

ELECTRO-CHEMISTRY

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical Cells can be classified as:

- (i) **Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.
- (ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

Electrochemical cell :

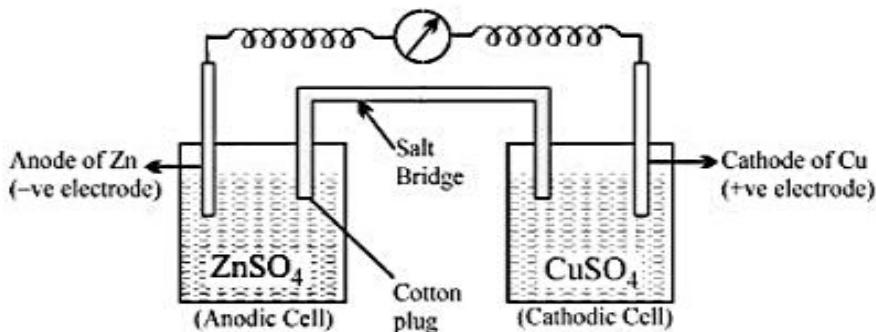
An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half cell -reaction take place.

A simple half-cell can be made from a metal strip that dips into a solution of its metal ion. An example is the zinc-zinc ion half-cell (often called simply a zinc electrode), which consists of a zinc metal strip dipping into a solution of a zinc ion salt. Another simple half-cell consists of a copper metal strip dipping into a solution of a copper ion salt (copper electrode).

In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.



The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate on as copper, the solution builds up a negative charge. The half cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated. The voltage would drop, and the battery would run down quickly.

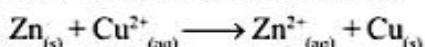
The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows.

The two half-cell reactions, as noted earlier, are



The first half cell -reaction, in which a species loses electrons, is the oxidation half cell-reaction. The electrode at which oxidation occurs is called the anode. The second half-reaction which a species gains electrons, is the reduction half cell-reaction. The electrode at which reduction occurs is called the cathode. These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.

Note that the sum of the two half cell-reaction



The net reaction that occurs in the voltaic cell, it is called the cell reaction.

Once you know which electrode is the anode and which is the cathode, you can determine the direction of electron flow in the external portion of the circuit. Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.



Note :

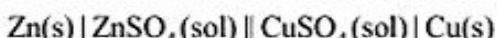
1. The salt-bridge contains solution of strong ionic salts like NaCl, NaNO₃, KNO₃, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.
2. Salt bridge carries whole of the current across the boundary ; more over the K⁺ and NO₃⁻ ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions completes the electrical circuit & permits the ions to migrate.
3. It maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.

In a galvanic cell, cathode is positive with respect to anode.

REPRESENTATION OF A CELL (IUPAC CONVENTIONS)

Let us illustrate the convention taking the example of Daniel cell.

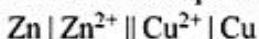
- (i) Anodic half cell is written on left and cathodic half cell on right hand side.



- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.

- (iii) EMF (electromotive force) may be written on the right hand side of the cell.

- (iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.



- (v) Inert electrodes are represented in the bracket



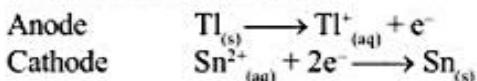
Illustration

1. Writing the cell Reaction from the Cell Notation



Problem strategy: The cell notation gives the species involved in each half-reaction. When you are going to add half cell- reaction balance half cell reaction in such a way that both have same number of electron.

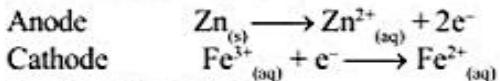
- Sol. (a) The half-cell reactions are



Multiplying the anode reaction by 2 and then summing the half-cell reactions gives



- (b) The half cell reactions are

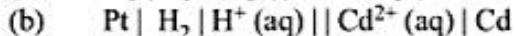
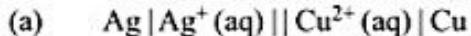


and the cell reaction is :



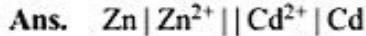
Exercise

1. Write cell reaction of the following cells :



Ans. (a) $2\text{Ag} + \text{Cu}^{2+} \longrightarrow 2\text{Ag}^+ + \text{Cu}$, (b) $\text{H}_2 + \text{Cd}^{2+} \longrightarrow \text{Cd} + 2\text{H}^+$

2. Write cell representation for following cells:

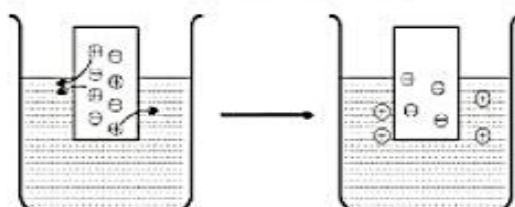


ELECTRODE POTENTIAL

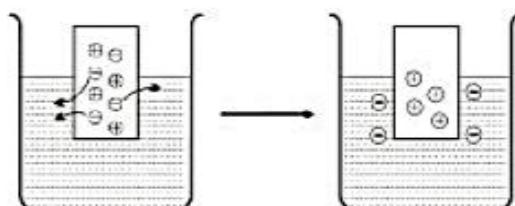
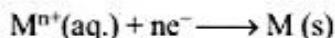
When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential**.

