F} = 73,770C$$

(v) Calculate the time using the current and the coulombs of charge.

$$20.0 \text{ amps} \times t = 73,770C; \quad t = 3,688s \text{ or } 1.03h$$

Calculating the Current required

To determine the amount of current necessary to produce a known quantity of substance in a given amount of time:

(i) Find the quantity of substance produced/or consumed in moles.

(ii) Write the equation for the half-reaction taking place.

(iii) Calculate the number of moles of electrons required.

(iv) Convert the moles of electrons into coulombs of charge.

(v) Calculate the current required.

Example: What amount of current is required to produce 400.0 L of hydrogen gas, measured at STP, from the electrolysis of water in 1 hour (3600 s)?

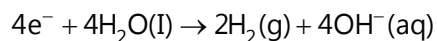
Sol:

(i) Calculate the number of moles of H_2 . (Remember, at STP, 1 mole of any gas occupies 22.4 L)

$$400.0L H_2 \times \frac{1 \text{ mole } H_2}{22.4L H_2} = 17.9 \text{ mole } H_2$$

(ii) Write the equation for the half-reaction that takes place.

Hydrogen is produced during the reduction of water at the cathode. The equation for this half-reaction is:



(iii) Calculate the number of moles of electrons. According to the stoichiometry of the equation, 4 mole of e^- are required to produce 2 moles of hydrogen gas, or 2 moles of e^- s for every one mole of hydrogen gas.

$$17.9 \text{ mole } H_2 \times \frac{2 \text{ mole } e^-}{1 \text{ mole } H_2} = 35.8 \text{ mole } e^-$$

(iv) Convert the moles of electrons into coulombs of charge.

$$35.8 \text{ mole } e^- \times \frac{1F}{1 \text{ mole } e^-} = 35.8F; \quad 35.8F \times \frac{96,485C}{1F} = 3.45 \times 10^6 C$$

(v) Calculate the current required. $I \times 3600s = 3.45 \times 10^6 C$; $I = 958 C / s = 958 \text{ amps}$

MASTERJEE CONCEPTS

As one faraday (96500 coulombs) deposits one gram equivalent of the substance, hence electrochemical equivalent can be calculated from the equivalent weight,

$$\text{i.e., } Z = \frac{\text{Eq. wt. of the substance}}{96500}$$

Note: Knowing the weight of the substance deposited (W gram) on passing a definite quantity of electricity

(Q coulombs), the equivalent weight of the substance can be calculated, i.e., $\text{Eq. wt.} = \frac{W}{Q} \times 96500$

MASTERJEE CONCEPTS

Tip: The quantity of electricity actually passed is calculated from the current and time as follows:

Quantity of electricity in coulombs = Current amperes × time in seconds

Thus, knowing the quantity of electricity passed, the amount of substance deposited can be calculated.

Faraday's first law and second law can be combined to give a mathematical relation as follows:-

$$W = ZQ = \frac{E}{F} \times Q = \frac{Q}{F} \times E = \frac{Q}{F} \times \frac{M}{z} = \frac{C \times t}{F} \times \frac{M}{z}$$

z = Electrochemical equivalent; Q = Quantity of electricity passed, E = Eq. wt. of the metal, F = 1 Faraday, M = Atomic mass of the metal; z = Valency of the metal; C = Current passed, t = Time for which current is passed.

Saurabh Gupta (JEE 2010 AIR 443)

Illustration 3: Electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP. **(JEE MAIN)**

Sol: Here current and time is given so from this first calculate quantity of electricity passed (charge) and from this calculate the amount of chlorine liberated. Volume of Cl_2 liberated at NTP can be determined by multiplying the amount of chlorine liberated by 22.4 L

The reaction taking place at anode is: $2\text{Cl}^- \xrightarrow{71.0\text{g}} \text{Cl}_2 + 2\text{e}^-$ $Q = I \times t = 100 \times 5 \times 60 \times 60$ coulomb
71.0g 71.0g 1mole 2x96500 coulomb

The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60$ coulomb of electric charge

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole Volume of } \text{Cl}_2 \text{ liberated at NTP} = 9.3264 \times 22.4 = 201\text{L}$$

Illustration 4: How much electric charge is required to oxidize (a) 1 mole of H_2O to O_2 and (b) 1 mole of FeO to Fe_2O_3 ? **(JEE MAIN)**

Sol: Charge = No of electrons involved in the reaction x faradays constant

So first find out the no of electron reaction involved in the reaction by writing the chemical reaction, balancing it and then calculate the charge.

(a) The oxidation reaction is: $\text{H}_2\text{O} \xrightarrow{1\text{mole}} \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$; $Q = 2 \times F = 2 \times 96500 = 193000$ coulomb
1mole 2mole

(b) The oxidation reaction is: $\text{FeO} + \frac{1}{2}\text{H}_2\text{O} \xrightarrow{1\text{mole}} \frac{1}{2}\text{Fe}_2\text{O}_3 + \text{H}^+ + \text{e}^-$; $Q = F = 96500$ coulomb

Illustration 5: An aqueous solution of sodium chloride on electrolysis gives $\text{H}_2(\text{g})$, $\text{Cl}_2(\text{g})$ and NaOH according to the reaction. $2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O} \longrightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$.

A direct current of 25 ampere with a current efficiency 62% is passed through 20 L of NaCl solution (20% by mass). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1 kg of Cl_2 ? What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.

(JEE ADVANCED)

Sol: Time can be calculated by using charge and current relationship. Effective current is determined by using current efficiency. Here it is given that we have to find out the molarity of the solution with respect to hydroxide ion. Volume is given. We have to find out the no of moles of oxygen.

This can be achieved by calculating the no of mole of Cl_2 present in 1 kg.

Reactions at anode and cathode are: $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$ (at anode)

$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$ (at cathode) $1\text{kg of Cl}_2 = \frac{1000}{71.0} = 14.08$ mole

Charge to produce one mole of $\text{Cl}_2 = 2 \times 96500$

Charge to produce 14.08 mole of $\text{Cl}_2 = 2 \times 96500 \times 14.08$

Effective current = $\frac{62}{100} \times 25.0 = 15.5$ ampere

Time = $\frac{\text{Charge}}{\text{Current}} = \frac{2 \times 96500 \times 14.08}{15.5} = 175318.7$ second = 48.699 hour

OH⁻ ions produced = 2 × moles of $\text{Cl}_2 = 2 \times 14.08 = 28.16$

Molarity = $\frac{\text{Mole}}{\text{Volume}} = \frac{28.16}{20} = 1.408\text{M}$

Illustration 6: An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with volume of solution kept at 100 mL and the current at 1.2 amp. Calculate the gases evolved at NTP during the entire electrolysis. **(JEE ADVANCED)**

Sol: 0.4 g of $\text{Cu}^{2+} = \frac{0.4}{31.75} = 0.0126\text{g}$ – equivalent

At the same time, the oxygen deposited at anode = $\frac{8}{32} \times 0.0126\text{g} = 0.00315\text{g}$ – mole

After the complete deposition of copper, the electrolysis will discharge hydrogen at cathode and oxygen at anode. The amount of charge passed = $1.2 \times 7 \times 60 = 504$ coulomb

So, Oxygen liberated = $\frac{1}{96500} \times 504 = 0.00523\text{g}$ – equivalent = $\frac{8}{32} \times 0.00523 = 0.001307\text{g}$ – mole

Hydrogen liberated = 0.00523g – equivalent = $\frac{1}{2} \times 0.00523 = 0.00261\text{g}$ – mole

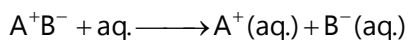
Total gases evolved = $(0.00315 + 0.001307 + 0.00261)\text{g}$ – mole = 0.007067g – mole

Volume of gases evolved at NTP = $22400 \times 0.007067\text{mL} = 158.3\text{mL}$

4. ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the properties of electrolytic solutions, Arrhenius put forth a comprehensive theory. The main postulates of the theory are:

- (a) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed as cations and negatively charged as anions.



