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CHEMISTRY

Target : JEE (Main)

ELECTROCHEMISTRY



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ELECTROCHEMISTRY

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JEE(MAIN) SYLLABUS

Electrolytic and metallic conduction, conductance in electrolytic solutions, specific and molar conductivities and their variation with concentration; Kohlrausch's law and its applications. Electrochemical cells – Electrolytic and Galvanic cells, different types of electrodes, electrode potentials including standard electrode potential, half – cell and cell reactions, emf of a Galvanic cell and its measurement; Nernst equation and its applications; Relationship between cell potential and Gibbs' energy change; Dry cell and lead accumulator; Fuel cells; Corrosion and its prevention.

JEE(ADVANCED) SYLLABUS

Electrochemical cells and cell reactions; Electrode potentials; Nernst equation and its relation to ΔG ; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductance, Kohlrausch's law; Concentration cells.

Electrochemistry

Introduction

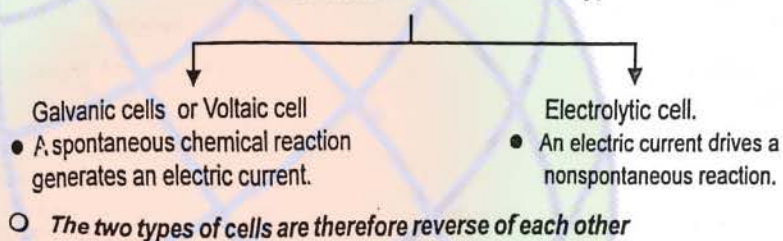
Batteries are everywhere in modern societies. They provide the electric current to start our automobiles and power a host of products such as pocket calculators, digital watches, heart pacemaker, radio, and tape recorders.

Electrochemistry is the area of chemistry concerned with the interconversion of chemical and electrical energy. A battery is an electrochemical cell, a device for interconverting chemical and electrical energy. A battery takes the energy released by a spontaneous chemical reaction and uses it to produce electricity.

Electrochemical cell :

It is a device for converting chemical energy into electrical energy.

Electrochemical cells are of two types



Construction/ Working principle

Whenever a metal strip is put in an electrolyte, the process of oxidation and reduction takes place simultaneously within the system. Due to this, there is a potential difference between the metal phase and the liquid phase.

On joining the metal strips through a wire (of negligible resistance), the current flows as long as the potential difference exists between the metal phase and the liquid phase.

I Anode :

Some metals (which are reactive) are found to have a tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions. For example: Zn rod is placed in ZnSO₄ solution.

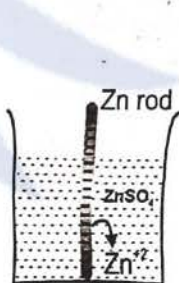
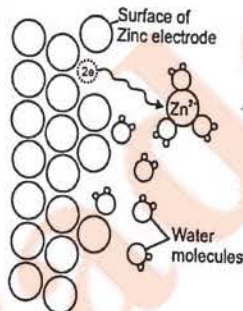


Figure : 1



How Zinc atoms become zinc ions at the electrode surface

Figure : 2

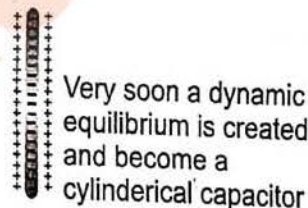


Figure : 3

The Zn atom or metal atoms will move into the solution to form Zn²⁺. After some time, following equilibrium will be established.



There will be an accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move into the solution. i.e. the solution will be saturated with Zn²⁺ ions.

The positive charge will be more concentrated near the rod.

The extra positive charge of the solution will be more concentrated around the negatively charged rod. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution, which is known as electrode potential.

Electrochemistry

This particular electrode is known as anode :

- On anode oxidation will take place. (release of electron).
- It is of negative polarity.

- To act as source of electrons.
- The electrode potential is represented by $E_{Zn(s) / Zn^{2+} (aq)}$

II Cathode :

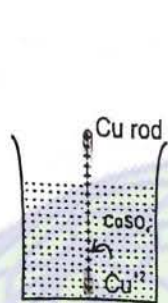


Figure : 1

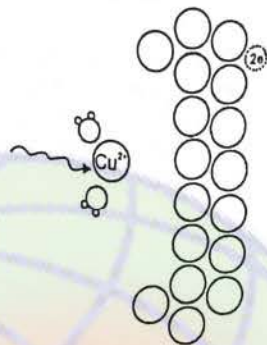


Figure : 2

Copper ion shed its solvating water accepts two electron and become a natural copper of the electrode.

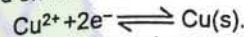


Very soon a dynamic equilibrium is created and become a cylindrical capacitor

Figure : 3

Some metals (Cu, Ag, Au etc..) are found to have the opposite tendency i.e. when placed in contact with their aqueous ions, the ions from the solution will get deposited on the metal rod.

The following equilibrium will be established :



So rod will have deficiency of electron (positive charge). Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential. This will be known as cathode.