The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution. The development of negative charge (as on zinc plate) or positive charge (as on copper plate) can be explained in the following manner.

- (a) **Oxidation** : Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.



- (b) **Reduction** : Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.



The magnitude of the electrode potential of a metal is a measure of its relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). The magnitude of potential depends on the following factors :

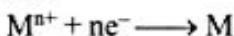
- (i) Nature of the electrode
- (ii) Concentration of the ion in solution
- (iii) Temperature.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types :

- (i) **Oxidation potential** : When electrode is negatively charged with respect to solution, i.e., it acts as anode. Oxidation occurs.



- (ii) **Reduction potential** : When electrode is positively charged with respect to solution. i.e., it acts as cathode. Reduction occurs.



It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally.

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called electromotive force (e.m.f.). EMF is called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

$$E_{\text{cell}} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$$E^\circ_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard reduction potential of anode}$$

$$E_{\text{cell}} = \text{R.P. (Cathode)} - \text{R.P. (Anode)}$$

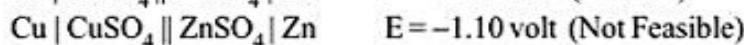
$$= \text{R.P. (Cathode)} + \text{O.P. (Anode)}$$



Which electrode of a galvanic cell corresponds to the higher potential energy.

SIGN CONVENTION OF EMF

EMF of cell should be positive otherwise it will not be feasible in the given direction.



Illustration

1. For the cell reaction $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$

E_{cell}° is 1.89 V. If $E_{\text{Co}^{2+}/\text{Co}}^\circ$ is -0.28 V, what is the value of $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ$?

Ans. 1.61 V

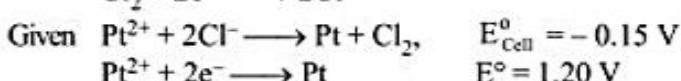
$$\text{Sol. } E_{\text{Cell}}^\circ = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ - E_{\text{Co}^{2+}/\text{Co}}^\circ$$

$$1.89 = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ - (-.28)$$

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ = 1.61 \text{ V}$$

Exercise

1. Determine the standard reduction potential for the half reaction :



Ans. 1.35 V

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RELATIONSHIP BETWEEN ΔG AND ELECTRODE POTENTIAL

Let n , Faraday charge is taken out from a cell of e.m.f. (E), then electrical work done by the cell may be calculated as,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

From thermodynamics, we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system.

$$\therefore \Delta G = -nFE$$

$$\text{Under standard state } \Delta G^{\circ} = -nFE^{\circ} \quad (\text{i})$$

- (i) From thermodynamics we know, $\Delta G =$ negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When $\Delta G =$ positive, $E =$ negative and the cell process will be non spontaneous.

Reactions	ΔG	E
Spontaneous	(-)	(+)
Non-spontaneous	(+)	(-)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E° (i.e., standard reduction potential of cathode- standard reduction potential of anode) in eq. (i) we may get ΔG° .

NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad .(1)$$

where ΔG and ΔG° are free energy and standard free energy change; 'Q' is reaction quotient.

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^{\circ} = nFE^{\circ}$$

Thus from Eq. (i), we get $-nFE = -nFE^{\circ} + RT \ln Q$

$$\text{At } 25^{\circ}\text{C}, \text{ above equation may be written as } E = E^{\circ} - \frac{0.0591}{n} \log Q$$

Where 'n' represents number of moles of electron involved in process.

In general, for a redox cell reaction involving the transference of n electrons
 $aA + bB \longrightarrow cC + dD$, the EMF can be calculated as:

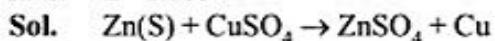
$$E_{\text{Cell}} = E_{\text{Cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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Illustration

1. Calculate the EMF of a Daniel cell when the concentration of ZnSO_4 and CuSO_4 are 0.001 M and 0.1M respectively. The standard EMF of the cell is 1.1V.

Ans. $E = 1.159\text{V}$



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right] = 1.1 - \frac{0.0591}{2} \log \frac{10^{-3}}{10^7} = 1.159 \text{ V}$$

Exercise

1. The EMF of the cell $M | M^{n+} (0.01\text{M}) \parallel H^+ (1\text{M}) | H_2(\text{g}) (1 \text{ atm})$, Pt at 25°C is 0.82V. Calculate the valency of the metal if the standard oxidation potential of the metal is 0.76V.

Take $\frac{2.303 \text{ RT}}{F} = 0.06$ at 25°C .

Ans. $n = 2$



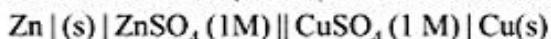
What will happen to the cell emf as cell start operating from standard condition.



Can the Nernst equation be used at temperature other than room temperature ? What will happen to cell emf as temperature is increased slightly ?

THERMODYNAMIC TREATMENT OF NERNST EQUATION**(i) Prediction and feasibility of spontaneity of a cell reaction.**

Let us see whether the cell (Daniel) is feasible or not: i.e. whether Zinc will displace copper or not.



