

2. ELECTROCHEMISTRY

Electrochemistry is the field of chemistry which deals with the results in the generation of an electric current or because by passing an electric current. Electrochemistry can be divided into two categories

1. USE of electrical energy to produce chemical change which is known as electrolysis.
2. conversion of chemical energy into electrical energy.

There are two types of electrical conductors present,

Metallic conductors

Metals are the best conductors, in them the passage of current is not accompanied by an movement of matter.

Ex:- copper, aluminium, silver, platinum

Electrolytic conductors

In these conductors, electricity is conducted due to the migration of ions or transport of ions to oppositely charged ions.

Ex:- aqueous solution of NaOH/KOH & fused solutions of NaCl/KCl

write the differences b/w metallic & electrolytic conductors

Metallic

Electrolytic

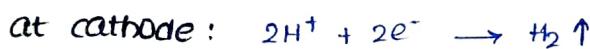
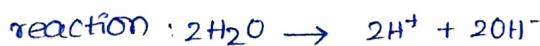
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|---|---|
| 1. It occurs due to flow of electrons. | 1. In the soln or fused state current is conducted due to movement of ions. |
| 2. This is only a physical change in the conductor. | 2. It involves a chemical change. This change occurs at electrode |
| 3. NO transfer of matter takes place | 3. This involves transfer of matter in the form of ions. |
| 4. Resistance increase with a raise in temperature | 4. It shows a decrease in resistance with a raise in temp. |

Electrolysis

Electrolysis takes place in the electrolytic cell which contains an electrolyte and two electrodes i.e., anode & cathode connected to a battery. The positive pole or electrode is called as anode and oxidation takes place at this electrode. The negative electrode is called as cathode and reduction takes place at this electrode i.e., in electrochemical cell Redox reactions take place.

Ex-1 : Electrolysis of water

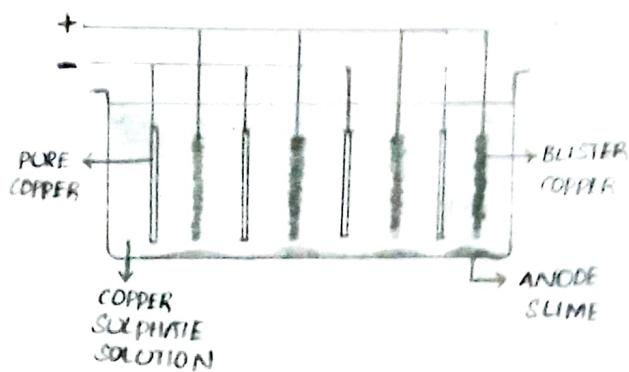
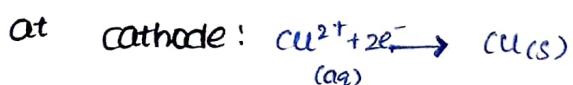
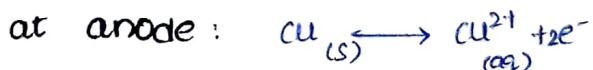
water may be the electrolyte and pure water is bad conductor. If we add the little amount of dilute H_2SO_4 then it is a good conductor of electricity, when we pass the current through the water, hydrogen gas is evolved at cathode and oxygen gas is liberated at anode in the 2:1 ratio. And the following reactions take place



Electrorefining of copper

Impure copper obtained by the ores is known as blister copper, and it can be purified by electrorefining process. In this process pure copper rods act as cathodes & blister copper act as anodes and Cu^{2+} ions act as electrolyte. On passing the current the Cu^{2+} ions from the solution deposited on cathode and at the same time pure Cu^{2+} ions are anti-entered from blister copper to solution. On prolonged electrolysis all the copper from the blister copper rods are deposited on the cathode and the impurities are settled down in the bottom of the cell.

The reactions are,



FARADAY'S LAWS OF ELECTROLYSIS

1st Law:

The weight of a chemical substance deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte ie,

$$w \propto Q$$

where, w = wgt of the substance deposited

Q = quantity of electricity passed in coulombs.

WKT,

$$Q = C_A t \text{ (sec)}$$

$$\therefore Q \propto w \Rightarrow w \propto ct$$

$$w = Z \cdot ct. \quad Z \Rightarrow \text{Electrochemical constant.}$$

If we keep $C=1 \text{ amp}$ and $t=1 \text{ sec}$, then

$$w = Z$$

\therefore The electrochemical equivalent is defined as the amount of the substance deposited by passing 1amp current per 1 sec ie,

$$Z = \frac{\text{Eq. wgt}}{96500}$$

2nd LAW:

It states that the weight of the different substances produced by the same quantity of electricity is proportional to the equivalent of the substance.

If w_1 & w_2 are weights of two elements deposited by passing certain quantity of electricity through their salt solutions of E_1, E_2 are the equivalent wghts then

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \quad [w \propto E]$$

Example:

when the same amount of current passed through solutions of three electrolytic cells like dil H_2SO_4 , $CuSO_4$ and $AgNO_3$ which are connected in a series and the relation b/w amount of substance deposited is,

$$\frac{\text{mass of Cu deposited}}{\text{mass of } H_2 \text{ liberated}} = \frac{\text{Eq wgt of Cu}}{\text{Eq wgt of } H_2}$$

$$\Rightarrow \frac{w_{Cu}}{w_{H_2}} = \frac{E_{Cu}}{E_{H_2}}$$

$$\text{Similarly, } \Rightarrow \frac{w_{Ag}}{w_{Cu}} = \frac{E_{Ag}}{E_{Cu}}$$

The relation can be explained in terms of equivalent wgt,

$$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

In other words, $E \propto Z \Rightarrow F = F \times Z$, when F is called the proportionality constant called as Faraday.

$$F = 96540 C.$$

Faraday (F)

One Faraday may be defined as the quantity of electricity which can deposit one gram equivalent of the element present in electrolyte.