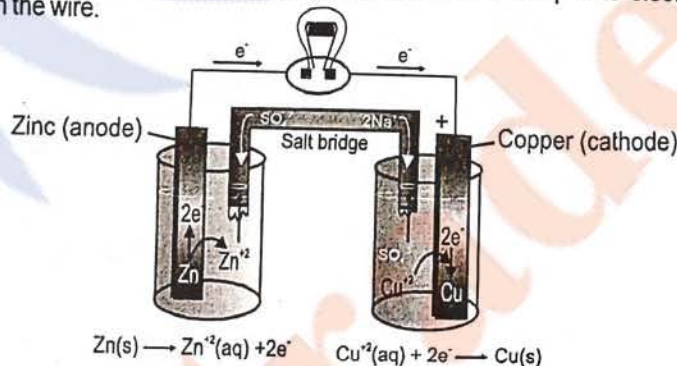
- At cathode reduction will take place. (gain of e^- will take place)
- To act as sink of electron.
- Positive polarity will be developed.
- Their electrode potential can be represented by : $E_{Cu^{2+}(aq)/Cu(s)}$

Anode : { Is where oxidation occurs
Is where electrons are produced
Has a negative sign

Cathode : { Is where reduction occurs
Is where electrons are consumed
Has a positive sign

Construction of Cell :

- It has two half-cells, each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called **electrodes** and are connected by an conducting wire.
- Two solutions are connected by a **salt bridge**.
- The oxidation and reduction half reactions occur at a separate electrodes and electric current flows through the wire.



Selection of electrolyte for Salt Bridge :

- The electrolyte in salt bridge should be such that speed of it's cation equals speed of it's anion in electrical field.
 - For that charge and sign of the ions should be almost equal.
- Transport number of cation = Transport number of anion

Mobility of cation = Mobility of anion

KCl is generally preferred but KNO_3 or NH_4NO_3 can also be used.

Electrochemistry



- If Ag^+ , Hg_2^{2+} , Pb^{2+} , TI^+ ions are present in a cell then in salt bridge KCl is not used because there can be formation of precipitate of AgCl , Hg_2Cl_2 , PbCl_2 or TlCl at mouth of tube which will prevent the migration of ions and its functioning will stop.

Functions of Salt Bridge :

- A salt bridge is a U-shaped inverted tube that contains a gel permeated with an inert electrolyte.
- It connects the solution of two half cell to complete the circuit.
- It minimise the liquid junction potential. The potential difference between the junction of two liquids.
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.
- The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.
- If the salt bridge is removed then voltage drops to zero.
- The ions of the inert electrolyte do not react with other ion in the solution and the ions are not oxidised or reduced at the electrodes.
- Generally tube is filled with a paste of agar-agar powder with a natural electrolyte/generally not common to anionic/cathodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solution.

Electrode Potential :

- The driving force that pushes the negative charge electrons away from the anode and pulls them towards the cathode is an electrical potential called **electromotive force** also known as **cell potential** or the **cell voltage**. Its unit is volt
- The potential difference developed between metal electrode and its ions in solution is known as electrode potential.
- Electrode potential depends upon :
 - Concentration of the solution.
 - Nature of the metal.
 - Nature of the electrolyte.
 - Pressure temperature conditions.
- The potential difference developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is known as standard electrode potential.

Oxidation Potential (O.P.) :

- The electrode potential for oxidation half reaction
- Tendency to get oxidised.
- **Greater the O.P. then greater will be tendency to get oxidised.**

Reduction Potential (R.P.)

- The electrode potential for reduction half reaction
- Tendency to get reduced.
- **Greater the R.P. greater will be tendency to get reduced.**

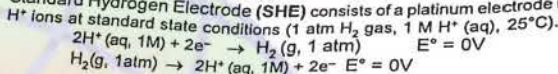
Type of Electrode	Electrode reaction in standard condition	Representation
1. Metal electrode (Zn electrode, Cu electrode etc.)	Reduction : $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$ Oxidation : $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	$E_{\text{Zn}^{2+}/\text{Zn(s)}}^0$ (SRP) $E_{\text{Zn(s)}/\text{Zn}^{2+}}^0$ (SOP)
2. Hydrogen peroxide electrode	Reduction : $2\text{e}^- + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O}$ Oxidation : $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	$E_{\text{H}_2\text{O}_2/\text{H}_2\text{O}}^0$ $E_{\text{H}_2\text{O}_2/\text{O}_2}^0$
3. Redox electrode	Reduction : $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0$
4. Metal Metal salt insoluble electrode	Reduction : $\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-$ Oxidation : $\text{Ag(s)} + \text{Cl}^- \rightarrow \text{AgCl(s)} + \text{e}^-$	$E_{\text{AgCl(s)}/\text{Ag(s)}/\text{Cl}^-}^0$ $E_{\text{Ag(s)}/\text{AgCl(s)}/\text{Cl}^-}^0$



Electrochemistry

Reference electrode :

- The potential of a single electrode cannot be determined what were the potential difference between two electrodes can be accurately measured using a reference electrode.
- An electrode is chosen as a reference with respect to which all other electrodes are valued.
- Standard Hydrogen Electrode (SHE) is taken as standard reference electrode. Its electrode potential is arbitrarily assumed to be 0.00 volt.
- Standard Hydrogen Electrode (SHE) consists of a platinum electrode in contact with H₂ gas and aqueous H⁺ ions at standard state conditions (1 atm H₂ gas, 1 M H⁺ (aq), 25°C).