$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ volt} ; E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34 \text{ volt}$$

$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

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

Since $E^0 = +\text{ve}$, hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

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- (ii) **Determination of equilibrium constant :** We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \quad \dots(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

\therefore From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti log} \left[\frac{nE^0}{0.0591} \right]$$

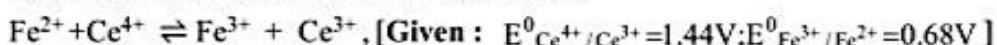
Illustration

1. Calculate E^0 and E for the cell $\text{Sn} | \text{Sn}^{2+} (1\text{M}) \parallel \text{Pb}^{2+}(10^{-3}\text{M}) | \text{Pb}$, $E^0 (\text{Sn}^{2+} | \text{Sn}) = -0.14\text{V}$, $E^0 (\text{Pb}^{2+} | \text{Pb}) = -0.13\text{V}$. Is cell reaction is feasible?

Ans. No, $E_{cell} = -0.078\text{V}$

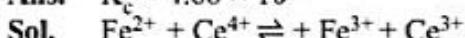
$$\begin{aligned} \text{Sol. } E_{cell} &= -E_{\text{Sn}^{2+}/\text{Sn}}^0 + E_{\text{Pb}^{2+}/\text{Pb}}^0 - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \\ &= +0.14 - 0.13 - \frac{0.059}{2} \log 10^3 \\ &= +0.01 - \frac{0.059}{2} \times = -0.078 \text{ V} \end{aligned} \quad \text{Cell will not work}$$

2. Calculate the equilibrium constant for the reaction



$$\text{Take } \frac{2.303 \text{ RT}}{\text{F}} = 0.06 \text{ at } 25^\circ\text{C}, \log 4.68 = 0.67$$

Ans. $K_c = 4.68 \times 10^{12}$



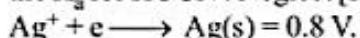
$$E^0 = 1.44 - 0.68 = 0.76\text{V} = \frac{0.06}{1} \log K_C \quad K_C = 4.64 \times 10^{12}$$

Exercise

1. For the galvanic cell : $\text{Ag} | \text{AgCl(s)} | \text{KCl (0.2M)} \parallel \text{KBr (0.001 M)} | \text{AgBr(s)} | \text{Ag}$, Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C . [$K_{sp(\text{AgCl})} = 2.8 \times 10^{-10}$; $K_{sp(\text{AgBr})} = 3.3 \times 10^{-13}$]

Ans. -0.037 V

2. Voltage of the cell $\text{Pt}, \text{H}_2(1\text{ atm}) | \text{HOCl} (1.3 \times 10^{-3} \text{ M}) || \text{Ag}^+(0.8 \text{ M}) | \text{Ag(s)}$ is 0.982 V . Calculate the K_a for HOCl. Neglect $[\text{H}^+]$ because of oxidation of $\text{H}_2(\text{g})$.



Ans. $K_a = 6.99 \times 10^{-4}$

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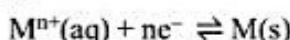
DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

- (1) **Gas-Ion Half Cell :** In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H₂gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.



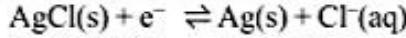
$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^0 - \frac{0.0591}{1} \log \frac{(\text{pH}_2)^{1/2}}{[\text{H}^+]}$$

- (2) **Metal-Metal Ion Half Cell :** This type of cell consist of a metal M in contact with a solution containing Mⁿ⁺ ions.



$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^0 - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]}$$

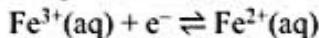
- (3) **Metal-Insoluble Salt - Anion Half Cell :** In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell: This half cell is represented as Cl⁻/AgCl/Ag. The equilibrium reaction that occurs at the electrode is



$$E_{\text{Cl}^-/\text{AgCl/Ag}} = E_{\text{Cl}^-/\text{AgCl/Ag}}^0 - \frac{0.0591}{1} \log [\text{Cl}^-]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as Reference Electrode.

- (4) **Oxidation-reduction Half Cell:** This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. Fe²⁺ - Fe³⁺ half cell.



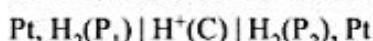
$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - \frac{0.0591}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

CONCENTRATION CELL

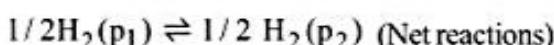
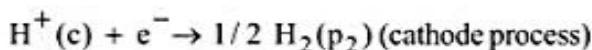
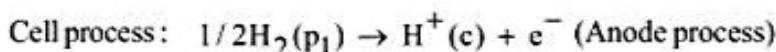
The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell . For such cell, E^o_{cell}=0.

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(i) **Electrode Gas concentration cell :**



Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.



$$\therefore E = -\frac{2.303RT}{F} \log \left[\frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

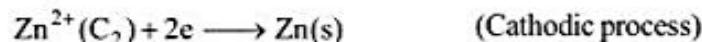
$$\text{or At } 25^\circ\text{C, } E = \frac{0.0591}{2} \log \left[\frac{\text{p}_1}{\text{p}_2} \right]$$

For spontaneity of such cell reaction, $\text{p}_1 > \text{p}_2$

(ii) **Electrolyte concentration cells:**



In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



\therefore From Nernst equation, we have

$$E = \frac{2.303RT}{2F} \log \left[\frac{\text{C}_2}{\text{C}_1} \right]$$

For spontaneity of such cell reaction, $\text{C}_2 > \text{C}_1$

Can you Explain Why ?