Applications of electrolysis

1 DETERMINATION OF EQUIVALENT MASSES OF ELEMENTS.

According to 2nd law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of metals deposited on cathodes of two cells are proportional to their equivalent masses of respective metals. If the amounts of metals deposited on cathodes be w_A and w_B respectively then

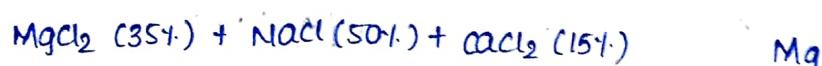
$$\frac{w_A}{w_B} = \frac{\text{Eq. wgt of A}}{\text{Eq. wgt of B}}$$

2 Electro Metallurgy

The metals like sodium, potassium, magnesium, calcium, aluminium etc are obtained by electrolysis of fused electrolytes.

Fused electrolyte

metal isolated.



3. Manufacture of Non-metals

Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

4. Electro-refining of metals

The metals like copper, silver, gold, aluminium, tin etc are refined by electrolysis.

5. Manufacture of compounds

Compounds like NaOH , KOH , Na_2CO_3 , KClO_3 , KMnO_4 etc are manufactured by electrolysis.

6. Electroplating

The process of coating an inferior metal with a superior metal, by electrolysis is known as electroplating. Its uses are

- (a) To prevent the inferior metal from oxidation.
- (b) To make it more attractive in appearance.

The object to be electroplated is made the cathode and block of metal to be deposited is made anode in electrolytic bath containing a solution of a salt of anodic metal. On passing electric current in cell, metal of anode dissolves out & is deposited on cathode - particle in the form of thin film.

* FOR electroplating	Anode	cathode	Electrolyte
with copper	cu	object	$\text{CuSO}_4 + \text{dil H}_2\text{SO}_4$
with silver	Ag	"	$\text{K[Ag(CN)}_2]$
with Nickel	Ni	"	Nickel ammonium Sulphate
with Gold	Au	"	$\text{K[Au(CN)}_2]$
with Zinc	Zn	Iron Object	ZnSO_4
with Tin	Sn	"	SnSO_4

Conductance in Electrolytic Solutions

Ohm's Law

The electrolytic solutions obey ohm's law just as metallic conductors do. According to this law, the current flowing through an electrolyte (I) is inversely proportional to its resistance (R).

$$I \propto \frac{1}{R} \text{ (or) } I = \frac{V}{R}$$

In electrochemistry, the term conductance (C) is used. It is reciprocal of electrical resistance.

$C = 1/R$, C is expressed in ohm⁻¹ (or) siemen in SI system.

$$1S = 1\Omega^{-1}$$

Specific Resistance (ρ)

The resistance of a conductor is directly proportional to its length (l) and is inversely proportional to Area (A).

$$R \propto l \quad R \propto 1/A$$

$$R \propto \frac{l}{A} \Rightarrow R = S \cdot \frac{l}{A}$$

$$\boxed{S = R \cdot \frac{A}{l}}$$

$$\text{when, } l = 1\text{cm} \text{ & } A = 1\text{cm}^2 \rightarrow \boxed{R = S}$$

* SI units are ohm.m.

Specific conductance (K)

The conductance of a solution taken in a cell in which the electrodes are at unit distance and have unit area of cross section and it is reciprocal of Specific Resistance. It is denoted by K .

$$K = 1/\rho$$

* The units are ohm⁻¹m⁻¹ or ohm⁻¹cm⁻¹

Cell constant

The ratio of length of electrolytic conductor (l) and the area of cross section.

$$\text{cell constant} = \left[\frac{l}{A} \right]$$

* Units of cell constant are cm^{-1} or m^{-1} (SI)

Equivalent conductivity (Λ_{eq})

The conductivity of all the ions present in the electrolytic solution containing one gram equivalent of a substance denoted by Λ .

* If volume of solution is V in cm^3 then $\boxed{\Lambda = K \cdot V}$

* If normality of solution is ' c ' then $\boxed{\Lambda = K \times \frac{1000}{c}}$

Molar conductance (Λ)

The conductivity of all the ions present in an electrolytic solution containing 1 gm molecular weight of a substance. It is represented by Λ .

Relation b/w Λ & μ

The molar & equivalent conductors are related by

$$\boxed{\Lambda = \frac{\mu}{Z}}$$

Z = no. of individual charges carried by ions.

Degree of Ionization or dissociation (α)

This is the ratio b/w the equivalent conductivity at a given concentration to equivalent conductivity at infinite dilution.

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty}$$

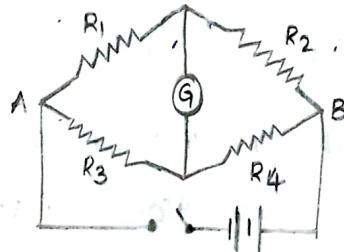
FOR strong electrolyte, $\alpha = 1$

weak, $\alpha < 1$

Measurement of electrolytic conductance

conductance of an electrolytic solution is measured using wheatstone bridge principle. The electrolyte is taken in conductivity cell. The cell is kept instead of one resistor in the wheatstone bridge.

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$



Strong & weak electrolytes

A solution which contains larger no. of ions as compared to another solution of same concentration at the same temperature is called a strong electrolyte

Ex:- HCl, KCl, NaOH etc.

An electrolyte which has low degree of dissociation is known as weak electrolyte

Ex:- CH₃COOH, NH₄OH, HCN etc.

Effect of dilution on equivalent conductivity:

For all electrolytes, the equivalent conductivity increases on dilution and reaches a limiting value. This limiting value is known as equivalent conductivity at infinite dilution, represented by Λ_0 or Λ_∞ .