(b) The process of splitting of the molecules into ions of an electrolyte is called **ionization**. The fraction of the total number of molecules present in solution as ions is known as **degree of ionizations** or **degree of dissociation**. It is denoted by ' α '

(c)
$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

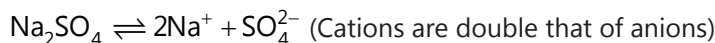
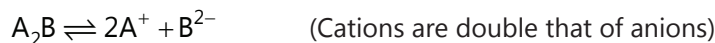
(d) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized and non-ionized molecules, i.e. $AB \rightleftharpoons A^+ + B^-$

(e) Applying the law of mass action to the above equilibrium $\frac{[A^+][B^-]}{[AB]} = K$. K is known as ionization constant. The

electrolytes having high value of K are termed **strong electrolytes** and those having low value of K as **weak electrolytes**.

(f) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs. **The ions are discharged always in equivalent amounts, no matter what their relative speeds are.**

(g) The electrolytic solution is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.



(h) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.

Limitations of Arrhenius Theory

- (i) You cannot apply Ostwald's dilutions law which is based on Arrhenius theory to strong electrolytes.
- (ii) Strong electrolytes conduct electricity in a fused state, i.e., in the absence of water. This is in contradiction of Arrhenius theory which states that the presence of solvent is imperative for ionization.
- (iii) Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

4.1 Factors Affecting Degree of Ionization

- (a) **Nature of solute:** When the ionizable parts of a molecule of a substance are held more by covalent bonding than by electrovalent bonding, less ions are furnished in solution.
- (b) **Nature of solvent:** The main function of the solvent is to weaken the electrostatic forces of attraction between the two ions and separate them.
- (c) **Dilution:** The extent of ionization of an electrolyte is inversely proportional to the concentration of its solution. Thus, degree of ionization increases with the increase of dilution of the solution, i.e., decreasing the concentration of the solution.

- (d) **Temperature:** The degree of ionization increases with the increase in temperature. This is due to the fact that at higher temperatures molecular speed is greater than before which overcomes the forces of attraction between the ions.

5. ELECTRICAL CONDUCTANCE

The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance, i.e.

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{R} \quad \dots \text{(i)}$$

It is expressed in the unit called reciprocal ohm (ohm^{-1} or mho) or Siemens.

5.1 Specific Conductance or Conductivity

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

$$\text{i.e. } R \propto \frac{l}{a} \text{ or } R = \rho \frac{l}{a} \quad \dots \dots \text{(ii)}$$

Where, ρ is called the specific resistance. If $l = 1 \text{ cm}$ and $a = 1 \text{ cm}^2$, then $R = \rho$... (iii)

The specific resistance is, thus, defined as the resistance of one centimeter cube of a conductor.

The reciprocal of specific resistance is termed the **specific conductance** or it is the conductance of one centimeter cube of a conductor. It is denoted by the symbol κ , Thus,

$$\kappa = \frac{1}{\rho}, \kappa = \text{kappa} - \text{The specific conductance} \quad \dots \text{(iv)}$$

Specific conductance is also called conductivity.

$$\text{From eq. (ii), we have } \rho = \frac{a}{l} \cdot R \text{ or } \frac{1}{\rho} = \frac{l}{a} \cdot \frac{1}{R}; \kappa = \frac{l}{a} \times C \left(\frac{l}{a} = \text{cell constant} \right)$$

or Specific conductance = conductance \times cell constant

5.2 Equivalent Conductance

Equivalent conductance is defined as the conductance of all the ions produced by **one gram-equivalent** of an electrolyte in a given solution. It is denoted by Λ .

$$\text{In general } \Lambda = \kappa \times V \quad \dots \text{(v)}$$

Where, V is the volume in mL containing 1 g-equivalent of the electrolyte.

In case the concentration of the solution is c g-equivalent per liter, then the volume containing

1 g-equivalent of the electrolyte will be $1000/c$.

$$\text{So, equivalent conductance } \Lambda = \kappa \times \frac{1000}{c} \quad \dots \text{(vi)}$$

$$\Lambda = \kappa \times \frac{1000}{N}; \text{ where, } N = \text{normality. The unit of equivalent conductance is } \text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}.$$

5.3 Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionization of **1 g-mole** of an electrolyte when present in V ml of solution. It is denoted by μ .

$$\text{Molar conductance } \mu = \kappa \times V \quad \dots \text{(vii)}$$

Where, V is the volume in mL containing 1 g-mole of the electrolyte. If c is the concentration of the solution in g-mole per liter, then $\mu = \kappa \times \frac{1000}{c}$ Its unit is $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}; \text{ where, } n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Illustration 7: 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq. cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution. **(JEE MAIN)**

Sol: As Equivalent conductivity = $\kappa \times V$

In order to find equivalent conductivity we have to calculate specific conductance.

Specific conductance (κ) is given as $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

Given, $l = 2.1 \text{ cm}$, $a = 4.2 \text{ sq. cm}$, $R = 50 \text{ ohm}$. Specific conductance, $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

Or $\kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{cm}^{-1}$; Equivalent conductivity = $\kappa \times V$

$V =$ The volume containing 1 g-equivalent = 1000 mL

So, Equivalent conductivity = $0.01 \times 1000 = 10 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$

Illustration 8: The specific conductivity of 0.02M KCl solution at 25°C is $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{cm}^{-1}$. The resistance of this solution at 25°C when measured with a particular cell was 250.2 ohm. The resistance of 0.01 M CuSO_4 solution at 25°C measured with the same cell was 8331 ohm. Calculate the molar conductivity of the copper sulphate solution. **(JEE ADVANCED)**

Sol: Molar conductivity is given by = $\text{Sp. cond.} \times \frac{1000}{C}$ so first we have to calculate specific conductivity of the solution. Sp.conductivity is given as a product of cell constant and conductance. Now cell constant is not provided; we can calculate it from the conductance and Sp.conductivity of KCl solution.

$$\text{Cell constant} = \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}} = \frac{2.768 \times 10^{-3}}{1/250.2} = 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M CuSO_4 solution

$$\text{Sp. Conductivity} = \text{Cell constant} \times \text{Conductance} = 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

$$\text{Molar conductance} = \text{Sp. cond.} \times \frac{1000}{C} = \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} = 8.312 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

6. KOHLRAUSCH'S LAW

At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte, irrespective of the nature of the ion with which it is associated and the value of molar conduction of its constituent ions, i.e., $\Lambda = \lambda_+ + \lambda_-$ λ_c and λ_a are called the ionic conductance of cation and anion at infinite dilution respectively. The ionic conductance are proportional to their ionic mobilities. Thus, at infinite dilution, $\lambda_c = k u_c$ and $\lambda_a = k u_a$, where, u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 C, i.e., one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte, it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionized at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

$$\text{Degree of dissociation } \alpha = \frac{\Lambda}{\Lambda_{\infty}} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

Ionic Mobility, μ : It is the distance travelled by an ions per second under a potential gradient of 1 volt per meter.

1. For an, $\mu = \lambda^{\circ} / F$
2. Ionic mobility of an ion depends on its charge, size, viscosity of solvent, temperature, etc.
3. For aqueous solution, greater the charge or smaller the size of gaseous ion, greater will be the size of aqueous ion. When such a big ion moves in solution, it experiences greater resistance by the size of solvent particles. This results in a decrease in its conductance as well as ionic mobility. Following are the increasing order of ionic mobilities of some ions:
 $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+; \text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-; \text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$
4. The size of gaseous H^+ ion is smallest among all the ions and hence its ionic mobility should be minimum but among all the ions, it is maximum. The ion with second highest ionic mobility is OH^- . The very high ionic mobilities of these ions are due to interchange of hydrogen bonds and covalent bonds, by which migration of charge occurs without any large displacement in the ions (Grotthus mechanism).