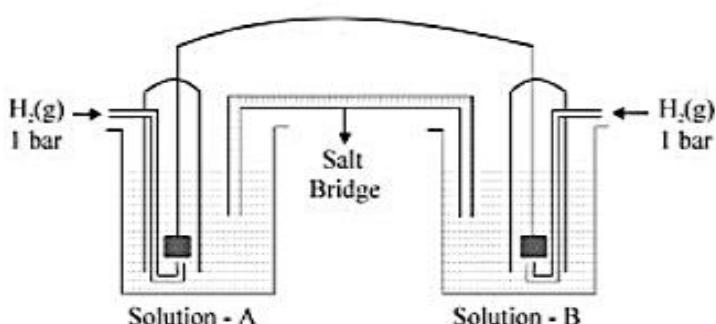


- (i) Like other thermodynamic properties, ΔH , ΔS and ΔG , the sign of E° changes but the magnitude of E° remains the same when we reverse the cell reaction.
- (ii) Changing the stoichiometric coefficients of a half-cell reaction does not affect the value of E° .

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Illustration

1. Carefully observe the given figure and using data provided find the EMF of shown Galvanic cell (in volt):



Solution A is 0.1 M each in NH_4OH and NH_4Cl and solution B is 0.1 M CH_3COONa .

[Given : $K_a(\text{CH}_3\text{COOH}) = 10^{-5}$, $K_b(\text{NH}_4\text{OH}) = 10^{-5}$ and $\frac{2.303RT}{F} = 0.06 \text{ volt}$]

- (A) 0.24 V (B) 0.12 V (C) 0.06 V (D) 0 V

Ans. (D)

Sol. pH of solution (A) : Solution A is a basic Buffer

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow \text{pOH} = 5$$

$$\Rightarrow \text{pH} = 9 \Rightarrow [\text{H}^+]_A = 10^{-9} \text{ M}$$

pH of solution (B)

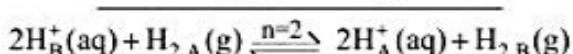
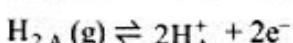
$$\text{pH} = \frac{1}{2} [\text{pK}_w + \text{pK}_a + \log C] \Rightarrow \frac{1}{2} [14 + 5 - 1]$$

$$\text{pH} \Rightarrow 9$$

$$\Rightarrow [\text{H}^+]_B = 10^{-9}$$

Now, The cell is a concentration cell

Cell reaction : $2\text{H}_B^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_{2,B}(\text{g})$



Nearest Equation for cell

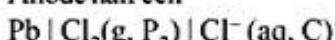
$$E_{\text{Cell}} = 0 - \frac{0.06}{2} \log \frac{[\text{H}^+]_A^2}{[\text{H}^+]_B^2} \Rightarrow 0 \text{ Volt Ans.}]$$

2. $\text{Pt} | \text{Cl}_2(\text{g}, P_2) | \text{Cl}^-(\text{aq}, C) \parallel \text{Cl}^-(\text{aq}, C) | \text{Cl}_2(\text{g}, P_1) | \text{Pt}$
EMF of cell is positive if

- (A) $P_1 > P_2$ (B) $P_2 > P_1$ (C) $P_1 = P_2$ (D) We cannot predict

Ans. (A)

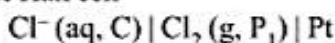
[Sol.] Anode half cell



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$$E_{ox} = E_{ox}^o - \frac{0.0591}{2} \log \frac{P_2}{C} \quad \dots(i)$$

Cathode Half cell



$$E_{red} = E_{red}^o - \frac{0.0591}{2} \log \frac{C}{P_1} \quad \dots(ii)$$

$$E_{cell} = E_{ox} + E_{red}$$

$$= E_{ox}^o + E_{red}^o - \frac{0.0591}{2} \log \frac{P_2}{C} \cdot \frac{C}{P_1}$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$$

for spontaneous reaction

$$P_1 > P_2 \quad \text{Ans. (A)} \quad]$$

3. Calculate the standard e.m.f. of the reaction $Fe^{3+} + 3e^- \rightarrow Fe_{(s)}$ $E_f^\theta = ?$

$$\text{Given } Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E_f^1 = 0.771V \quad Fe^{2+} + 2e^- \rightarrow Fe_{(s)} \quad E_f^2 = -0.44V$$

Sol. With the help of calculation of free energy

$$\Delta G_1^0 = -nFE^o = -(1)(F)(0.771V) = -0.771V$$

$$\Delta G_2^0 = -(2)(F)(0.44) = 0.88FV$$

$$\Delta G_3^0 = -(3)(F)(E^o) = -3FE^oV$$

The free energy change for the unknown process can be obtained as

$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-3FE^o = -0.771V + 0.88F = 0.109V$$

$$\text{or } E^o = -\frac{0.109}{3} = -0.036V$$

4. The standard electrode potentials of the electrode $Cu^{2+}|Cu$ and $Ag^+|Ag$ are 0.34V and 0.7991V respectively. What would be the concentration of Ag^+ in a solution containing 0.06M of Cu^{2+} ion such that both the metals can be deposited together. Assume that activity coefficients are unity and both silver and copper do not dissolve among themselves.

Sol. The individual reactions are :



The electrode potentials given by Nernst equation

$$E(Cu^{2+} | Cu) = E^o = \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} = 0.037 - \frac{(0.0591)}{2} \log \frac{1}{0.06} = 0.037 - 0.036 = 0.301$$

$$E(Ag^+ | Ag) = 0.7991 - \frac{0.0591}{1} \log \frac{1}{[Ag^+]}$$

Two metals will be deposited together when the electrode potentials are equal i.e.