The equivalent conductivity of a strong electrolyte can be determined by extrapolation method. Most of the procedures are based on formula,

$$\Lambda = \Lambda_\infty - b\sqrt{c} \quad (b = \text{const})$$



But for weak electrolytes, Kohlrausch's law is utilized.

Kohlrausch law

This is also known as law of independent migration of ions. It is defined as the equivalent conductance at infinite dilution of an electrolyte is composed of two independent quantities, one attributed by anion and the other by cation.

$$\Lambda_{\infty} = [\lambda_a^{\circ} + \lambda_c^{\circ}]$$

At infinite dilution the dissociation of all electrolytes is complete. The interionic interactions disappear. The each ion migrates independently.

Applications of Kohlrausch law

- * determination of equivalent conductance of a weak electrolyte at infinite dilution.

There are several methods to determine Λ_{∞} for the weak electrolyte (acetic acid).

Calculation of Λ_{∞} of CH_3COOH



consider the dissociation of HCl, NaCl and CH_3COONa .

$$\Lambda_{\infty}^{\circ}_{\text{HCl}} = \lambda^{\circ}_{\text{H}^+} + \lambda^{\circ}_{\text{Cl}^-} \rightarrow (1)$$

$$\Lambda_{\infty}^{\circ}_{\text{NaCl}} = \lambda^{\circ}_{\text{Na}^+} + \lambda^{\circ}_{\text{Cl}^-} \rightarrow (2)$$

$$\Lambda_{\infty}^{\circ}_{\text{CH}_3\text{COONa}} = \lambda^{\circ}_{\text{CH}_3\text{COO}^-} + \lambda^{\circ}_{\text{Na}^+} \rightarrow (3)$$

The given electrolyte CH_3COOH is a weak acid n^othg but weak electrolyte at infinite dilution,

$$\Lambda_{\infty}^{\circ}_{\text{CH}_3\text{COOH}} = \lambda^{\circ}_{\text{CH}_3\text{COO}^-} + \lambda^{\circ}_{\text{H}^+}$$

To get this value doing (1) + (3) - (2)

$$\begin{aligned}&= \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} + \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{Na^+} - \lambda^{\circ}_{Na^+} - \lambda^{\circ}_{Cl^-} \\&= \lambda^{\circ}_{H^+} + \lambda^{\circ}_{CH_3COO^-}\end{aligned}$$

By using the Kohlrausch's law we can calculate the degree of dissociation of weak electrolyte

- The degree of dissociation is given by $\alpha = \frac{\Lambda c}{\Lambda_{\infty}}$, in this eqn Λ_{∞} value can be calculated by this law and can be used to calculate α .
- * The ionic product of water can be calculated from Kohlrausch Law.
- * We can also calculate conductivity of individual ions.
- * The solubility product also can be calculated by Kohlrausch Law.

Electrochemical cells

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge to the external circuit.

Ex:- Electrolytic cell

Galvanic or voltaic cells.

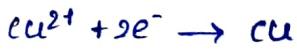
Electrolytic cell

It is a device in which electrolysis reaction involving oxidation and reduction is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

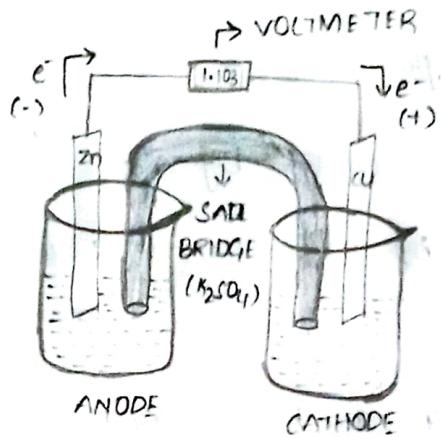
Galvanic or voltaic cell

It is a device used to convert the chemical energy produced in a Redox reaction into electrical energy.

Ex:- The Redox reaction b/w Zn & CuSO₄ is



If a Redox reaction is allowed to take place in such a way that the oxidation half reaction takes place in one beaker and the reduction half reaction in another beaker. Then electrons will flow from the former to the latter and a current will flow.



Representation of an electrochemical cell

An electrochemical cell is represented by taking the oxidation half reaction on the left hand side ; reduction half reaction on the right hand side, which can be separated by two vertical lines indicated salt bridge with their concentration.

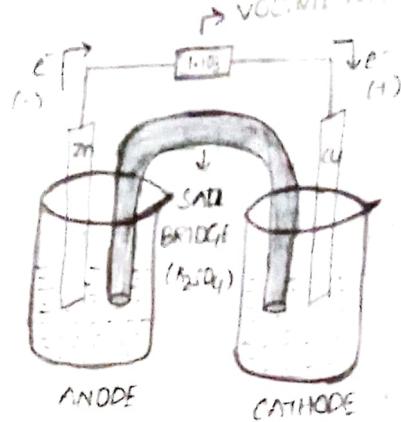
Ex:

Cell potential (or) emf of a cell

The difference b/w electrode potentials of two half cells is known as cell potential or cell voltage or emf.

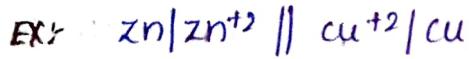
$$E_{cell} = E_{PMS} - E_{LHS}$$

Single electrode



Representation of an electrochemical cell

An electrochemical cell is represented by taking the oxidation half reaction on the left hand side & reduction half reaction on the right hand side, which can be separated by two vertical lines indicated salt bridge with their concentration.



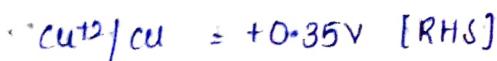
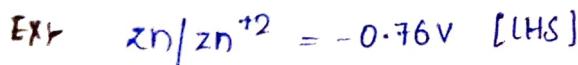
Cell potential (or) emf of a cell

The difference b/w electrode potentials of two half cells is known as cell potential or cell voltage or emf.