Cell potential :

- The difference in electrode potentials of the two half cell reactions (oxidation half cell and reduction half cell) is known as emf of the cell or cell potential.
- The emf of the cell or cell potential can be calculated from the values of electrode potential of the two half cell constituting the cell. The following three methods are in use :
 - When oxidation potential of anode and reduction potential of cathode are taken into account :

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}}(\text{anode}) + E^\circ_{\text{red}}(\text{cathode})$$
 - When reduction potential of both electrodes are taken into account :

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$
 both are reduction potential.
 - When oxidation potential of both electrodes are taken into account :

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}}(\text{anode}) - E^\circ_{\text{ox}}(\text{cathode})$$
- The standard cell potential E^o is the cell potential when both reactants and products are in their standard states – solutes at 1 M concentration, gases at a potential pressure of 1 atm, solids and liquids in pure form, with all at a specified temperature, usually 25°C.
- E^o_{cell} is intensive property so on multiplying/dividing cell reaction by any number, the E^o_{cell} value would not change.

Free energy changes for cell reaction :

- The free energy change ΔG (a thermochemical quantity) and the cell potential E (an electrochemical quantity) both measure the driving force of a chemical reaction.
- The values of ΔG and E are directly proportional and are related by the equation.

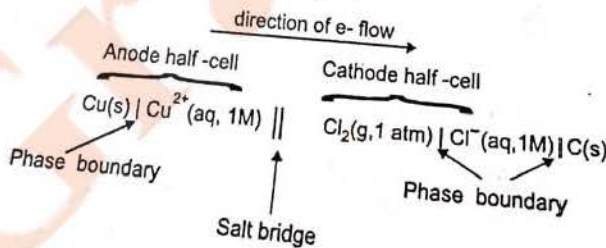
$$\Delta G = -nFE$$

where n = Number of moles of electron transferred in the reaction.

F = Faraday constant = 96485 C/mole e⁻ ≈ 96500 C/mole e⁻

Short Hand Notation for Galvanic Cells

- We require two half cells to produce an electrochemical cell, which can be represented by following few rules;
 - The anode half-cell is always written on the left followed on the right by cathode half cell.
 - The separation of two phases (state of matter) is shown by a vertical line.
 - The various materials present in the same phase are shown together using commas.
 - The salt bridge is represented by a double slash (||).
 - The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
- For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode. (i.e Pt H₂ / H⁺ or H⁺ / H₂ Pt)



Electrochemistry

Solved Examples

Ex.1 Write short hand notation for the following reaction, $\text{Sn}^{2+}(\text{aq}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Ag}(\text{s})$.
Sol. The cell consists of a platinum wire anode dipping into an Sn^{2+} solution and a silver cathode dipping into an Ag^+ solution therefore $\text{Pt}(\text{s}) | \text{Sn}^{2+}(\text{aq}), \text{Sn}^{4+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$.

Ex.2 Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell ?

- (a) $\text{Zn} | \text{Zn}^{2+} || \text{Br}^-, \text{Br}_2 | \text{Pt}$
 (b) $\text{Cr} | \text{Cr}^{3+} || \text{I}^-, \text{I}_2 | \text{Pt}$
 (c) $\text{Pt} | \text{H}_2, \text{H}^+ || \text{Cu}^{2+} | \text{Cu}$
 (d) $\text{Cd} | \text{Cd}^{2+} || \text{Cl}^-, \text{AgCl} | \text{Ag}$

Sol.

(a) Oxidation half cell reaction, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
 reduction half cell reaction, $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$
 Net cell reaction, $\text{Zn} + \text{Br}_2 \rightarrow \text{Zn}^{2+} + 2\text{Br}^-$ (Positive terminal : cathode Pt)

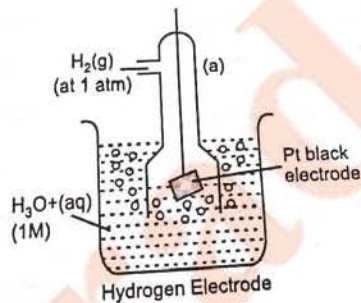
(b) Oxidation half reaction, $[\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-] \times 2$
 reduction half reaction, $[\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-] \times 3$
 Net cell reaction, $2\text{Cr} + 3\text{I}_2 \rightarrow 2\text{Cr}^{3+} + 6\text{I}^-$ (Positive terminal : cathode Pt)

(c) Oxidation half reaction, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
 reduction half reaction, $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 Net cell reaction, $\text{H}_2 + \text{Cu}^{2+} \rightarrow \text{Cu} + 2\text{H}^+$ (Positive terminal : cathode Cu)

(d) Oxidation half reaction, $\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$
 reduction half reaction, $[\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-] \times 2$
 Net cell reaction, $\text{Cd} + 2\text{AgCl} \rightarrow \text{Cd}^{2+} + 2\text{Ag} + 2\text{Cl}^-$ (Positive terminal : cathode Ag)

Calculation of electrode potential :

- | | |
|---|--|
| <p>At Anode</p> $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$ <ul style="list-style-type: none"> Oxidation potential O.P. = $E_{\text{H}_2(\text{g})/\text{H}^+(\text{aq})}$ under standard state $E_{\text{H}_2(\text{g})/\text{H}^+(\text{aq})}^0 = \text{SOP}$ | <p>At Cathode</p> $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ <ul style="list-style-type: none"> Reduction Potential (R.P.) $E_{\text{H}^+/\text{H}_2(\text{g})} = \text{RP}$ under standard state. $E_{\text{H}^+/\text{H}_2(\text{g})}^0 = \text{SRP}$ |
|---|--|



- For SHE reference potential is taken to be zero at all temperature.
 $\text{SOP} = -\text{SRP} = 0$ for SHE.
- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and its potential is measured that gives the value of electrode potential of that electrode.