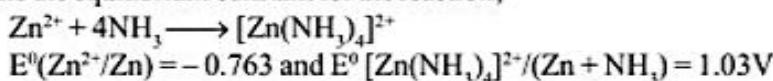
$$\frac{0.301 - 0.7991 - 0.0591 \log \frac{1}{[Ag^+]}}{i.e. \log \frac{1}{[Ag^+]}} = \frac{0.7991 - 0.301}{0.0591} = 8.428$$

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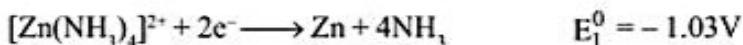
$$\frac{1}{[\text{Ag}^+]} = 10^{8.428}$$

or $[\text{Ag}^+] = 10^{-8.428} = 0.37 \times 10^{-8} \text{ mol dm}^{-3}$

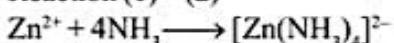
5. Calculate the equilibrium constant for the reaction,



Sol. The electrode reactions for the given electrodes, can be written as



Reaction (1) – (2)



The standard emf of this reaction = $E_1^\circ - E_2^\circ = -0.763 \text{ V} - (-1.03) = 0.267 \text{ V}$

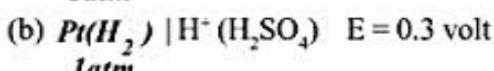
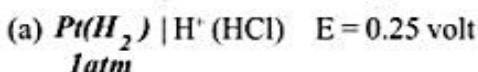
According to Nernst equation $E = E^\circ - \frac{RT}{2F} \ln \frac{a_{[\text{Zn}(\text{NH}_3)_4]^{2-}}}{a_{\text{Zn}^{2+}} \cdot a}$

If the process is equilibrium, $E = 0$ at 25°C $\frac{0.0591}{2} \log K = 0.267$

$$\log K = \frac{(0.267)(2)}{0.0591} = 9.036 \Rightarrow K = 10^{-9.036} 10^9 = 1.09 \times 10^9$$

The equilibrium constant is also called the "Stability Constant" of the complex. If the reaction is written in a reverse manner, it will be "instability constant".

6. Calculate the pH of the following half cells solutions.



Sol. (a) $\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$

$$E_{\text{H}_2/\text{H}^+} = E_{\text{H}_2/\text{H}^+}^\circ - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} = 0.0 - 0.0591 \log \frac{[\text{H}^+]}{1}$$

$$0.25 = 0.0591 \text{ pH}$$

$$\text{pH} = \frac{0.25}{0.0591} = 4.23$$

(b) $E_{\text{H}_2/\text{H}^+} = E_{\text{H}_2/\text{H}^+}^\circ - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} = 0.0 - 0.0591 \log \frac{[\text{H}^+]}{1}$

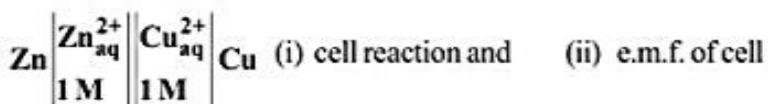
$$0.3 = 0.0591 \text{ pH}$$

$$\text{pH} = \frac{0.3}{0.0591} = 5.076$$

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Exercise

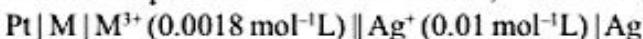
1. Calculate the values for cell



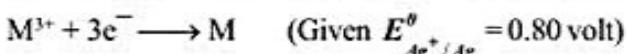
Given : $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.35 \text{ V}$; $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$

- Sol. (i) Cell reaction $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$
(ii) 1.11 V

2. To find the standard potential of M^{3+}/M electrode, the following cell is constituted.

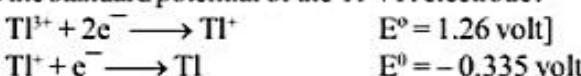


The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction,



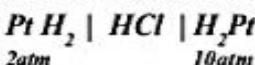
Ans. 0.32 volt

3. What is the standard potential of the Ti^{3+}/Ti electrode?



Ans. 0.728 volt

4. Calculate the emf of the following cell at 25 °C.



Ans. -0.0206 volt

5. Calculate the emf of the cell $\text{Zn}-\text{Hg}(\text{C}_1)/\text{Zn}^{2+}(\text{aq}) \mid \text{Zn}-\text{Hg}(\text{C}_2)$ at 25°C, if the concentration of the zinc amalgam are $\text{C}_1 = 2 \text{ gm per 100 gm of Hg}$ and $\text{C}_2 = 1 \text{ gm per 100 gm of Hg}$.

Ans. $8.8 \times 10^{-3} \text{ V}$

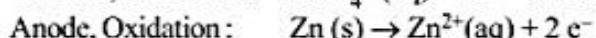
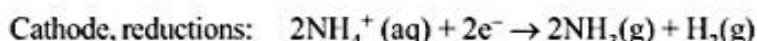
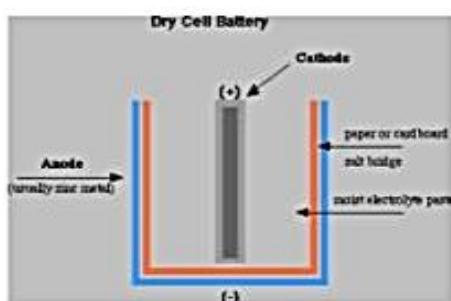
COMMERCIAL VOLTAIC CELLS

Batteries can be classified as primary and secondary. Primary batteries can not be returned to their original state by recharging, so when the reactants are consumed, the battery is "dead" and must be discarded. Secondary batteries are often called storage batteries or rechargeable batteries. The reactions in these batteries can be reversed; thus, the batteries can be recharged.