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}}$$

Single electrode

* The SI unit of emf is volt.



$$\text{emf} = 0.35 - (-0.76)$$

$$= 1.11\text{V.}$$

ELECTROCHEMICAL CELL (galvanic cell)

1. chemical energy \rightarrow electrical energy.
2. It is based on spontaneous Redox reaction.
3. two electrolytes same or different taken in two beakers.
4. Anode \Rightarrow -ve electrode, oxidation
cathode \Rightarrow +ve electrode, Reduction.

ELECTROLYTIC CELL (electrolysis)

1. Electrical energy \rightarrow chemical energy.
2. It is based on non-spontaneous Redox reaction.
3. only one electrolyte taken.
4. Anode = +ve electrode, oxidation
cathode = -ve electrode, Reduction.

Single electrode

A metal rod dipped in the aqueous solution of its salt solution is known as single electrode

(or)

A metal rod dipped in the aq. solution of its salt or a gaseous non-metal in contact with the solution containing its anions in the form of salt (or) acid or alkali functions as single electrode

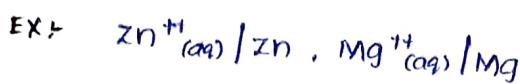
Ex:- Metal electrodes

1. Zinc electrode : $Zn^{++}_{(aq)} / Zn$
2. Copper electrode : $Cu^{++}_{(aq)} / Cu$
3. Magnesium Electrode : $Mg^{++}_{(aq)} / Mg$
4. Silver electrode : $Ag^{++}_{(aq)} / Ag$
5. Iron electrode : $Fe^{++}_{(aq)} / Fe$

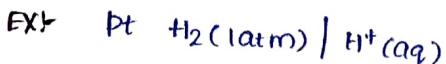
Ex:- Non-metal electrodes

1. Hydrogen electrode : $H^+_{(aq)} / H_2(g), Pt$
2. Chlorine electrode : $Pt, Cl_2(g) / Cl^-_{(aq)}$
3. Oxygen electrode : $Pt, O_2(g) / OH^-_{(aq)}$
4. Bromine electrode : $Pt, Br_2(g) / Br^-_{(aq)}$

* Generally the electrolyte in a single electrode is written in the form of the ions of concentrated metal (or) the non-metal while representing the half cell.



* In the case of non-metal electrodes a particular rod is placed in the concerned gas at atmosphere pressure is passed into the solution.



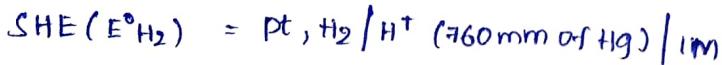
Standard Electrode potential (E°)

"when the concentration of solutes are 1M, the gas pressures are 1 atm and the temperature has specified value (298K or 25°C) the electrode potential is known as standard electrode potential (E°_{cell})

Ex:- when Zn-rod of any length is dipped in 1M ZnSO_4 solution, standard electrode potential developed is called standard zinc electrode potential. i.e,



Ex:- when the H_2 gas at a pressure of 1 atm is bubbled through HCl of 1M, standard electrode potential developed is called Standard Hydrogen Electrode



→ Here the gas at a pressure of 760 mm of Hg & the ions in the solution of 1 unit concentration.

→ The magnitude of SHE is considered to be zero.

NOTE:

The magnitude of the standard electrode potential is independent of temperature, it depends only on the concentration of the ions.

Standard Hydrogen Electrode (SHE) ; Normal Hydrogen Electrode (NHE) Reference Electrode

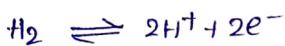
- * The absolute value of single electrode potential can't be determined
- * To overcome this difficulty the Standard hydrogen electrode (SHE) is taken as the standard reference electrode

SHE

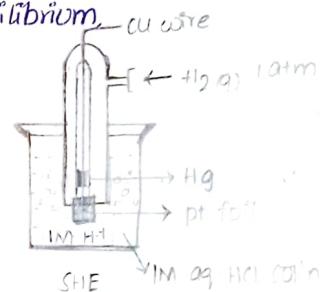
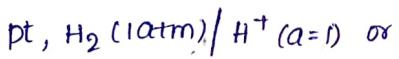
- * It is used as a primary reference electrode for measuring the Emf of other electrodes.
- * The Emf of SHE is taken as 0.00 V at all temperature

construction

- i, The SHE consists of a platinum electrode coated with platinum black.
- ii, The electrode is dipped in a 1M aq. solution of HCl
- iii, H₂ gas is bubbled through it at one atmosphere pressure



- iv, on platinum foil H₂ gas & H⁺ ions are in equilibrium
hydrogen electrode is represented as,



- v, Half Reactions \rightarrow If electrode act as cathode $\rightarrow pt, 2H^+ + 2e^- \rightarrow H_2$
 \rightarrow If electrode act as anode $\rightarrow 2H^+ \xrightarrow{Pt, H_2} 2H^+ + 2e^-$

Applications

- * The magnitude of SHE potential is considered as zero. It is used for
- 1. The determination of electrode potential of metal electrode system.
- 2. The determination of pH of the solution.

Limitations

1. It is rather difficult to regulate the pressure of H_2 gas to be exactly 1 atm and concentration of HCl at 1M throughout the experiment.
2. Pt foil gets easily poisoned by the impurities present in the H_2 gas. So, if the attachment of equilibrium is ensured by trial & error, HCl then the attachment of equilibrium is ensured by trial & error.
3. If the solution contains any oxidising agent the H_2 electrode can't be used.