Applications of Kohlrausch's Law:

(a) Determining Λ_m° of a weak electrolyte: In order to calculate Λ_m° of a weak electrolyte say CH_3COOH , we determine experimentally Λ_m° values of the following three strong electrolytes:

- (i) A strong electrolyte containing same cation as in the test electrolyte, say HCl
- (ii) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa
- (iii) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl .

$$\Lambda_m^{\circ} \text{ of } \text{CH}_3\text{COOH} \text{ is then given as: } \Lambda_m^{\circ}(\text{CH}_3\text{COOH}) = \Lambda_m^{\circ}(\text{HCl}) + \Lambda_m^{\circ}(\text{CH}_3\text{COONa}) - \Lambda_m^{\circ}(\text{NaCl})$$

$$\text{Proof: } \Lambda_m^{\circ}(\text{HCl}) = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} \quad \dots \text{ (i)}$$

$$\Lambda_m^{\circ}(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{Na}^+}^{\circ} \quad \dots \text{ (ii)}$$

$$\Lambda_m^{\circ}(\text{NaCl}) = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} \quad \dots \text{ (iii)}$$

Adding equation (I) and equation (II) and subtracting (III) from them:

$$\Lambda_{(\text{HCl})}^{\circ} + \Lambda_{(\text{CH}_3\text{COONa})}^{\circ} - \Lambda_{(\text{NaCl})}^{\circ} = \lambda_{(\text{H}^+)}^{\circ} + \lambda_{(\text{CH}_3\text{COO}^-)}^{\circ} = \Lambda_{\text{O}(\text{CH}_3\text{COOH})}$$

$$\text{(b) Determination of degree of dissociation } (\alpha): \alpha = \frac{\text{No. of molecules ionised}}{\text{Total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^{\circ}}$$

$$\text{(c) Determination of solubility of sparingly soluble salt: } \Lambda_m^{\circ} = \frac{1000\kappa}{C},$$

Where C is the molarity of solution and hence the solubility.

(d) Determination of ionic product of water: From Kohlrausch's law, we determine Λ_m° of H_2O where Λ_m° is the molar conductance of water at infinite dilution when one mole of water is completely ionized to give one mole of H^+ and one mole of OH^- ions i.e. $\Lambda_m^{\circ}(\text{H}_2\text{O}) = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ}$

$$\text{Again using the following } \Lambda_m = \frac{\kappa \times 1000}{C}, \text{ where } C = \text{molar concentration i.e. mole L}^{-1} \text{ or mole dm}^{-3}$$

$$\Rightarrow \Lambda_m = \frac{\kappa}{C}, \text{ where } C = \text{concentration in mole m}^{-3}$$

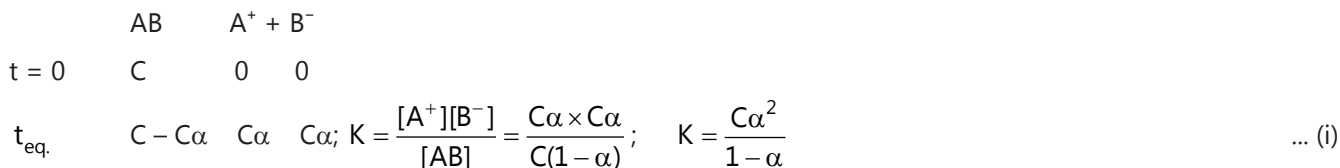
$$\text{Assuming that } \Lambda_m \text{ differs very little from } \Lambda_m^0; \Lambda_m^0 = \frac{\kappa}{C} \Rightarrow C = \frac{\kappa}{\Lambda_m^0}$$

Specific conductance (κ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation. K_w is then calculated as: $K_w = C^2$

7. THEORY OF WEAK ELECTROLYTES

(i) Electrolytes that are not completely ionized when dissolved in a polar medium like water are called weak electrolytes. There exists equilibrium between ions and unionized molecules. $AB \rightleftharpoons A^+ + B^-$

(ii) The Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.



For weak electrolytes, $\alpha \ll 1 \quad \therefore (1-\alpha) \approx 1$

Thus, equation (i) can be written as: $K = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}}$... (ii)

From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionization ' α ' increases. Both equivalent and molar conductance increase when at a high degree of ionization.

(iii) Degree of ionization can be calculated as: $\alpha = \frac{\Lambda_e^C}{\Lambda_e^\infty} = \frac{\Lambda_m^C}{\Lambda_m^\infty}$... (iii)

Λ_e^C, Λ_m^C = Equivalent and molar conductance at concentration 'C'

$\Lambda_e^\infty, \Lambda_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Substituting the values of ' α ' from eq. (iii) in eq. (i), we get $K = \frac{C \times \left(\frac{\Lambda_e^C}{\Lambda_e^\infty}\right)^2}{1 - \frac{\Lambda_e^C}{\Lambda_e^\infty}} = \frac{C(\Lambda_e^C)^2}{\Lambda_e^\infty(\Lambda_e^\infty - \Lambda_e^C)}$... (iv)

Similarly $K = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^C)}$... (v)

Equations (iv) and (v) are called **Ostwald equation**.

Illustration 9: A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductance of Na⁺ and Cl⁻ ions at the same temperature are 43.0 and 65.0 ohm⁻¹ respectively, calculate the degree of dissociation of NaCl solution. **(JEE MAIN)**

Sol: Degree of dissociation is calculated as equivalent conductance at a particular dilution divided by equivalent conductance at infinite dilution. so first we have to calculate Λ_∞

$\Lambda_v \cdot \Lambda_\infty$ is determined by summing up ionic conductance of each ion. Λ_v is product of specific conductance and dilution.

Equivalent conductance of N/10 NaCl solution

$$\Lambda_v = \text{Sp. conductivity} \times \text{dilution} = 0.0092 \times 10,000 = 92 \text{ ohm}^{-1};$$

$$\Lambda_\infty = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 43.0 + 65.0 = 108 \text{ ohm}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{92}{108} = 0.85$$

Illustration 10: At 18°C, the conductivities at infinite dilution of NH_4Cl , NaOH and NaCl are 129.8, 217.4 and 108.9 mho respectively. If the equivalent conductivity of N/100 solution of NH_4OH is 9.93 mho, calculate the degree of dissociation of NH_4OH at this dilution. **(JEE ADVANCED)**

Sol: Degree of dissociation is calculated as equivalent conductance at a particular dilution divided by equivalent conductance at infinite dilution. Λ_v is given. Λ_∞ is determined by summing up ionic conductance of each ion

$$\Lambda_{\infty\text{NH}_4\text{Cl}} = \lambda_{\text{NH}_4^+} + \lambda_{\text{Cl}^-} = 129.8 \quad \dots \text{ (i)}$$

$$\Lambda_{\infty\text{NaOH}} = \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-} = 217.4 \quad \dots \text{ (ii)}$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\Lambda_{\text{NH}_4^+} + \lambda_{\text{Cl}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} = \lambda_{\text{NH}_4^+} + \lambda_{\text{OH}^-} = 129.8 + 217.4 - 108.9$$

$$\Lambda_{\infty\text{NH}_4\text{OH}} = 238.3 \text{ mho. Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{9.93}{238.3} = 0.04167 \text{ or } 4.17\% \text{ dissociated.}$$

8. ELECTROCHEMICAL CELLS

8.1 Electrolytic Cells

Electrolytic cells are devices in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

8.2 Galvanic Cells

This is a device where a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity is obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode and the compartments containing the electrode and the electrolyte solution are called **half-cells**. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through the galvanometer, the electricity begins to flow. This is the simple form of voltaic cell.

8.3 Daniel Cell

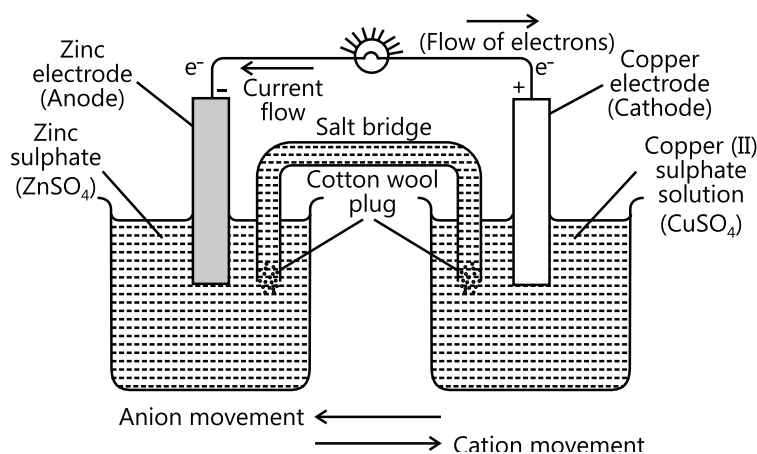


Figure 17.1: Representation of a daniel cell

Oxidation half reaction, $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq.}) + 2\text{e}^{-}$

Reduction half reaction, $\text{Cu}^{2+}(\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Cu(s)}$

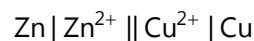
Net reaction $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq.}) \longrightarrow \text{Zn}^{2+}(\text{aq.}) + \text{Cu(s)}$

Salt Bridge: A Salt bridge is usually an inverted U-tube filled with a concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells.