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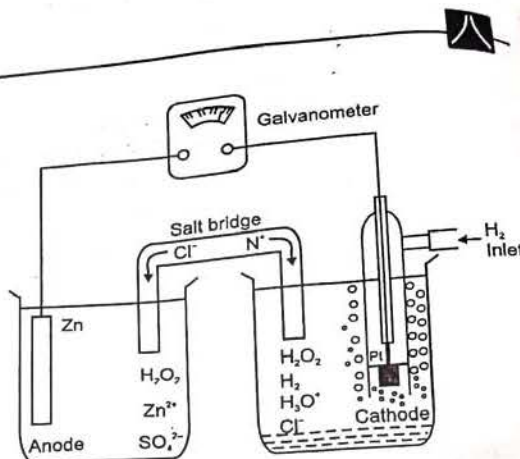
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MAINECH - 5

Electrochemistry

Anode : Zinc electrode
Cathode : SHE
Cell : Zinc electrode || SHE
Cell potential :
 $E_{cell} = E_{H^+/H_2(g)} - E^{\circ}_{Zn^{2+}/Zn}$
 $= 0.76 \text{ V (at 298 K experimentally)}$
 So, $E^{\circ}_{Zn^{2+}/Zn} = -0.76 \text{ V (SRP)}$
 $E^{\circ}_{Zn/Zn^{2+}(aq)} = 0.76 \text{ V (SOP)}$

- So, w.r.t. H_2 , Zn has greater tendency to get oxidised.
 In similar manner reduction potentials (SRP) at 298 K for many other electrodes are calculated and are arranged in a series increasing order known as electrochemical series.



A galvanic cell measuring the $Zn^{2+}|Zn$ half-cell potential

Electrochemical Series :

Increasing strength of reducing agent

Electrode	Reaction	SRP (at 298 K)
* Li	$Li^+ + e^- \rightarrow Li(s)$	-3.05 V
K	$K^+ + e^- \rightarrow K(s)$	-2.93 V
Ba		
Ca	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87 V
Na	$Na^+ + e^- \rightarrow Na(s)$	-2.71 V
Mg	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.37 V
Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66 V
* Electrolytes (H_2O)	$H_2O(l) + e^- \rightarrow \frac{1}{2} H_2 + OH^-$	-0.828 V
* Zn	$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76 V
Cr	$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74 V
* Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44 V
Cd	$Cd^{2+} + 2e^- \rightarrow Cd(s)$	-0.40 V
Co		
Ni	$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.24 V
Sn	$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14 V
Pb	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13 V
* H_2	$2H^+ + 2e^- \rightarrow H_2(g)$	0.00 V
Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34 V
I_2		
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V
Hg	$Hg_2^{2+} + 2e^- \rightarrow Hg(l)$	0.79 V
Ag	$Ag^+ + e^- \rightarrow Ag$	0.80 V
Hg	$Hg^{2+} \rightarrow Hg(l)$	0.85 V
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	1.06 V
* Electrolytes	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O(l)$	1.23 V
* $Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33 V
* Cl_2	$Cl_2 + 2e^- \rightarrow 2 Cl^-$	1.36 V
* MnO_4^-	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51 V
* F_2	$F_2 + 2e^- \rightarrow 2F^-$	2.87 V

Increasing strength of oxidising agent

Electrochem

Ex.3 C 2

Sol.

Ex.4

Sol

Electrochemistry

Solved Examples

Ex.3 Calculate E°_{cell} of (at 298 K),
 $Zn(s) / ZnSO_4(aq) || CuSO_4(aq) / Cu(s)$
 given that $E^{\circ}_{Zn/Zn^{2+}(aq)} = 0.76 V$; $E^{\circ}_{Cu(s) / Cu^{2+}(aq)} = -0.34 V$

Sol. $E^{\circ}_{cell} = (S.R.P)_{cathode} - (S.R.P)_{anode}$
 $= 0.34 - (-0.76) = 1.1 V$

Ex.4 Given the cell $Ag | AgCl(s) | NaCl(0.05 M) || AgNO_3(0.30 M) | Ag$
 (a) Write half reaction occurring at the anode. (b) Write half reaction occurring at the cathode.
 (c) Write the net ionic equation of the reaction. (d) calculate E°_{cell} at 25°C.
 (e) Does the cell reaction go spontaneous as written?

Sol. (Given $E^{\circ}_{AgCl/Cl} = +0.22 \text{ volt}$; $E^{\circ}_{Ag^+/Ag} = +0.80 \text{ volt}$)
 (a) LHS electrode is anode and half reaction is oxidation.
 $Ag^+ + Cl^- \rightarrow AgCl(s) + e^-$... (i)

(b) RHS electrode is cathode and half reaction is reduction.
 $Ag + e^- \rightarrow Ag(s)$... (ii)

(c) From equation (i) and (ii) cell reaction is: $Cl^-(0.05 M) + Ag^+(0.30 M) \rightarrow AgCl(s)$
 (d) $E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left} = (0.80 - 0.22 \text{ volt}) = 0.58 \text{ volt}$
 (e) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell reaction.