Measurement of Electrode potential

- * The absolute value of a single electrode can't be measured experimentally. bcoz a half cell reaction can't take place independently.
- * we can measure only difference b/w the electrode potentials of any two half cell Reactions.
- * If the cell potential of the electrode potentials for one half reac'n are known, the electrode potential of the other electrode can be determined.
- * therefore, hydrogen electrode is chosen and all other cell reactions are compared with this standard & a set of E° values are obtained.

Ex:-

Measurement of electrode potential of Cu^{+2}/Cu electrode

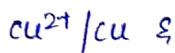
- * In a galvanic cell the cathode is positive electrode while the anode is negative electrode.
- * These two electrodes are connected to voltmeter readings are obtained when the terminals are properly connected.
- * when the half cell consisting of copper electrode immersed in 1M $CuSO_4$ solution & SHE are connected to voltmeter the Emf of the cell is observed to be 0.34 V.
- * Oxidation occurs to the SHE, which act as the anode where as reduction occurs at the copper electrode which act as the cathode.

The potential of the cell.

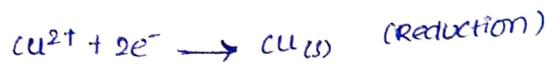
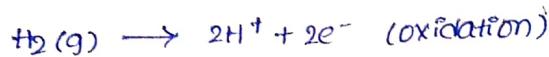
→ SHE denoted as



→ Cu electrode denoted as



* The two half cell reactions



* The Emf of the cell is, $E^\circ_{\text{cell}} = E^\circ_{\text{RHS}} - E^\circ_{\text{LHS}}$; $E^\circ_{\text{cell}} = 0.34\text{ V.}$

$$0.34 = E^\circ(Cu^{2+}/Cu) - E^\circ(H_2/H^+)$$

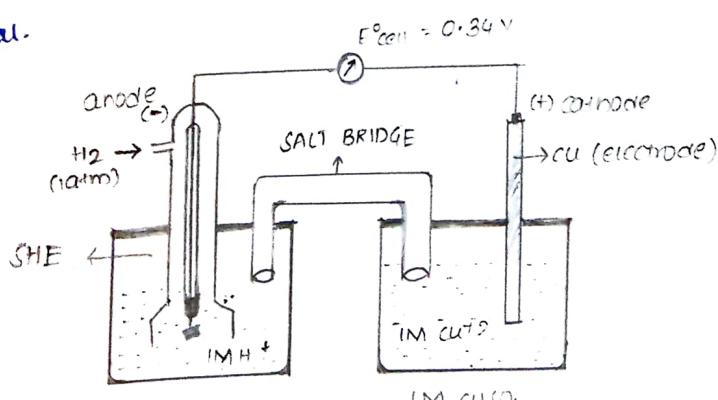
$$0.34 = E^\circ(Cu^{2+}/Cu) - 0$$

$$\therefore E^\circ(Cu^{2+}/Cu) = 0.34\text{ V.}$$

→ Thus the standard Electrode potential of Cu electrode is 0.34 V.

NOTE

- * The electron accepting tendency of the electrode is more than that of SHE gets a +ve sign.
- * The electron accepting tendency of the electrode is less than that of SHE gets a -ve sign.
- * The electrode at which reduction occurs w.r.t to SHE electrode has +ve reduction potential.
- * The electrode at which oxidation occurs wrt to SHE has -ve reduction potential.



Electrochemical Series

"The arrangements of the electrodes in order of increasing reduction potential values (or) standard electrode potential values is called Electrochemical Series".

standard reduction potentials at 298K

ELECTRODE	HALF CELL REA'N (Reduction)	E° (VOLTS)
$\text{Li} : \text{Li}^+$	$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05
$\text{K} : \text{K}^+$	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93
$\text{Ba} : \text{Ba}^{2+}$	$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	-2.90
$\text{Ca} : \text{Ca}^{2+}$	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.87
$\text{Na} : \text{Na}^+$	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.81
$\text{Mg} : \text{Mg}^{+2}$	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37
$\text{Al} : \text{Al}^{3+}$	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66
$\text{Zn} : \text{Zn}^{+2}$	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76
$\text{Fe} : \text{Fe}^{2+}$	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.44
$\text{Pb}, \text{PbSO}_4, \text{SO}_4^{-2}$	$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{-2}$	-0.31
$\text{Co} : \text{Co}^{+2}$	$\text{Co}^{+2} + 2e^- \rightarrow \text{Co}$	-0.28
$\text{Ni} : \text{Ni}^{+2}$	$\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni}$	-0.25
$\text{Sn} : \text{Sn}^{+2}$	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.14
$\text{Pb} : \text{Pb}^{+2}$	$\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb}$	-0.13
$\text{Pt}, \text{H}_2 ; \text{H}^+$	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.00
$\text{Cu} : \text{Cu}^{+2}$	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.34
$\text{I}_2 : \text{I}^-$	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.54
$\text{Fe}^{3+} ; \text{F}^{-2}$	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+0.180 0.177
$\text{Ag} ; \text{Ag}^+$	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.80
$\text{Cl}^- ; \text{Cl}_2, \text{Pt}$	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{Au} ; \text{Au}^{3+}$	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.5
$\text{F} ; \text{F}_2, \text{pt}$	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+2.87

Characteristics

- * Substances with stronger reducing power are placed above Hydrogen and those with weaker reducing power are placed below H.
- * If two metals form a cell, the metal that above Hydrogen undergoes oxidation and forms anode, while the other one below the hydrogen undergoes reduction form the cathode

Ex:- Zn - anode (-0.76 V)
Cu - cathode (+0.34 V)

Applications

1. To calculate the EMF of an electrochemical cell

Ex:- $Zn/Zn^{+2} \parallel Ag^+/Ag$

$$E^\circ_{cell} = E_R \text{ (cathode)} - E_L \text{ (anode)} \Rightarrow E^\circ_{cell} = E_R^\circ - E_L^\circ$$

$$E^\circ_{cell} = 0.80 - (-0.76) = +1.56 V.$$

2. To predict the relative strengths of oxidising & reducing agents.
→ the more positive is the value of E° , the better will be the oxidising agent.