Significance of salt bridge: The following are the functions of the salt bridge:

- (i) It connects the solutions of two half-cells and completes the cell circuit.
- (ii) It prevents transference or diffusion of the solutions from one half-cell to the other.
- (iii) It keeps the solutions in two half-cells electrically neutral.
- (iv) It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.



Electrode Potential: A metal placed in a solution of its ions obtains either a positive or negative charge with respect to the solution. On account of this, a definite potential is developed between the metal and the solution. This potential difference is called electrode potential. It depends on the nature of electrode, concentration of ions and temperature.

Oxidation Potential: It is the tendency of an electrode to get oxidized, i.e., to lose electrons.



Reduction potential: It is the tendency of an electrode to get reduced, i.e., to accept electrons.



Standard Electrode Potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25°C (278 K) is called standard electrode potential.

The magnitude of potential depends on the following factors:

- (i) Nature of the electrode,
- (ii) Concentration of the ions in solution,
- (iii) Temperature.

Standard Electrode Potential: While dipping an electrode in a solution in order to compare the electrode potentials of different electrodes, it is essential to first specify the ion concentration in the solution as well as the temperature of the half cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25°C (298 K) is called **standard electrode potential**. Standard oxidation potential = -Standard reduction potential

EMF of a cell: It is the difference in the potential across left and right electrodes due to which electrons flow from anode to cathode.

Standard EMF: The EMF values of an electrode under standard conditions (1 atm, 298 K) and the unit concentrations of its ions is called as standard EMF and is denoted by E_{cell}°

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \quad \text{or} \quad E_{\text{cell}}^{\circ} = E_{\text{right electrode}}^{\circ} - E_{\text{left electrode}}^{\circ}$$

8.4 Reference Electrode (Standard Hydrogen Electrode, SHE or NHE)

The potential of an individual half-cell cannot be measured but the difference in the potential of two half-cells can be measured experimentally. It is therefore, necessary to couple the electrodes with another electrode whose potential is known. This electrode is termed as reference electrode like standard hydrogen electrode (SHE). Which is standard electrode potential considered zero.

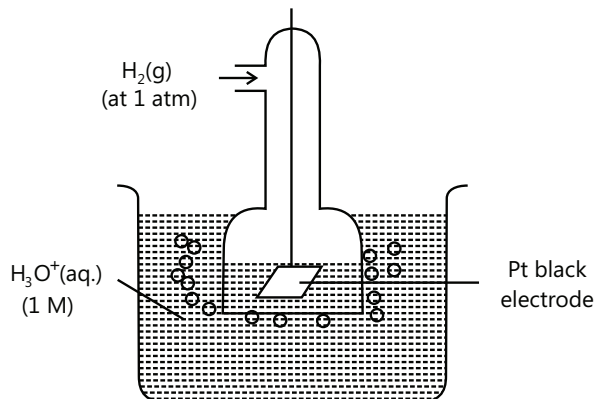
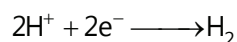
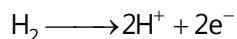


Figure 17.2: Representation of reference electrode

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. A voltaic cell is created when this half-cell is connected with any other half-cell. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction



Electrode potential

0.0 V (Anode)

0.0 V (Cathode)

8.5 Some other Reference Electrodes

(i) Calomel Electrode:

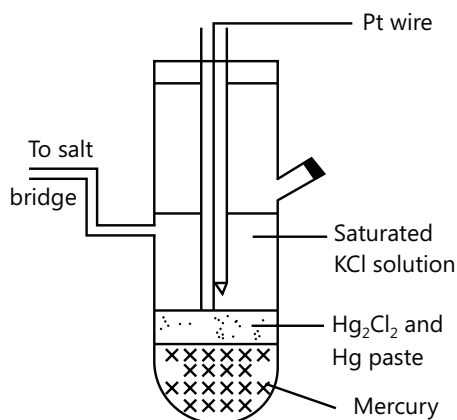


Figure 17.3: Representation of calomel electrode

Reaction when electrode act as cathode: $\frac{1}{2}\text{Hg}_2\text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Hg} + \text{Cl}^-$

(ii) **Silver-silver chloride electrode:** This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without inserting liquid junction.

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K. The electrode is represented as: $\text{Ag} | \text{AgCl} | \text{Cl}^-$

The electrode reaction is: $\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$

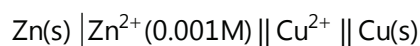
MASTERJEE CONCEPTS

$\text{InMnO}_4^- + 8\text{H}^+ + 5\text{e} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$, oxidant should be taken as $[\text{MnO}_4^-][\text{H}^+]^8$, i.e., all ions concentration present with oxidant should be reported accordingly in Nernst half-cell potential. Similarly for reductant, all ions present with reductant should be considered.

Aman Gour (JEE 2012 AIR 230)

8.6 Nernst Equation

Nernst Equation: Suppose, for example, that we reduce the concentration of Zn^{2+} in the Zn/Cu cell from its unit-activity value of around 0.5 M to a much smaller value:



This will reduce the value of Q for the cell reaction $\text{Zn(s)} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu(s)}$

The free energy change ΔG more negative than ΔG° , so than E would be more positive than E° .

The relation between the actual cell potential E and the standard potential E° is developed in the following way.

According to cell potential and Gibb's free energy change: $\Delta G^\circ = -nE^\circ F$; $\Delta G = -nEF$

These expressions can then be substituted into the relation $\Delta G = \Delta G^\circ + RT \ln Q$

Which gives $-nEF = -nE^\circ F + RT \ln Q$. Which can be rearranged to $E = E^\circ - \frac{RT}{nF} \ln Q$

This is Nernst Equation, which relates the cell potential to the standard potential E° . If Q is unity then at 25°C

Nernst Equation will be $E = E^\circ - \frac{0.059}{n} \log Q$

And for a general electrochemical reaction of the type $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

Nernst equation can be written as: $E_{\text{cell}} = E_{(\text{cell})}^\circ - \frac{RT}{nF} \ln Q = E_{(\text{cell})}^\circ - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$

MASTERJEE CONCEPTS

- The overall reaction and ΔG° for each cell is same.
- E_{cell}° and 'n' values are different for each cell.
- $E_{\text{cell}}^\circ \times n$ is same for each cell.
- ΔG° depends on cell reaction and E_{cell}° depends upon making up of a cell.

B Rajiv Reddy (JEE 2010 AIR 11)

8.7 Electrochemical Series

Characteristics of electrochemical series

- (a) Negative sign of SRP (standard reduction potential) indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. Similarly positive sign of SRP indicates that an electrode when joined with SHE acts as cathode and reduction occurs on this electrode.
- (b) In the series, those substances that are stronger reducing agents than hydrogen are placed above it.
- (c) The substances which are stronger oxidizing agents than H^+ ion are placed below hydrogen in the series.
- (d) The activity decreases from top to bottom and the metals on top are called active metals.

Application of electrochemical series

(i) Reactivity of metals

- Alkali metals and alkaline earth metals having high –ve values of SRP which are chemically active react with cold water, evolve hydrogen and readily dissolve in acids.
- Metals like Fe, Pb, Sn, Ni, Co etc. do not react with cold water but react with steam to evolve hydrogen.
- Metals Li, Be, Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) **Electropositive character of metals:** Electropositive character of metals decreases from top to bottom.

(iii) **Displacement reactions:** The metal having low SRP will displace the metal from its salt's solution which has higher value of SRP.

(iv) **Reducing power of metals:** Reducing nature decreases from top to bottom in the electrochemical series.

(v) **Oxidizing nature of non-metals:** Oxidizing nature increases from top to bottom in the electrochemical series.

(vi) **Thermal stability of metallic oxides:** The thermal stability of the metal oxide decreases from top to bottom.