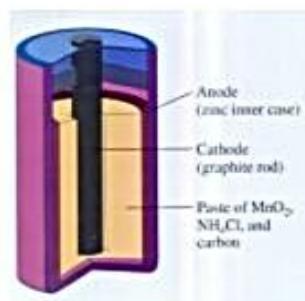
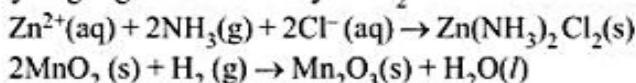
PRIMARY BATTERIES

Dry cells and alkaline batteries

Zinc serves as the anode, and the cathode is a graphite rod placed down the center of the device. These cells are often called "dry cells" because there is no visible liquid phase. However, water is present, so the cell contains a moist paste of NH_4Cl , ZnCl_2 and MnO_2 . The moisture is necessary because the ions present must be in a medium in which they can migrate from one electrode to the other. The cell generates a potential of 1.5 V using the following half-reactions:

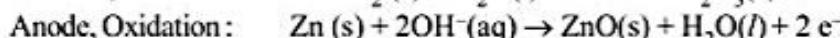
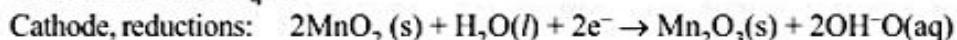


The two gases formed at the cathode will build up pressure and could cause the cell to rupture. This problem is avoided, however, by two other reactions that take place in the cell. Ammonia molecules bind to Zn^{2+} ions, and hydrogen gas is oxidized by MnO_2 to water.



LeClanche cells were widely used because of their low cost, but they have several disadvantages. If current is drawn from the battery rapidly, the gaseous products cannot be consumed rapidly enough, so the cell resistance rises, and the voltage drops. In addition, the zinc electrode and ammonium ions are in contact in the cell, and these chemicals react slowly. Recall that zinc reacts with acid to form hydrogen. The ammonium ion, $\text{NH}_4^+(\text{aq})$, is a weak Bronsted acid and reacts slowly with zinc. Because of this reaction, these voltaic cells cannot be stored indefinitely. When the zinc outer shell deteriorates, the battery can leak acid and perhaps damage the appliance in which it is contained.

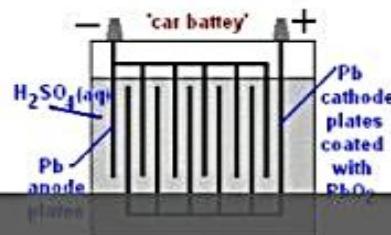
At the present time **alkaline batteries** are used the chemistry of alkaline cells is quite similar to that in a LeClanche cell, except that the material inside the cell is basic (alkaline). Alkaline cells use the oxidation of zinc and the reduction of MnO_2 to generate a current, but NaOH or KOH is used in the cell instead of the acidic salt NH_4Cl .



Alkaline cells, which produce 1.54 V (approximately the same voltage as the LeClanche cell), have the further advantage that the cell potential does not decline under high current loads because no gases are formed.

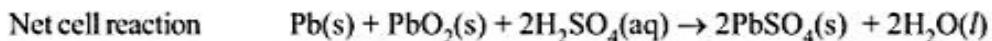
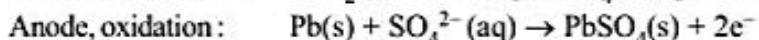
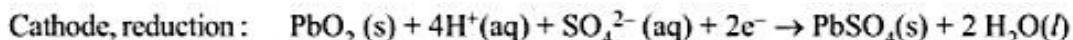
SECONDARY OR RECHARGEABLE BATTERIES

An automobile battery – the **lead storage battery** – is probably the best-known rechargeable battery figure. The 12-V version of this battery contains six voltaic cells, each generating about 2V. The lead storage battery can produce a large initial current, an essential feature when starting an automobile engine.

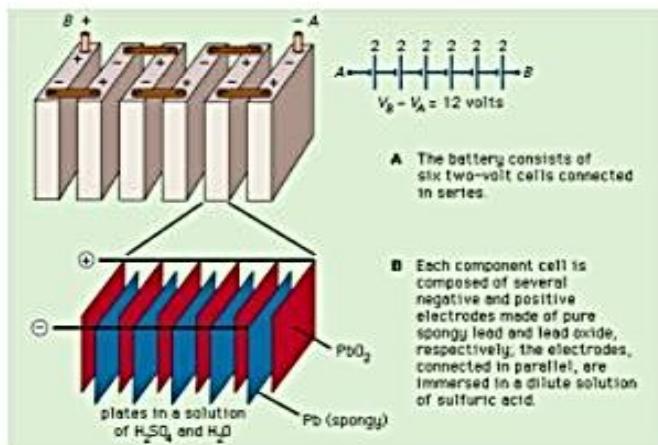


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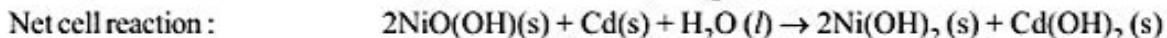
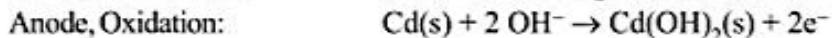
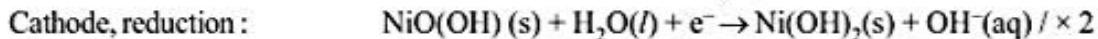
When the cell supplies electrical energy, the lead anode is oxidized to lead (II) sulfate, an insoluble substance that adheres to the electrode surface. The two electrons produced per lead atom move through the external circuit to the cathode, where PbO_2 is reduced to Pb^{2+} ions that, in the presence of H_2SO_4 , also form lead (II) sulfate.