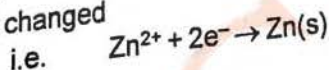
Ex.5 An aqueous solution containing Na^+ , Sn^{2+} , Cl^- & SO_4^{2-} ions, all at unit concentration, is electrolysed between a silver anode and a platinum cathode. What changes occur at the electrodes when current is passed through the cell? Given: $E^{\circ}_{Ag^+/Ag} = 0.799 V$,
 $E^{\circ}_{Sn^{2+}/Sn} = -0.14 V$, $E^{\circ}_{Cl_2/Cl^-} = 1.36 V$, $E^{\circ}_{S_2O_8^{2-}/SO_4^{2-}} = 2 V$, $E^{\circ}_{Sn^{4+}/Sn^{2+}} = 0.13 V$

(A) Sn^{2+} is reduced and Cl^- is oxidized (B) Ag is oxidized and Sn^{2+} is reduced
 (C) Sn^{2+} is reduced and Sn^{2+} is oxidized (D) H^+ is reduced and Sn^{2+} is oxidized

Sol. At anode either Ag can oxidised to Ag^+ or Sn^{2+} to Sn^{4+} or Cl^- to Cl_2 or SO_4^{2-} to $S_2O_8^{2-}$. Their respective oxidation potential values are $-0.799 V$, $0.13 V$, $-1.36 V$ and $-2 V$. From these values, it is evident that Sn^{2+} would be oxidised first, followed by Ag at anode. At cathode, either Na^+ can get reduced to Na. or Sn^{2+} to Sn or H^+ to H_2 . The reduction potential value for Na^+ is highly negative while for $Sn^{2+} | Sn$ is $-0.14 V$ and for H^+
 $e^- \rightarrow 1/2 H_2$ ($E_{H^+/H_2} = 0.059 \log \frac{1}{10^{-7}}$) is $-0.413 V$. Thus Sn^{2+} will get reduced at cathode followed by H^+

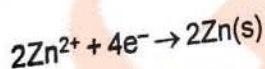
∴ (C)

- Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.
- Obtain the reaction of the 3rd electrode with the help of some algebraic operations on reactions of the given electrodes.
- Then calculate ΔG of the 3rd reaction with the help of some algebraic operations of ΔG° of 1st and 2nd reactions.
- Use $\Delta G^{\circ} = -nF E^{\circ}_{elec}$ to calculate unknown E.P.
- E°_{cell} is intensive property so if we multiply/Divide electrode reaction by any number the E°_{cell} value would not changed



$E^{\circ} = -0.76 V$

Multiply by 2



$E^{\circ} = -0.76 V$ (remain same)



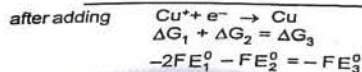
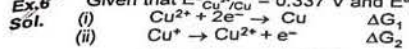
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MAINECH - 7

Electrochemistry

Solved Examples

Ex.6 Given that $E^{\circ}_{Cu^{2+}/Cu} = 0.337 V$ and $E^{\circ}_{Cu^{+}/Cu^{2+}} = -0.153 V$. Then calculate $E^{\circ}_{Cu^{+}/Cu}$

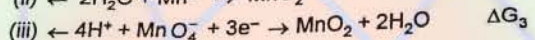
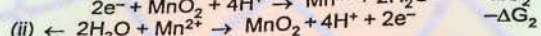
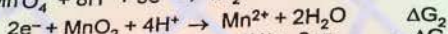
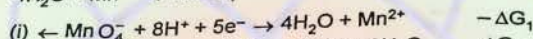
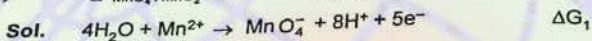


$E_3 = 2E_1^{\circ} + E_2^{\circ}$
 $= 2 \times 0.337 - 0.153 = 0.674 - 0.153 = 0.521 V$

$E^{\circ}_{Cu^{2+}/Cu} = 0.337V$

Ex.7 $E^{\circ}_{Mn^{2+}/MnO_4^{-}} = -1.51 V$; $E^{\circ}_{MnO_2/Mn^{2+}} = +1.23 V$

$E^{\circ}_{MnO_4^{-}/MnO_2} = ?$ (All in acidic medium)



(i) + (ii) = (iii)

$\Delta G_3 = -\Delta G_1 - \Delta G_2$

$-3E_3F = 5E_1^{\circ}F + 2E_2^{\circ}F$

$E = \frac{-[5E_1 + 2E_2]}{3} = \frac{-[5(-1.51) + 2(1.23)]}{3} = \frac{-[-7.55 + 2.46]}{3} = \frac{+5.09}{3} = 1.69 V$

Nernst Equation :

- Cell potentials depend on temperature and on the composition of the reaction mixtures.
- It depends upon the concentration of the solute and the partial pressure of the gas, if any.
- The dependence upon the concentration can be derived from thermodynamics.

From thermodynamics

$\Delta G = \Delta G^{\circ} + RT \ln Q$

$-nFE = -nFE^{\circ} + 2.303 RT \log Q$

$E = E^{\circ} - \frac{2.303RT}{nF} \log Q$

Take $T = 298 K$, $R = 8.314 J/mol K$, $F = 96500 C$

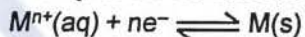
Now we get, $E = E^{\circ} - \frac{0.059}{n} \log Q$

Where $n =$ number of transferred electron, $Q =$ reaction quotient

- Nernst equation can be used to calculate cell potentials for non standard conditions also.
- Nernst equations can be applied to half cell reactions also.