(vii) **Products of electrolysis:** The ion which is a stronger oxidizing agent is discharged first at cathode.
 $K^+, Ca^{2+}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$ increasing order of deposition.

(viii) **Corrosion of metals:** Corrosion is defined as the deterioration of a substance because of its reaction with its environment. The corrosion tendency decreases from top to bottom.

(ix) **Extraction of metals:** Ag and Au extracted by cyanide process.

Table 17.3: Reduction potential of different ions

	Reaction (Oxidized form + ne^-)	→ Reduced form		E°/V
↑ Increasing strength of oxidizing agent	$F_2(g) + 2e^-$	→ $2F^-$	↓ Increasing strength of reducing agent	2.87
	$Co^{3+} + e^-$	→ Co^{2+}		1.81
	$H_2O_2 + 2H^+ + 2e^-$	→ $2H_2O$		1.78
	$MnO_4^- + 8H^+ + 5e^-$	→ $Mn^{2+} + 4H_2O$		1.51
	$Au^{3+} + 3e^-$	→ $Au(s)$		1.40
	$Cl_2(g) + 2e^-$	→ $2Cl^-$		1.36
	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	→ $2Cr^{3+} + 7H_2O$		1.33
	$O_2(g) + 4H^+ + 4e^-$	→ $2H_2O$		1.23
	$MnO_2(s) + 4H^+ + 2e^-$	→ $Mn^{2+} + 2H_2O$		1.23
	$Br_2 + 2e^-$	→ $2Br^-$		1.09
	$NO_3^- + 4H^+ + 3e^-$	→ $NO(g) + 2H_2O$		0.97
	$2Hg^{2+} + 2e^-$	→ Hg_2^{2+}		0.92
	$Ag^+ + e^-$	→ $Ag(s)$		0.80
	$Fe^{3+} + e^-$	→ Fe^{2+}		0.77
	$O_2(g) + 2H^+ + 2e^-$	→ H_2O_2		0.68
	$I_2 + 2e^-$	→ $2I^-$		0.54
	$Cu^+ + e^-$	→ $Cu(s)$		0.52
	$Cu^{2+} + 2e^-$	→ $Cu(s)$		0.34
	$AgCl(s) + e^-$	→ $Ag(s) + Cl^-$		0.22
	$AgBr(s) + e^-$	→ $Ag(s) + Br^-$		0.10
$2H^+ + 2e^-$	→ $H_2(g)$	0.00		
$Pb^{2+} + 2e^-$	→ $Pb(s)$	-0.13		
$Sn^{2+} + 2e^-$	→ $Sn(s)$	-0.14		
$Ni^{2+} + 2e^-$	→ $Ni(s)$	-0.25		

	Reaction (Oxidized form + ne^-)	→ Reduced form		E°/V
↑ Increasing strength of oxidizing agent ↓	$Fe^{2+} + 2e^-$	→ Fe(s)	↓ Increasing strength of reducing agent ↑	-0.44
	$Cr^{3+} + 3e^-$	→ Cr(s)		-0.74
	$Zn^{2+} + 2e^-$	→ Zn(s)		-0.76
	$2H_2O + 2e^-$	→ $H_2(g) + 2OH^-(aq)$		-0.83
	$Al^{3+} + 3e^-$	→ Al(s)		-1.66
	$Mg^{2+} + 2e^-$	→ Mg(s)		-2.36
	$Na^+ + e^-$	→ Na(s)		-2.71
	$Ca^{2+} + 2e^-$	→ Ca(s)		-2.87
	$K^+ + e^-$	→ K(s)		-2.93
	$Li^+ + e^-$	→ Li(s)		-3.05

Two important parameters that can be determined from a cell potential are the equilibrium constant for the cell reaction and the free energy change for the cell reaction.

1. Determining the equilibrium constant from E_{cell}°
2. Determining the standard state free energy change from E_{cell}°
3. Determining the non-standard free energy change

Determining the Equilibrium Constant from E_{cell}°

To calculate the equilibrium constant for an electrochemical cell we need to know:

1. The standard state potential for a cell
2. The half-reactions involved

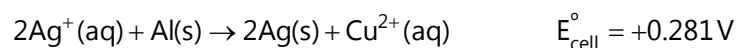
The Nernst equation is used in calculating the equilibrium constant. $E_{cell}^\circ = \frac{RT}{nF} \ln Q$

At equilibrium $Q = K$, Substituting in K for Q and the values for R , T and F we get:

$$E_{cell}^\circ = \frac{0.0257}{n} \ln K = \frac{0.0592}{n} \log K$$

Example: Find the value of the equilibrium constant at 25°C for the cell reaction for the following electrochemical cell: $Cu | Cu^{2+}(1M) || Ag^+(1M) | Ag$

Sol: (i) Write the equations for the cell half-reactions, calculate the standard cell potential and determine the number of electrons transferred.



$n = 2$ moles of electrons

(ii) Substitute into the above equations and solve for K .

$$E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log K; 0.281 = \frac{0.0592}{2} \log K; \log K = 9.49; K = 10^{9.49} = 3.1 \times 10^9$$

Note: values for the equilibrium constant for electrochemical cell reactions are sometimes very large.

Determining the Standard State Free Energy Change from E_{cell}°

To determine the standard state free energy change for a cell reaction

1. Determine the E_{cell}°
2. Determine the number of moles of electrons transferred in the reaction.
3. Solve for ΔG° using the equation $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$

ΔG° = standard state free energy change (joules); n = number of moles of electrons transferred

F = Faraday's constant (96,485 C/mole e^{-}); E_{cell}° = standard state cell potential (volts or joules/C)

Example: Find the value of the equilibrium constant at 25°C for the cell reaction for the following electrochemical cell: $\text{Cu} | \text{Cu}^{2+} (1\text{M}) || \text{Ag}^{+} (1\text{M}) | \text{Ag}$

(The solution for the determination of the E_{cell}° and the number of moles of electrons, n , are shown in the example in the previous section.)

1. Determine the E_{cell}° . $E_{\text{cell}}^{\circ} = +0.281$ volts
2. Determine the number of moles of electrons transferred. $n = 2$ moles of e^{-}
3. Substitute into the equation and solve.

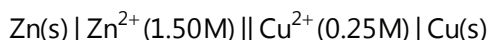
$$\Delta G^{\circ} = -(2\text{mole}^{-})(96,485\text{C} / \text{mole}^{-})0.281\text{J} / \text{C}; \Delta G^{\circ} = -54,200\text{J} \text{ or } -54.2\text{kJ}$$

Determining the Non-Standard State Free Energy Change

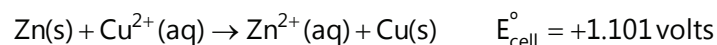
To determine the non-standard state free energy change:

1. Calculate the standard cell potential, E_{cell}°
2. Determine the number of moles of electrons transferred, n
3. Calculate the reaction quotient, Q
4. Calculate the non-standard cell potential, E_{cell} , using the Nernst equation
5. Calculate the non-standard free energy change using the equation: $\Delta G = -nFE_{\text{cell}}$

Example: Calculate the free energy change for the following electrochemical cell.



1. Calculate E_{cell}° .



2. Determine "n". $n = 2$ moles of electrons

3. Calculate Q ; $Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1.50}{0.25} = 6.0$

4. Calculate E_{cell} ; $E_{\text{cell}} = 1.101 \text{ volts} - \frac{0.0257}{2} \ln 6 = 1.078 \text{ volt}$

5. Calculate ΔG .

$$\Delta G = -nFE_{\text{cell}} = -(2 \text{ mole } e^-)(96,485 \text{ C / mole } e^-)(1.078 \text{ volts}); \Delta G = -208,000 \text{ joules or } -208 \text{ kJ}$$

8.8 Corrosion

The weakening and deterioration of a substance because of its reaction with its environment is called as corrosion. This is also defined as the process by which metals have the tendency to go back to their combined state, i.e., reverse of extraction of metals.