The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.



Nickel - Cadmium ("Ni - Cad") batteries, used in variety of cordless appliances such as telephones, video camcorders, and cordless power tools, are lightweight and rechargeable. The chemistry of the cell utilizes the oxidation of cadmium and the reduction of nickel (III) oxide under basic conditions.



As the active masses of all reaction components are independent of their amount. The cell delivers constant EMF throughout.

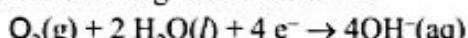
FUEL CELLS AND HYBRID CARS

An advantage of voltaic cells is that they are small and portable, but their size is also a limitation. The amount of electric current produced is limited by the quantity of reagents contained in the cell. When one of the reactants is completely consumed, the cell will no longer generate a current. Fuel cells avoid this limitation because the reactants (fuel and oxidant) can be supplied continuously to the cell from an external reservoir.

In a Hydrogen - Oxygen fuel cell figure, hydrogen is pumped into the anode of the cell, and O_2 (or air)

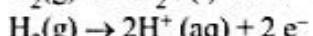
is directed to the cathode where the following reactions occur :

Cathode, reduction :

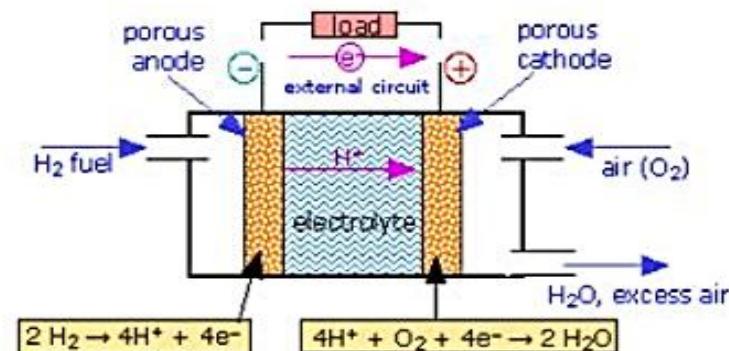


$$E^\circ = 1.23 \text{ V}$$

Anode, Oxidation :



$$E^\circ = 0 \text{ V}$$



Schematic diagram
of a modern
hydrogen-oxygen
fuel cell.

Commonly used
electrolytes are
NaOH solution,
phosphoric acid, or
solid oxides. A
major limitation of
any oxygen-
consuming fuel cell
is the slow rate of
the reduction of
this element at a
cathode. The best
cathode surfaces
are usually made
of platinum, which
is a major cost
factor in fuel cell
design.

EFFICIENCY OF A FUEL CELL

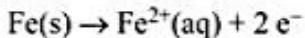
$$\eta = \frac{(\Delta G)}{(\Delta H)} \times 100$$

CORROSION CELLS AND REACTIONS

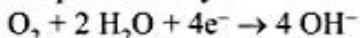
Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $\text{M} \rightarrow \text{M}^+ + \text{e}^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a depolarizer.

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient. A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like



and the cathodic steps can be any of



where M is a metal. Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

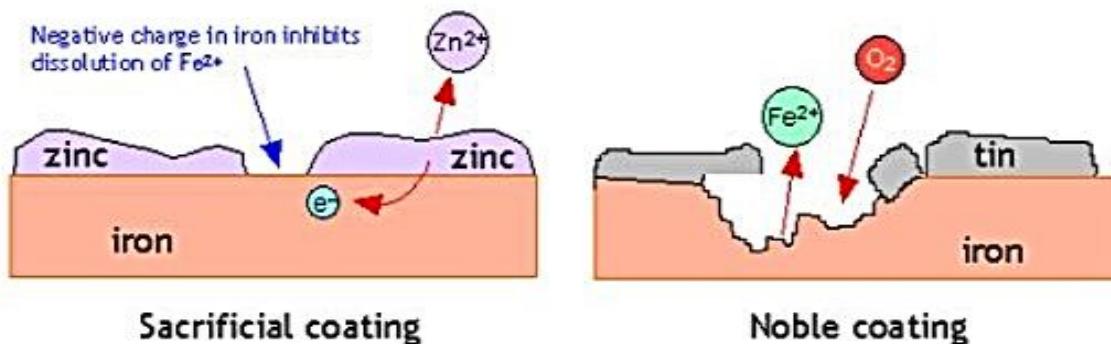
CONTROL OF CORROSION

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads.

A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction $M \rightarrow M^{2+} + 2 e^-$ to take place.

SACRIFICIAL COATINGS

One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.