Applications of Nerst equation

- Nernst Equation for Electrode Potential



$E_{Red^n} = E_{red}^{\circ} - \frac{RT}{nF} \ln \left[\frac{M(s)}{M^{n+}} \right]$

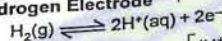
$E_{Red^n} = E_{red}^{\circ} - \frac{2.303RT}{nF} \log \left[\frac{M(s)}{M^{n+}} \right]$

at 298K,

$E_{Red^n} = E_{Red^n}^{\circ} - \frac{0.059}{n} \log \left[\frac{1}{M^{n+}} \right]$

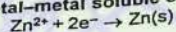
Electrochemistry

Hydrogen Electrode



$$E = E^0 - \frac{0.0591}{2} \log \left[\frac{(H^+)^2}{P_{H_2}} \right]$$

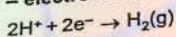
Metal-metal soluble salt electrode.



$$E_{Red^n} = E_{Red}^0 - \frac{2.303RT}{nF} \log \left(\frac{1}{Zn^{+2}} \right) \text{ at } 298K$$

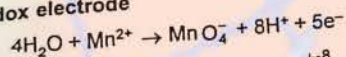
$$E_{Red^n} = E_{Red}^0 - \frac{0.059}{2} \log \left(\frac{1}{Zn^{+2}} \right)$$

Gas - electrode Hydrogen electrode.



$$E_{Red^n} = E_{Red}^0 - \frac{0.059}{2} \log \left(\frac{P_{H_2}}{(H^+)^2} \right)$$

Redox electrode

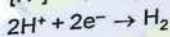


$$E_{Ox} = E_{Ox}^0 - \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{+2}]}$$

Solved Examples

Ex.8 Calculate R.P. of hydrogen electrode at 298K which is prepared with the help of aq. solution of acetic acid with 0.1 M conc at 1 atm pressure $K_a = 1.8 \times 10^{-5}$.

Sol. $[H^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8 \times 10^{-6}}$



$$E_{Red^n} = E_{Red}^0 - \frac{0.059}{2} \log \frac{P_{H_2}}{(H^+)^2} \quad (E_{Red}^0 = 0)$$

$$E_{Red^n} = -\frac{0.059}{2} \log \left(\frac{1}{1.8 \times 10^{-6}} \right) = -\frac{0.059}{2} [6 - \log(1.8)]$$

$$E_{Red^n} = -\frac{0.059}{2} \times 5.74 = -0.169 \text{ V}$$

Ex.9 Which is stronger oxidizing agent

(i) $K_2Cr_2O_7$ in solution in which $[Cr_2O_7^{2-}] = 0.1 \text{ M}$, $[Cr^{3+}] = 10^{-2} \text{ M}$ and $[H^+] = 10^{-1} \text{ M}$

(ii) $KMnO_4$ in a solution in which $[MnO_4^-] = 10^{-1} \text{ M}$, $[Mn^{2+}] = 10^{-2} \text{ M}$, $[H^+] = 10^{-2} \text{ M}$

$$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33 \text{ V} \quad E^0_{MnO_4^-/Mn^{2+}} = 1.51 \text{ V}$$

Sol. (i) $14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 6e^-$

$$E_{Red^n} = 1.33 - \frac{0.059}{6} \log \left[\frac{10^{-4} \times 10}{10^{-14}} \right] = 1.33 - \frac{0.059}{6} \times 11$$

$$E_{Red^n} = 1.33 - \frac{0.649}{6} = 1.330 - 0.108 = 1.222 \text{ V}$$

(ii) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$$E_{Red^n} = 1.51 - \frac{0.059}{5} \log \left[\frac{10^{-2}}{10^{-16} \times 10^{-1}} \right] = 1.51 - 0.059 \times 3 = 1.51 - 0.18 = 1.33 \text{ V}$$

E_{Red^n} is more so, good oxidising agent

Electrochemistry

• Nernst Equation for cell Potential :



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

n - no. of electrons which gets cancelled out while making cell reaction.

Equilibrium in electrochemical cell.

$$\Delta G^{\circ} = -nF E_{\text{cell}}^{\circ}$$

$$\Delta G = -nF E_{\text{cell}}$$

From thermo dynamics

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

at chemical equilibrium $\Delta G = 0$

$$E_{\text{cell}} = 0 \rightarrow \text{cell will be of no use}$$

$$\text{so, } \Delta G^{\circ} = -RT \ln K_{\text{eq}}$$

$$\text{at equilibrium } -nF E_{\text{cell}}^{\circ} = -2.303 RT \log (K_{\text{eq}})$$

$$\log K_{\text{eq}} = \frac{nF}{2.303RT} E_{\text{cell}}^{\circ}$$

at 298 K and R = 8.314 J/mol K

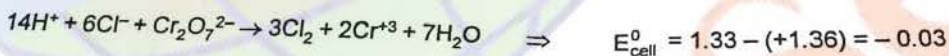
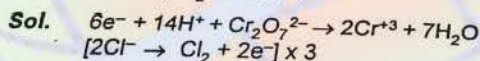
$$\log K_{\text{eq}} = \frac{n}{0.059} E_{\text{cell}}^{\circ}$$

Solved Examples

Ex.10 Calculate E_{cell} of $\text{Pt(s)} \left| \text{Cl}_2(\text{g}) \right| \text{Cl}^-(\text{aq}) \left| \text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+}(\text{in H}_2\text{SO}_4) \right| = 0.05\text{M}$
 $\left. \begin{array}{l} 0.1\text{atm} \\ 10^{-2}\text{M} \end{array} \right| \left. \begin{array}{l} 0.01\text{M} \\ 0.1\text{M} \end{array} \right|$

given that $E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^{\circ} = 1.33\text{ V}$

$$E^{\circ} \text{Cl}^- / \text{Cl}_2 = -1.36\text{ V}$$



$$E_{\text{cell}} = -0.03 - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2 [\text{P}_{\text{Cl}_2}]^3}{[\text{H}^+]^{14} [\text{Cl}^-]^6 [\text{Cr}_2\text{O}_7^{2-}]} = -0.03 - \frac{0.059 \times 23}{6}$$

$$E_{\text{cell}} = -0.26\text{ V}$$

Ex.11 The E_{cell}° for the reaction $\text{Fe} + \text{Zn}^{2+} \rightleftharpoons \text{Zn} + \text{Fe}^{2+}$, is -0.32 volt at 25°C . What will be the equilibrium concentration of Fe^{2+} , when a piece of iron is placed in a 1 M Zn^{2+} solution ?