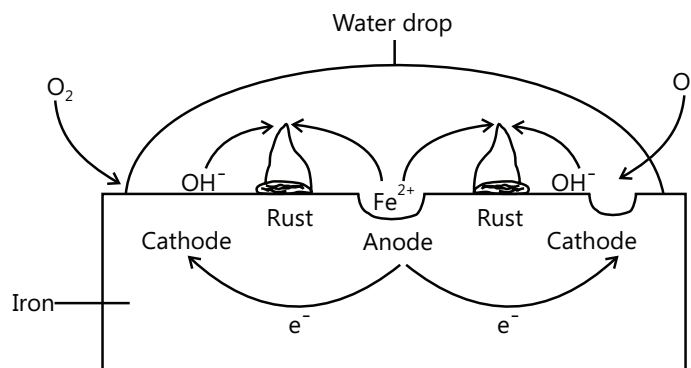
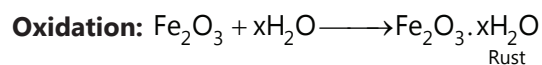
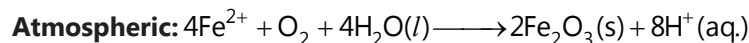


Figure 17.4 : Process of corrosion

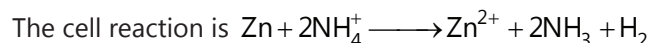
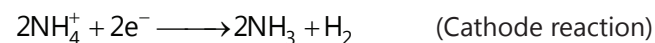


8.9 Dry Cell

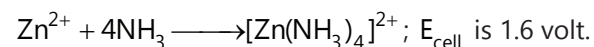
In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy.

As the cell operates, the zinc is oxidized to Zn^{2+} ; $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$ (Anode reaction)

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.



Ammonia produced at cathode combines with zinc ions to form complex ion.



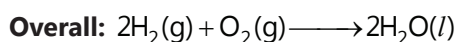
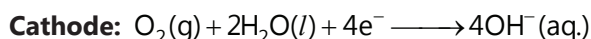
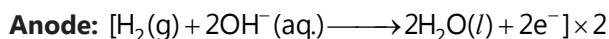
MASTERJEE CONCEPTS

- These are called dry cells but are not actually dry. These contain moist paste and operate only as long as the paste in it remains wet.
- In alkaline cells, e.m.f. is independent of concentration of alkali because redox reaction does not involve $[\text{OH}^-]$.
- Alkaline cells retards corrosion as corrosion is favored more in H^+ ions.
- Alkaline cells show more efficient ion transport because of alkaline electrolyte and thus give rise to more stable current and voltage.

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8.10 Fuel Cell

Fuel cells are another means to convert chemical energy to electrical energy. The main disadvantage of a primary cell is that it can deliver current for a short period only. This is because the quantity of oxidizing agent and reducing agent is limited. But energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell. The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with electrodes that are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution. Hydrogen is oxidized at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:



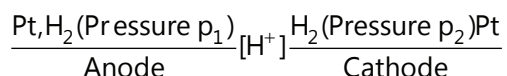
These type of cells are used in space-crafts. Fuel cells are efficient and pollution free.

Thermodynamic efficiency of fuel cells is the ratio of the electrical free energy to the enthalpy of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

8.11 Concentration Cell

- (a) **Electrode concentration cells:** In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressures in the same solution of hydrogen ions constitute a cell of this type.



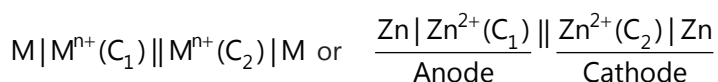
If $p_1 > p_2$, oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{(p_1)}{(p_2)} \text{ at } 25^\circ\text{C}$$

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution. $\text{M}(\text{HgC}_1) | \text{M}^{n+} | \text{Zn}(\text{HgC}_2)$

The e.m.f of the cell is given by the expression $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_1}{C_2}$ at 25°C

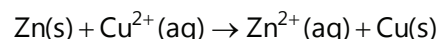
(b) Electrolyte concentration cells: In these cells, electrodes are identical but these are immersed in a solution of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the beginning, the e.m.f of the cell is at its maximum and it gradually falls to zero. Such a cell is represented in the following manner: (C_2 is greater than C_1).



The e.m.f of the cell is given by the following expression: $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2(\text{RHS})}}{C_{1(\text{LHS})}}$ at 25°C

The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.

Example: Find the standard cell potential for an electrochemical cell with the following cell reaction.



Sol:

(i) Write the half-reactions for each process. $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$; $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

(ii) Look up the standard potentials for the reduction half-reaction. $E_{\text{reduction}}^\circ$ of $\text{Cu}^{2+} = +0.339\text{V}$

(iii) Look up the standard reduction potential for the reverse of the oxidation reaction and change the sign.

$E_{\text{reduction}}^\circ$ of $\text{Zn}^{2+} = -0.762\text{V}$, $E_{\text{oxidation}}^\circ$ of $\text{Zn} = -(-0.762\text{V}) = +0.762\text{V}$

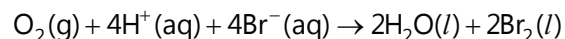
(iv) Add the cell potentials together to get the overall standard cell potential.

Oxidation: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ $E_{\text{oxidation}}^\circ = -E_{\text{reduction}}^\circ = -(-0.762\text{V}) = +0.762\text{V}$

Reduction: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$ $E_{\text{reduction}}^\circ = +0.339\text{V}$

Overall: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$ $E_{\text{cell}}^\circ = +1.101\text{V}$

Example: Predict the cell potential for the following reaction when the pressure of the oxygen gas is 2.50 atm, the hydrogen ion concentration is 0.10 M and the bromide ion concentration is 0.25 M.



Sol: (i) Calculate the standard cell potential for the reaction, E_{cell}° , using the tabled values:

Oxidation: $4\text{Br}^-(\text{aq}) \rightarrow 2\text{Br}_2(\text{l}) + 4\text{e}^-$ $E_{\text{oxidation}}^\circ = -E_{\text{reduction}}^\circ = -(+1.077\text{V}) = -1.077\text{V}$

Reduction: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ $E_{\text{reduction}}^\circ = +1.229\text{V}$

Overall: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{Br}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{Br}_2(\text{l})$ $E_{\text{cell}}^\circ = +0.152\text{V}$

(ii) Determine the new cell potential resulting from the changed conditions.

(iii) Calculate the value for the reaction quotient, Q. (Note: We calculate Q using molar concentrations for solutions and pressures for gases. Water and bromine are both liquids, therefore they are not included in the calculation of Q.)

$$Q = \frac{1}{P_{O_2} [H^+]^4 [Br^-]^4}; \quad Q = \frac{1}{(2.50 \text{ atm})(0.10 \text{ M})^4 (0.25 \text{ M})^4}; \quad Q = 1.02 \times 10^6$$

(iv) Calculate the number of moles of electrons transferred in the balanced equation, n .

$n = 4$ moles of electrons

(v) Substitute values into the Nernst equation and solve for the non-standard cell potential, E_{cell} .

$$E_{\text{cell}} = +0.152 \text{ V} - (0.0257 / 4) \ln(1.02 \times 10^6), E_{\text{cell}} = 0.063 \text{ V}$$

Illustration 11: Reaction $\rightarrow 2\text{Ag} + \text{Cd}^{2+}$. The standard electrode potentials for $\text{Ag}^+ \rightarrow \text{Ag}$ and $\text{Cd}^{2+} \rightarrow \text{Cd}$ couples are 0.80 volt and -0.40 volt respectively

(i) What is the standard potential E° for this reaction?

(ii) For the electrochemical cell, in which this reaction takes place which electrode is negative electrode?

(JEE MAIN)

Sol: First write down the two half-cell. Standard potential E° for the cell is given by standard potential of reducing electrode + standard potential of oxidising electrode. The electrode having less electrode potential act as negative electrode.