3. To predict the feasibility of Reaction.

→ In general, If $E^\circ_{cell} = +ve$, the reaction is feasible

4. To predict whether a metal will react with acid to give the gas.

→ Any metal placed above the hydrogen is a strong reducing agent & will displace H_2 from a dilute acid.



5. To predict whether a metal will displace another a metal from its Salt solution or not.

→ A metal which placed higher up in the series will displace all metals which are kept below it from solutions of their salts.

Gibb's Free energy of the Reaction

- If we want to obtain maximum work from a galvanic cell then the charge has to be passed reversibly.
 - The reversible work done by a galvanic cell is equal to decrease in its Gibb's free energy.
- ∴ Decrease in free energy = Electrical work. → (1)

- In an electrochemical cell,

Electrical work done = quantity of current \times Emf of the cell produced

$$W = nF \times E_{\text{cell}}. \rightarrow (2)$$

$n \Rightarrow$ no. of moles of electrons

$F \Rightarrow$ faraday current ($1 \text{ F} = 96,500 \text{ coulomb}$)

$$\text{emf} = E_{\text{cell}}$$

18.0

$$\text{From (1) \& (2)} \quad -\Delta G^\circ = nF \cdot E_{\text{cell}}$$

This is the relation b/w cell potential (EMF) & Gibb's free energy.

Relation b/w Gibb's free Energy & Equilibrium constant.

For equilibrium establishment in a Redox Reaction, the decrease in the free energy is given by,

$$\Delta G^\circ = -nFE_{\text{cell}} \quad \therefore E_{\text{cell}} = \frac{RT}{nF} \ln K_c$$

$$\Delta G^\circ = -RT \ln K_c \quad K_c \Rightarrow \text{Equilibrium constant}$$

$$\Delta G^\circ = -2.303 RT \cdot \log K_c$$

NERNST EQUATION

"This equation tells us the effect of temperature and concentration of the electrolyte on electrode potential."

For the reduction reaction : $M^{n+} + ne^- \rightarrow M$

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[\text{products}]}{[\text{reactants}]} \quad \text{or}$$

$$E = E^\circ = \frac{-2.303 RT}{nF} \log \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

Electrode reaction is, $M^{n+} + ne^- \rightleftharpoons M$

$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]} \rightarrow (1)$$

where, E = electrode potential

E° = standard electrode potential

R = gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = temperature in K (298 K)

F = Faraday (96500 coulombs)

n = no. of e^- 's involved in reaction.

Substitute these values in the eqn we get,

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[M]}{[M^{n+}]}$$

For pure solids (or) liquids or gases at 1 atm the concentration is unity

$$[M=1] \Rightarrow E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$\boxed{E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]} \text{ or}$$

$$E = E^{\circ} + \frac{0.0591}{n} \log [c] \quad c \rightarrow \text{concentration of electrolyte}$$

Ex- Nernst equation for Zn-ZnSO₄ electrode

Electrode reaction $\rightarrow \text{Zn}^{12+} + 2e^- \rightarrow \text{Zn}$

$$\therefore E = E^{\circ} - \frac{0.0591}{2} \log \left[\frac{1}{\text{Zn}^{12+}} \right]$$

$$E = E^{\circ} + \frac{0.0591}{2} \log [\text{Zn}^{12+}]$$

NOTE!

* Nernst eqn for metal electrode, $E = E^{\circ} + \frac{2.303 RT}{nF} \log c$

* For non-metal electrode, $E = E^{\circ} - \frac{2.303 RT}{nF} \log c$.

1. Nernst Equation for EMF of cell

Let us consider a cell represented as,



$$\therefore E_{\text{cell}} = E^{\circ} - \frac{0.0591}{n} \log \frac{[X]^p [Y]^q}{[A]^s [B]^s}$$

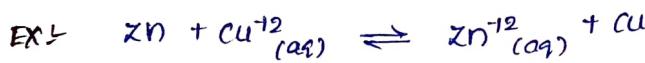
$$[\text{Zn}] = \text{[Cu]} = 1 \quad (\text{they are pure solids})$$

$$E_{\text{cell}} = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

2 Equilibrium constant (K_c) from Nernst Equation.

Both the electrode potentials are equal. Current stops flowing and the cell is said to have attained equilibrium.

$$\therefore E = E^{\circ} - \frac{0.0591}{n} \log K_c$$



$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log K_c \quad K_c \rightarrow \text{Equilibrium constant.}$$

$$0 = E^{\circ} - \frac{0.0591}{n} \log K_c \quad \text{at equilibrium, } E_{\text{cell}} = 0.$$

$$\boxed{\log K_c = \frac{nE^{\circ}}{0.0591}}$$

Significance of K_c

- It tells us about the extent to which the reaction has been completed.
- K_c for Zn-Cu cell at 298K is 2×10^7 which shows that the reaction has nearly gone to completion.

SOME COMMERCIAL CELLS

Mostly electrochemical cells (galvanic cells) are used for the generation of electrical energy and commonly known as batteries.

Battery

A number of electrochemical cells connected in series forms a battery and should have these properties

- (i) Light & compact
- (ii) Reasonably long life
- (iii) Voltage of the battery shouldn't vary appreciably during its use

commercial cells

3) primary cells - In these Redox reaction occurs only once & cannot be used again

Ex:- dry cell, mercury cell.

2) Secondary cells - these can be recharged by passing current & can be used again & again.

Ex:- lead storage cell, Ni-Cd storage cell.