Sol. We have the Nernst equation at equilibrium at 25°C

$$E^{\circ} = \frac{0.0591}{n} \log K \dots (i)$$

Since E_{cell}° for the given reaction is negative, therefore, the reverse reaction is feasible for which E_{cell}° will be $+0.32\text{ V}$, Thus for $\text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Fe} + \text{Zn}^{2+}$; $E_{\text{cell}}^{\circ} + 0.32\text{ V}$

$$\text{Now, } E^{\circ} = \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} \text{ or } 0.32 = \frac{0.0591}{2} \log \frac{1}{[\text{Fe}^{2+}]}$$

$$\log [\text{Fe}^{2+}] = -10.829$$

$$[\text{Fe}^{2+}] = 1.483 \times 10^{-11}\text{ M}$$

Taking antilog,

Electrochemistry

Work done by a c

(i) Let

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(ii) W

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Ex.12 Calcula

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Electrochemistry

Work done by a cell :

- (i) Let 'n' faraday charge be taken out of a cell of EMF 'E'; then work done by the cell will be calculated as : $\text{work} = \text{Charge} \times \text{Potential} = nFE$
- (ii) Work done by cell = Decrease in free energy
 so $-\Delta G = nFE$
 or $W_{\text{max}} = + nFE^\circ$ where E° is standard EMF of the cell

Solved Examples

Ex.12 Calculate the maximum work that can be obtained from the Daniell cell given below -

$\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$. Given that $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ and $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$.

Sol. Cell reaction is : $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$ Here $n = 2$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (\text{On the basis of reduction potential})$$

$$= +0.34 - (-0.76) = 1.10 \text{ V}$$

We know that : $W_{\text{max}} = \Delta G^\circ = -nFE^\circ$
 $= -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (1.10 \text{ V}) = -212300 \text{ C.V.} = -212300 \text{ J}$
 or $W_{\text{max}} = -212300 \text{ J}$

Concentration cells :

- A concentration cell consists of two electrodes of the same material, each electrode dipping in a solution of its own ions and the solution being at different concentrations.
- The two solutions are separated by a salt bridge.

e.g. $\text{Ag(s)} | \text{Ag}^+(a_1) || \text{Ag}^+(a_2) | \text{Ag(s)}$ ($a_1 < a_2$) a_1, a_2 are concentrations of each half cell

At LHS electrode Anode : $\text{Ag(s)} \longrightarrow \text{Ag}^+(a_1) + e^-$

At RHS electrode Cathode : $\text{Ag}^+(a_2) + e^- \longrightarrow \text{Ag(s)}$

The net cell reaction is : $\text{Ag}^+(a_2) \longrightarrow \text{Ag}^+(a_1)$

for concentration cells $E^\circ_{\text{Cell}} = 0$.

The Nernst eq. is

$$E_{\text{cell}} = -\frac{0.059}{n} \log \frac{a_1}{a_2} \quad (\text{Here } n = 1, \text{Temp, } 298 \text{ K})$$

- Likewise, the e.m.f. of the cell consisting of two hydrogen electrodes operating at different pressure P_1 and P_2 ($P_1 > P_2$) and dipping into a solution HCl is :

$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{P_1}{P_2} \quad (\text{at } 298 \text{ K})$$

Electrolysis & Electrolytic cell :

Electrolysis :

- Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- This is possible due to the movement of ions from which it is made of and electrolyte.
- The process of using an electric current to bring about chemical change is called electrolysis.
- Electrolysis is a process of oxidation and reduction due to current in the electrolyte.
- The product obtained during electrolysis depends on following factors.
 - The nature of the electrolyte
 - The concentration of electrolyte
 - The charge density flowing during electrolysis.
 - The nature of the electrode

Active vs Inactive electrodes :

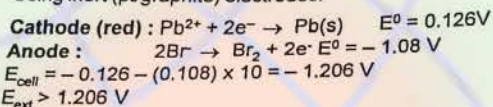
- The electrodes in the cell that are active because the metals themselves are components of the half reactions.
- As the cell operates, the mass of the zinc electrode gradually decreases, and the $[\text{Zn}^{2+}]$ in the anode half - cell increases. At the same time, the mass of the copper electrode increases and the $[\text{Cu}^{2+}]$ in the cathode half - cell decreases; we say that the Cu^{2+} „plates out“ on the electrode.

Electrochemistry

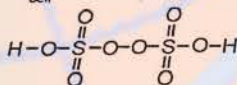
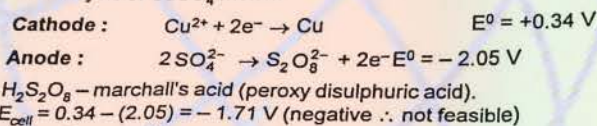
- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half-reactions.
- In a voltaic cell based on the following half reactions, for instance, the species cannot act as electrodes:
 $2I^-(aq) \rightarrow I_2(s) + 2e^-$ [anode; oxidation]
 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ [cathode; reduction]
 Therefore, each half-cell consists of inactive electrodes immersed in an electrolyte solution that contains all the species involved in that half-reaction. In the anode half-cell, I^- ions are oxidized to solid I_2 . The electrons released flow into the graphite anode, through the wire, and into the graphite cathode. From there, the electrons are consumed by MnO_4^- ions as they are reduced to Mn^{2+} ions.