(i) The half reactions are: $2\text{Ag}^+ + \underset{\substack{\text{Reduction} \\ \text{(Cathode)}}}{2e^-} \longrightarrow 2\text{Ag}$

$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ volt}$ (Reduction potential); $\text{Cd} \longrightarrow \underset{\substack{\text{Oxidation} \\ \text{(Anode)}}}{\text{Cd}^{2+} + 2e^-}$

$E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ volt}$ (Reduction potential) or $E^\circ_{\text{Cd}/\text{Cd}^{2+}} = +0.40 \text{ volt}$

$$E^\circ = E^\circ_{\text{Cd}/\text{Cd}^{2+}} + E^\circ_{\text{Ag}^+/\text{Ag}} = 0.40 + 0.80 = 1.20 \text{ volt}$$

Illustration 12: The standard oxidation potential of zinc is 0.76 volt and of silver is -0.80 volt. Calculate the e.m.f of the cell:

$\text{Zn} | \text{Zn}(\text{NO}_3)_2 \parallel \text{AgNO}_3 | \text{Ag}$ At 25°C .
0.25M 0.1M

(JEE MAIN)

Sol: First calculate the standard potential for reaction which is calculated as

$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} - E^\circ_{\text{reduction}}$$

After calculating E°_{cell} e.m.f of the cell can be easily calculated using following equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

The cell reaction is $\text{Zn} + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Zn}^{2+}$; $E^\circ_{\text{oxidation}}$ of Zn = 0.76 volt

$E^\circ_{\text{reduction}}$ of Ag = 0.80 volt; $E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}}$ of Zn + $E^\circ_{\text{reduction}}$ of Ag = 0.76 + 0.80 = 1.56 volt

We know that, $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$

$$= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{0.25}{0.1 \times 0.1} = 1.56 - \frac{0.0591}{2} \times 1.3979 = (1.56 - 0.0413) \text{ volt} = 1.5187 \text{ volt}.$$

Illustration 13: Calculate the e.m.f of the cell. $\text{Mg(s)} | \text{Mg}^{2+} (0.2\text{M}) || \text{Ag}^+ (1 \times 10^{-3}) | \text{Ag}$

$$E_{\text{Ag}^+/\text{Ag}}^\circ = +0.8 \text{ volt}, E_{\text{Mg}^{2+}/\text{Mg}}^\circ = -2.37 \text{ volt}$$

What will be the effect on e.m.f if concentration of Mg^{2+} ion is decreased to 0.1 M?

(JEE MAIN)

Sol: First calculate the standard potential for reaction which is calculated as

$$E_{\text{cell}}^\circ = E_{\text{oxidation}}^\circ - E_{\text{reduction}}^\circ$$

After calculating E_{cell}° e.m.f of the cell can be easily calculated using following equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

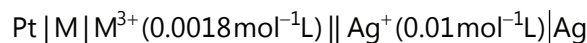
$$E_{\text{cell}}^\circ = E_{\text{Cathode}}^\circ - E_{\text{Anode}}^\circ = 0.80 - (-2.37) = 3.17 \text{ volt}$$

$$\text{Cell reaction, } \text{Mg} + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Mg}^{2+}; E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

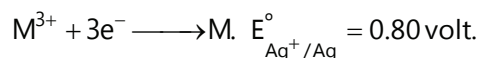
$$= 3.17 - \frac{0.0591}{2} \log \frac{0.2}{[1 \times 10^{-3}]^2} = 3.17 - 0.1566 = 3.0134 \text{ volt when } \text{Mg}^{2+} = 0.1\text{M}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{0.1}{(1 \times 10^{-3})^2} = (3.17 - 0.1477) \text{ volt} = 3.0223 \text{ volt.}$$

Illustrations 14: To find the standard potential of M^{3+} / M electrode, the following cell is constituted:



The e.m.f of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction

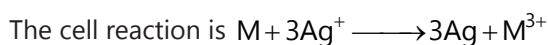


(JEE MAIN)

Sol: Here e.m.f is given we have to calculate standard potential of anode. So first we have to calculate standard potential of the cell and subtract it from the provided standard potential of cathode.

Standard potential of cell can be determined using following expression, Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{3} \log \frac{[\text{M}^{3+}]}{[\text{Ag}^+]^3}$$



$$\text{Applying Nernst equation, } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{3} \log \frac{[\text{M}^{3+}]}{[\text{Ag}^+]^3}$$

$$0.42 = E_{\text{cell}}^\circ - \frac{0.0591}{3} \log \frac{(0.0018)}{(0.01)^3} = E_{\text{cell}}^\circ - 0.064; E_{\text{cell}}^\circ = (0.42 + 0.064) = 0.484 \text{ volt}$$

$$E_{\text{cell}}^\circ = E_{\text{Cathode}}^\circ - E_{\text{Anode}}^\circ \text{ or } E_{\text{Anode}}^\circ = E_{\text{Cathode}}^\circ - E_{\text{Cell}}^\circ = (0.80 - 0.484) = 0.32 \text{ volt.}$$

PROBLEM-SOLVING TACTICS

(a) Related to electrolysis: Electrolysis comprises of passing an electric current through either a molten salt or an ionic solution. Thus the ions are "forced" to undergo either oxidation (at the anode) or reduction (at the cathode). Most electrolysis problems are really stoichiometry problems with the addition of some amount of electric current. The quantities of substances produced or consumed by the electrolysis process is dependent upon the following:

- (i) Electric current measured in amperes or amps
- (ii) Time measured in seconds
- (iii) The number of electrons required to produce or consume 1 mole of the substance

(b) To calculate amps, time, coulombs, faradays and moles of electrons:

Three equations related these quantities:

- (i) Amperes \times time = Coulombs
- (ii) 96,485 coulombs = 1 Faraday
- (iii) 1 Faraday = 1 mole of electrons

The through process for interconverting amperes and moles of electrons is:

Amps and time \longleftrightarrow Coulombs \longleftrightarrow Faradays \longleftrightarrow Moles of electrons

Use of these equations are illustrated in the following sections.

(c) To calculate the quantity of substance produced or consumed: To determine the quantity of substance either produced or consumed during electrolysis, given the time a known current flowed:

- (i) Write the balanced half-reactions involved.
- (ii) Calculate the number of moles of electrons that were transferred.
- (iii) Calculate the number of moles of substance that was produced/consumed at the electrode.
- (iv) Convert the moles of substance to desired units of measure.

(d) Determination of standard cell potentials: A cell's standard state potential is the potential of the cell under standard state conditions, and it is approximated with concentrations of 1 mole per liter (1 M) and pressures of 1 atmosphere at 25°C.

- (i) To calculate the standard cell potential for a reaction.
- (ii) Write the oxidation and reduction half-reactions for the cell.
- (iii) Look up the reduction potential, $E_{\text{reduction}}^{\circ}$, for the reduction half-reaction in a table of reduction potentials.
- (iv) Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction, $E_{\text{oxidation}}^{\circ} = -E_{\text{reduction}}^{\circ}$.
- (v) Add the potentials of the half-cells to get the overall standard cell potential.

$$E_{\text{cell}}^{\circ} = -E_{\text{reduction}}^{\circ} + E_{\text{oxidation}}^{\circ}$$

(e) For determining non-standard state cell potentials: To determine the cell potential when the conditions are other than standard state (concentrations not 1 molar and/or pressures not 1 atmosphere):

- (i) Determine the standard state cell potential.
- (ii) Determine the new cell potential resulting from the changed conditions.
- (iii) Determine Q, the reaction quotient.

- (iv) Determine n , the number of electrons transferred in the reaction “ n ”.
- (v) Determine E_{cell} , the cell potential at the non-standard state conditions using the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT / nF) \ln Q$$

E_{cell} = cell potential at non-standard state conditions; E_{cell}° = standard state cell potential

R = constant (8.31 J/mole K); T = absolute temperature (Kelvin scale)

F = Faraday's constant (96,485 C/mole e^{-})

n = Number of moles of electrons transferred in the balanced equation for the reaction occurring in the cell;

Q = Reaction quotient for the reaction. $aA + bB \rightarrow cC + dD$, $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

If the temperature of the cell remains at 25°C, the equation simplifies to:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0257 / n) \ln Q \text{ or in terms of } \log_{10}; E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0592 / n) \log Q$$

POINTS TO REMEMBER

S.No.		Description
1	Electrolyte	Any substance which dissolves in water to form a solution that will conduct an electric current (ionic substances). Electrolytes may be classified as strong (NaCl, HCl, NaOH) or weak (NH ₄ OH, CH ₃ COOH, HF). Solutions that do not conduct electricity at all are called non-electrolytes.
2	Strong and Weak Electrolytes	Strong electrolyte - Solutions in which the substance dissolved (solute) is present entirely as ions. Weak electrolyte - A solute that yields a relatively low concentration of ions in solution.
3	Dissociation	The separation of ions that occurs when an ionic substance dissolves: $\text{CaCl}_2(\text{s}) + \text{H}_2\text{O} \rightarrow \text{Ca}^{+2}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$.
4	Electrochemical Cells	A system of electrodes and electrolytes in which a spontaneous or non-spontaneous redox reaction occurs.
5	Components of Electrochemical cells	<ul style="list-style-type: none"> a. Electrode: An electrical conductor (metal strip) used to establish contact with a non-metallic part of the circuit (usually an electrolyte). b. Anode: The electrode at which oxidation occurs. c. Cathode: The electrode at which reduction occurs. d. Electrolyte: A liquid, paste, or gel that serves to conduct charge by moving ions in the cell. e. Half-cell: A single electrode immersed in a solution of its ions. f. Salt bridge: A device (porous disk or bridge i.e. U-tube containing inert electrolytic solution, KCl, NH₄NO₃, etc.) placed between the cells which maintains electrical neutrality by allowing ions to migrate between the cells. g. External circuit: The part of the cell where charge is conducted as a current of moving electrons. h. Standard Electrode Reduction Potential E°: The measurement, in volts, of the tendency for a half reaction to occur as a reduction half reaction.