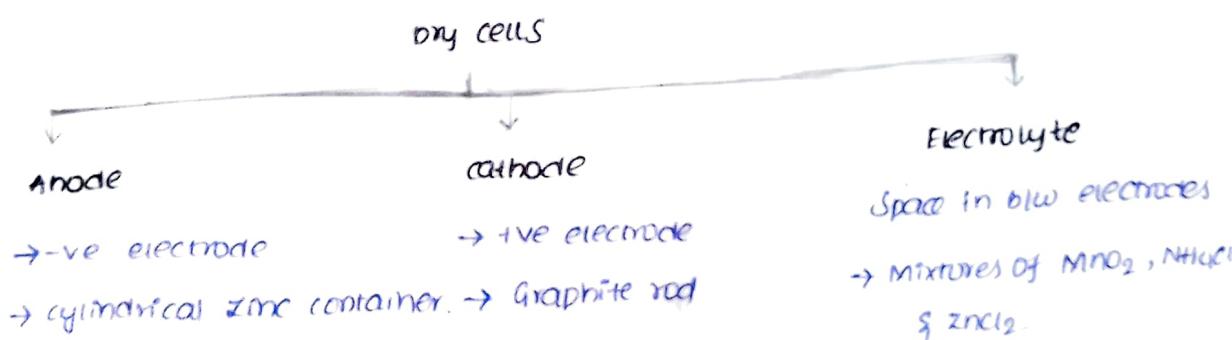
3) Fuel cells - Energy produced by combustion of fuels like H_2 , CO , CH_4 can be directly converted to electric energy.

Ex:- $H_2 - C_2$ fuel cell

I. primary cells

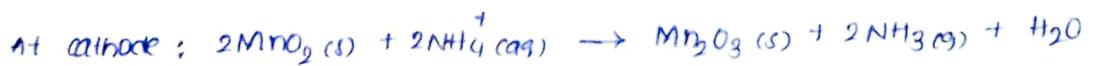
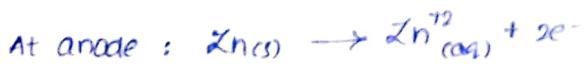
1. Dry cell (a) Leclanche cell

It is the compact form of the Leclanche cell.



* Electrolyte (or) Space in b/w the electrodes is filled with NH_4Cl & ZnCl_2 . The graphite rod is surrounded by MnO_2 & Carbon.

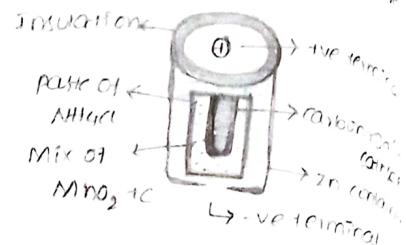
cell reactions



overall reaction

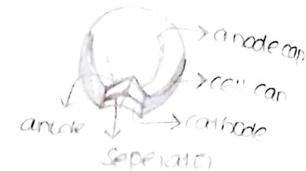


- * Voltage Range : 1.25 V to 1.5 V
- * used in torches, toys, calculators, flashlights etc
- * It doesn't have a long life bcoz the acidic NH_4Cl corrodes Zn container.

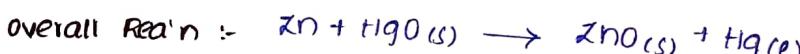
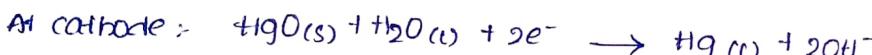
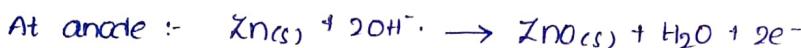


Mercury cell

- Anode → zinc container
- cathode → carbon rod
- Electrolyte → moist HgO mixed with KOH



Cell reactions



Voltage Range

The cell shows a constant potential of 1.35 V throughout as it doesn't involve any ion whose concentration changes.

- These cells are used in small electric devices like hearing aids & watches.

II Secondary cell

1. Lead Storage Battery

- A Secondary cell after its use can be recharged and can be used again.
- A good Secondary cell undergoes a large number of discharging & charging cycle.
- The most important Secondary cell in use is the lead storage battery or cell.

→ It consists of

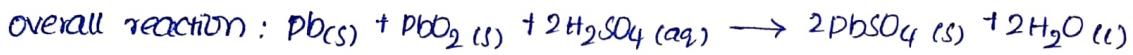
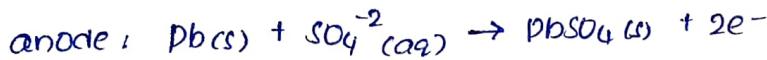
Anode : Lead

Cathode : Lead dioxide (PbO_2)

Electrolyte : 38-1. sol'n of dil. H_2SO_4

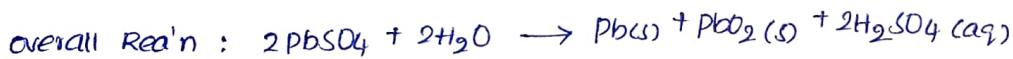
→ The electrodes are arranged alternately separated by thin wooden or fiber glass sheet.

→ The cell reactions when the battery is in use (discharging) are



→ These reactions occur during discharge i.e., during use

* During charging, reverse reactions takes place



* Lead storage battery commonly used in automobiles & invertors.