Examples of Electrolysis

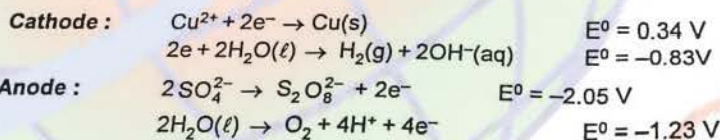
Using inert (pt/graphite) electrodes.



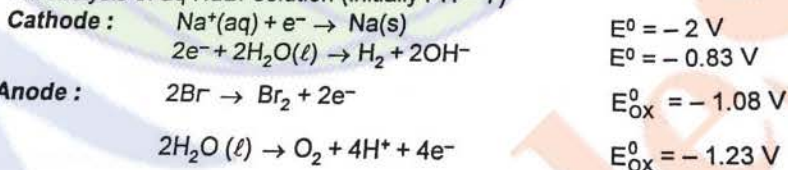
Electrolysis of $CuSO_4$ molten



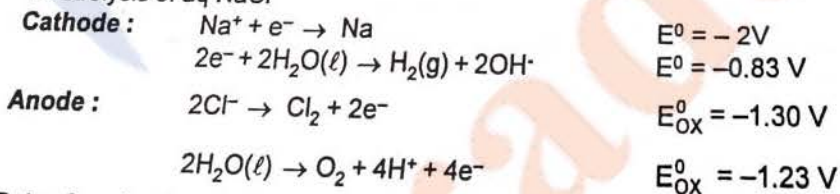
Electrolysis of aq $CuSO_4$



Electrolysis of aq $NaBr$ solution (initially PH = 7)



Electrolysis of aq $NaCl$



Rate of production of Cl_2 is more than rate of production of O_2 gas.

Note: According to thermodynamics, oxidation of H_2O to produce O_2 should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase it's rate, the greater potential difference is applied called over voltage or over potential but because of this oxidation of Cl^- ions also become feasible and this takes place on anode.

Electrochemistry

Electrolysis using attachable (reactive) electrodes.

- Electrolysis of aq. CuSO_4 using Cu electrode.
 - Cathode (reduction): $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ $E^0 = +0.34 \text{ V}$
 - $2\text{H}_2\text{O}(\ell) + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$ $E^0 = -0.83 \text{ V}$
 - Anode (oxidation): $\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2e^-$ $E^0_{\text{ox}} = -2.05 \text{ V}$
 - $2\text{H}_2\text{O}(\ell) \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$ $E^0 = -1.23 \text{ V}$
 - $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+} + 2e^-$ $E^0 = -0.34 \text{ V}$

electrolytic refining

- $\text{AgNO}_3(\text{aq})$ using Cu cathode & Ag anode.
 - Cathode: $\text{Ag}^+ + e^- \rightarrow \text{Ag}(\text{s})$ $E^0 = 0.8 \text{ V}$
 - $2\text{H}_2\text{O}(\ell) + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$ $E^0 = -0.83 \text{ V}$
 - Anode: $\text{NO}_3^- \rightarrow \text{X}$ (No reaction) $E^0 = -1.23 \text{ V}$
 - $2\text{H}_2\text{O}(\ell) \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$ $E^0 = -0.80 \text{ V}$
 - $\text{Ag}(\text{s}) \rightarrow \text{Ag}^+(\text{aq}) + e^-$

Faraday's Law of Electrolysis :

- 1st Law : The mass deposited/released/produced of any substance during electrolysis is proportional to the amount of charge passed into the electrolyte.

$W \propto Q$
 $W = ZQ$

Z - electrochemical equivalent of the substance.

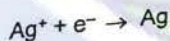
Unit of Z = $\frac{\text{mass}}{\text{coulomb}} = \text{Kg/C or g/C}$

Z = Mass deposited when 1 C of charge is passed into the solution.

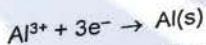
Equivalent mass (E) : mass of any substance produced when 1 mole of e^- are passed through the solution during electrolysis.

$E = \frac{\text{Molar mass}}{\text{no. of } e^- \text{ involved in oxidation / reduction}}$

e.g.



$E = \frac{M}{1}$
 $E = \frac{M}{3}$



1 mole of $e^- = 1$ Faraday of charge.

$\therefore 96500 \text{ C} = \text{Charge deposited } E \text{ gram metal charge}$

$\therefore 1\text{C} \rightarrow \left(\frac{E}{96500}\right) \text{g}$ $Z = \frac{E}{96500}$

$W = \frac{EQ}{96500} = \frac{\text{Molar mass}}{(\text{no. of } e^- \text{ involved})} \times \frac{Q}{96500}$

$\int dQ = i \int dt$

$Q = it$

$W = \frac{i \times t}{96500} \times \frac{\text{Molar mass}}{(\text{no. of } e^- \text{ involved})}$

- 2nd Law : When equal charge is passed through 2 electrolytic cells and these cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

$W = ZQ = \frac{EQ}{96500}$

$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2} \text{ (Q = same)}$

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