S.No.		Description																		
6	Voltaic/Galvanic Cells	Redox reactions are spontaneous and chemical energy is transformed into electrical energy. The cell potential E° is positive and the anode is the negative electrode. i.e. batteries $Zn(s) Zn^{+2}(1M) Cu^{+2}(1M) Cu(s)$ anode cathode																		
7	Electrolytic Cells	Cell in which an external electric current is required to drive a non-spontaneous redox reaction. The cell potential (E°) is negative and the anode is the positive electrode. i.e. electrolysis, electroplating, etc. $Cu(s) Cu^{+2}(1M) Cu^{+2}(1M) Cu(s)$ anode cathode																		
8	Quick Comparison of Electrolytic Cells	<table border="1"> <thead> <tr> <th>Type of redox reaction cell potential (E°_{cell}) Electron flow</th> <th>Galvanic/Voltaic</th> <th>Electrolytic</th> </tr> </thead> <tbody> <tr> <td>Site of oxidation</td> <td>Spontaneous (E°_{cell} is positive)</td> <td>Non-spontaneous (E°_{cell} is negative)</td> </tr> <tr> <td>Site of reduction</td> <td>Creates one</td> <td>Requires one</td> </tr> <tr> <td>Positive electrode</td> <td>Anode</td> <td>Anode</td> </tr> <tr> <td>Negative electrode</td> <td>Cathode</td> <td>Cathode</td> </tr> <tr> <td>Flow of electrons</td> <td>Cathode Anode Anode to cathode (negative to positive) Batteries</td> <td>Anode Cathode Anode to cathode (positive to negative) Electrolysis, electroplating</td> </tr> </tbody> </table>	Type of redox reaction cell potential (E°_{cell}) Electron flow	Galvanic/Voltaic	Electrolytic	Site of oxidation	Spontaneous (E°_{cell} is positive)	Non-spontaneous (E°_{cell} is negative)	Site of reduction	Creates one	Requires one	Positive electrode	Anode	Anode	Negative electrode	Cathode	Cathode	Flow of electrons	Cathode Anode Anode to cathode (negative to positive) Batteries	Anode Cathode Anode to cathode (positive to negative) Electrolysis, electroplating
Type of redox reaction cell potential (E°_{cell}) Electron flow	Galvanic/Voltaic	Electrolytic																		
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Negative electrode	Cathode	Cathode																		
Flow of electrons	Cathode Anode Anode to cathode (negative to positive) Batteries	Anode Cathode Anode to cathode (positive to negative) Electrolysis, electroplating																		
9	Faraday's First law of Electrolysis	The amount of electrolyte discharged at an electrode is directly proportional to the quantity of electricity passed: $W \propto Q$ where, $Q = I \cdot t$ I = Current strength in ampere T = time in seconds $\Rightarrow W = ZQ = Zit$ Z is a constant called electrochemical equivalence (ECE)																		
10	Electrochemical Equivalent	It is the amount of an electrolyte discharged on passing one coulomb of electricity.																		
11	Faraday's Constant	It is the charge possessed by 1.0 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 number of faraday's passed. $\Rightarrow W = E \left(\frac{Q}{96500} \right)$ where, E = Equivalent weight																		
12	Faraday's Second Law	Second Law: If same quantity of electricity is passed through different cells connected in series, same number of gram equivalent of electrolytes are discharged at each of the electrodes: $\Rightarrow \frac{W_1}{W_2} = \frac{E_1}{E_2}$ Where, W_1 and W_2 are the weights of electrolytes discharged at two different electrodes in two different cells connected in series and E_1 and E_2 are their respective equivalent weights.																		

S.No.		Description
13	Nernst Equation	$E_{\text{half-cell}} = E^{\circ}_{\text{half-cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$ <p>At 298 K, the Nernst equation can be written as,</p> $E_{\text{half-cell}} = E^{\circ}_{\text{half-cell}} - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$

Solved Examples

JEE Main/Boards

Example 1: Zn and iron can replace Cu in a solution but Pt and Au cannot. Why?

Sol: Both Zn and iron have more E°_{OP} than Cu, whereas Pt and Au have less E°_{OP}

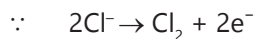
Example 2: Which of the following metals cannot be obtained by the electrolysis of their aqueous salt solution and why?

Al, Na, Cu, Ag.

Sol: Al and Na cannot be obtained because they have higher E°_{OP} than H and thus, reduction of Cu^{2+} and Ag^+ will give Cu and Ag.

Example 3: Calculate the no. of electron lost or gained during electrolysis of 2 g Cl^- from NaCl (aq) to give Cl_2 at anode.

Sol: First calculate the equivalent of Cl^- used during the reaction and on multiplying it with avogadro number will give us the no of electron lost during the reaction



Eq. of Cl^- used = $2/35.5$

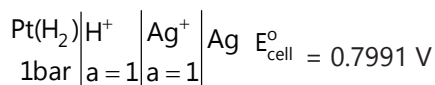
\therefore 1 eq. of an element involves 1 faraday charge or N electrons

\therefore $(2/35.5)$ eq. of an element involves

$$= \frac{N \times 2}{35.5} \text{ electrons} = \frac{6.023 \times 10^{23} \times 2}{35.5}$$

$$= 3.4 \times 10^{22} \text{ electrons}$$

Example 4: Evaluate the $E^{\circ}_{\text{Ag}^+/\text{Ag}}$ and $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}$ from the given values:



Sol: Since platinum electrode has zero reduction potential the standard electrode potential will be equal to the standard electrode potential of the cell.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{H}^+/\text{H}^+} + E^{\circ}_{\text{RP}_{\text{Ag}^+/\text{Ag}}}$$

$$\text{Or } 0.7991 = 0 + E^{\circ}_{\text{RP}_{\text{Ag}^+/\text{Ag}}} \quad \therefore E^{\circ}_{\text{RP}_{\text{Ag}^+/\text{Ag}}} = 0.7991 \text{ V}$$

Example 5: Standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, $K_{\text{sp}} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of $\text{I}^-/\text{AgI}/\text{Ag}$ electrode.

Sol: Here solubility product is given from this calculate the concentration of silver ions. Now substituting this value in Nernst equation determine $E^{\circ}_{\text{Ag}^+/\text{Ag}}$

As we have found out $E^{\circ}_{\text{Ag}^+/\text{Ag}}$, $E^{\circ}_{\text{I}^-/\text{AgI}/\text{Ag}}$ can find out by using the value of solubility product.

$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = E^{\circ}_{\text{Ag}^+/\text{Ag}} + (0.059/1) \log [\text{Ag}^+] \quad \dots \text{ (i)}$$

$$\text{Also, } K_{\text{spAgI}} = [\text{Ag}^+][\text{I}^-]$$

$$\therefore [\text{Ag}^+] = [\text{I}^-] \quad (\text{for a saturated solution})$$

$$\therefore [\text{Ag}^+] = \sqrt{K_{\text{spAgI}}} = \sqrt{8.7 \times 10^{-17}}$$

$$= 9.32 \times 10^{-19} \quad \dots \text{ (ii)}$$

\therefore By Eq. (i),