2) Nickel-cadmium storage cell

→ Another important secondary cell is the Ni-cd cell

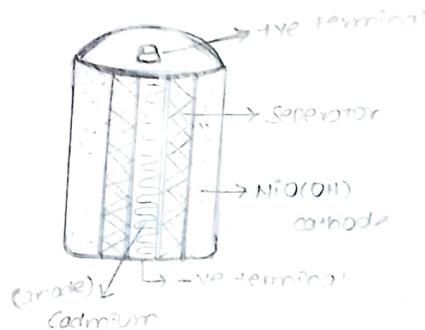
→ which has longer life than the lead storage cell. But is more expensive to manufacture

→ It consists of

Anode : Cadmium

Cathode : $NiO_2 \rightleftharpoons NiO(OH)$

Electrolyte : KOH Nickel-oxyl-hydroxide

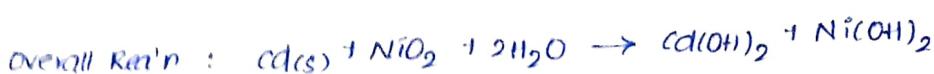
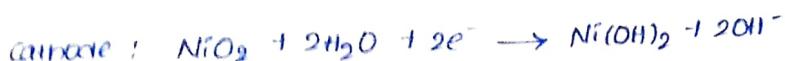
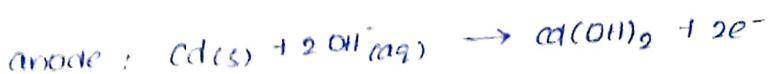


III

Fuel cells

ZNHS

* The following reactions takes place during discharging



* They are mainly used in calculators.

Fuel cells.

It is an electrochemical cell which converts about 74.1% chemical energy to electrical energy.

"These devices which are designed to convert the energy of combustion of fuels like H_2 , CO, methane, methanol etc. directly into electrical energy are called fuel cells."

→ The most successful fuel cell is the $\text{H}_2\text{-O}_2$ fuel cell.

→ It is used in the Apollo space programme; the water produced used as drinking water for astronauts.

* For $\text{H}_2\text{-O}_2$ fuel cell

Electrodes - containing Pt, Ag or Co

Electrolyte \rightarrow NaOH or KOH solution.

* Catalysts like finely divided platinum (or) palladium is incorporated into electrodes.

CORROSION

The process of atmospheric gases attack on the surface of metal resulting into formation of compounds such as oxides, sulphides, carbonates etc., causing decomposition of metal called corrosion.

Ex: Trinishing of Ag.

Development of a green coating on Cu (or) Bronze

→ A metal loses electrons to oxygen & is oxidised.

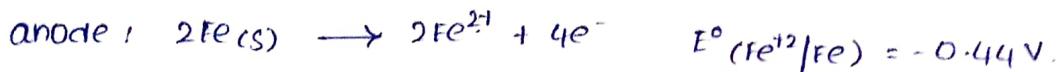
$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

→ Corrosion of iron is called 'Rusting of Iron' rust is hydrated ferric oxide

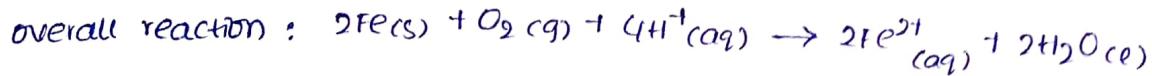
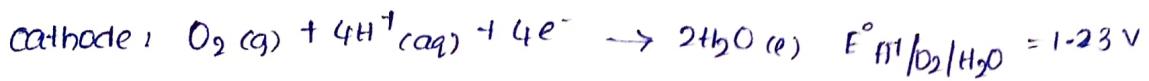
→ Rusting is an electrochemical process.

Mechanism (on theory of rusting (corrosion))

- The chemistry of corrosion is quite complex.
- It is considered essentially as an electrochemical change
- At a particular spot of an object made of Iron, oxidation takes place and that spot behaves as anode

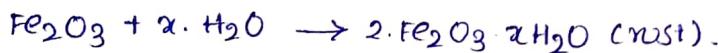
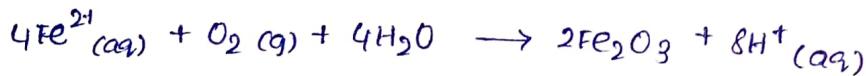


- Electrons released at anodic spot move through the metal & go to another spot on the metal & reduce O_2 or in the presence of H^+ this spot behaves as cathode



$$E_{\text{cell}} = 1.67\text{ V.}$$

- The ferrous ions are further oxidised by atmospheric O_2 to ferric ions, which come out as rust in the form of hydrated ferric oxide (rust).



Factors which promote corrosion

1. Reactivity of metal. → more active metals are actively corroded.
2. presence of Impurities → pure metals do not corrode
3. presence of air & moisture → air, moisture & gases like SO_2 , CO_2 catalyse the process of corrosion.
4. presence of Electrolytes → electrolytes in water increase rate of corrosion
5. strains in metals → corrosion takes place rapidly at bends, at scratches, nicks & cuts in the metal

Prevention of Rusting

Prevention of corrosion is of prime importance anti-corrosion techniques save loss of lives through accidents & money with extended life of materials.

1. Barrier protection

The metal surface is not allowed to come in contact with moisture, O_2 & CO_2 . This can be achieved by

- a) Coating the metal surface with paint or some chemicals.
- b) Applying the ~~met~~ thin film of oil or grease on metal surface
- c) Electroplating with (alkaline earth) metals like tin, nickel, zinc, chromium, aluminium etc
- d) Coating with alkaline earth phosphate (anti-rust) solution used in car radiators to prevent rusting.

2. Sacrificial protection

In this method Iron is covered with a more electropositive metal than Fe. The more electropositive metal loses electrons & as long as the coating is present, Fe is protected.

Ex:-

- * Galvanization - covering iron with zinc (reduction potential = 0.76V) corrosion thermodynamically takes place than Iron.

The zinc also forms a protective coating of $ZnO_2 \cdot Zn(OH)_2$

3. Electrical protection (cathodic protection)

- * This method is used when iron articles are in contact with water such as underground water pipes, storage tanks, canals etc.
- * The article of iron is connected with more active metals like magnesium, Zinc or aluminium which act as anode. ($Mg = -2.363 V$)
- * Iron pipe act as cathode in this case