The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

CATHODIC PROTECTION

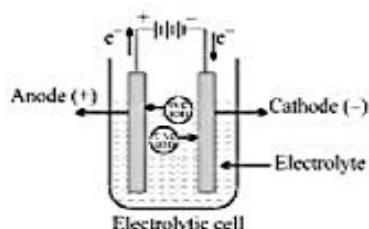
A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as cathodic protection. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a piece of zinc or aluminum buried in the ground nearby.

ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell

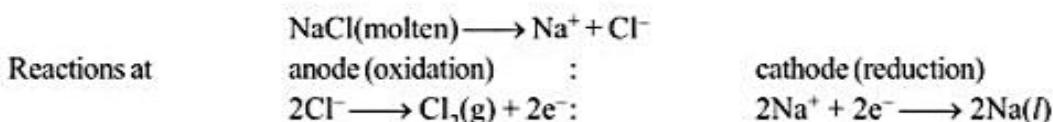


ELECTRODES

The metal strip at which positive current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

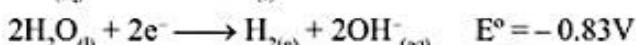
ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE



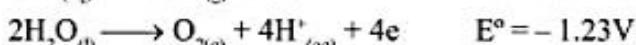
There are two types of electrodes used in the electrolytic cell, namely attackable and non - attackable. The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.

ELECTROLYSIS OF SODIUM CHLORIDE SOLUTIONS

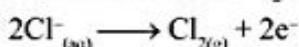
When you electrolyze an aqueous solution of sodium chloride, NaCl, the possible species involved in half-reactions are Na^+ , Cl^- and H_2O . The possible cathode half-reactions are



Under standard conditions, you expect H_2O to be reduced in preference to Na^+ , which agrees with what you observe. Hydrogen is evolved at the cathode.

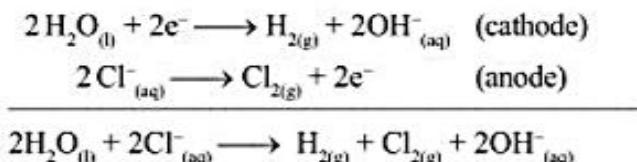


Under standard-state conditions, you might expect H_2O to be oxidized in preference to Cl^- . However, the potentials are close and over voltages at the electrodes could alter this conclusion. It is possible nevertheless to give a general statement about the product expected at the anode. Electrode potentials, as you have seen, depend on concentrations. It turns out that when the solution is concentrated enough in Cl^- , Cl_2 is the product; but in dilute solution, O_2 is the product. To see this, you would simply apply the Nernst equation of the $\text{Cl}^-|\text{Cl}_2$ half reaction.



Starting with very dilute NaCl solutions, you would find that the oxidation potential of Cl^- is very negative, so H_2O is reduced in preference to Cl^- . But as you increase the NaCl concentration, you would find that the oxidation potential of Cl^- increases until eventually Cl^- is oxidized in preference to H_2O . The product changes from O_2 to Cl_2 .

The half-reactions and cell reaction for the electrolysis of aqueous sodium chloride to chlorine and hydroxide ion are as follows:



Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is Na^+ . When you evaporate the electrolyte solution at the cathode, you obtain sodium hydroxide NaOH .

QUALITATIVE ASPECTS OF ELECTROLYSIS

- (i) Of the two cations, that cation is liberated at the cathode which has higher reduction potential.
Of the two anions, that anion will be discharged at the anode which has lower reduction potential.
- (ii) If electrode is active at cathode, metal goes on depositing on cathode and at anode metal is dissolved.
- (iii) It must be noted that it is not the SRP of a cation that decides its discharge, but its reduction potential. The SRP's should be used only when the concentration of ions are 1M. For concentrations other than 1M, the reduction potentials for each cation at the concentration is calculated and then the discharge of an ion can be predicted.
- (iv) The discharge of NO_3^- , PO_4^{3-} and SO_4^{2-} ions at anode does not commonly take place from aqueous solution.



Electrolysis of water is often done with a small amount of sulphuric acid added to water.

Why?

FARADAY'S LAWS OF ELECTROLYSIS

(i) *First law of electrolysis :*

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called **electrochemical equivalent**.

Let 1 ampere current is passed till 't' seconds.

Then, $Q = It \quad \therefore w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulomb.

$\therefore 1 \text{ Coulomb will liberate } \frac{E}{96500} \text{ gm; By definition, } Z = \frac{E}{96500}$

$$\therefore W = \frac{ItE}{96500}$$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where V = volume of liberated gas, V_e = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at 1 atm & 0°C.

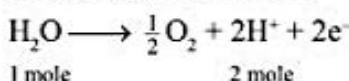
(ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

Illustration

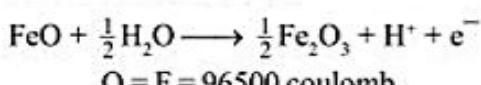
- 1** How much electric charge is required to oxidise :
 (a) 1 mole of H_2O to O_2 , (b) 1 mole of FeO to Fe_2O_3 ?

Sol. (a) The oxidation reaction is:



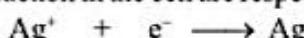
$$O = 2F = 2 \times 96500 = 1.93 \times 10^5 C$$

(b) The oxidation reaction is



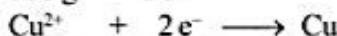
2. Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing AgNO_3 , second CuSO_4 and third FeCl_3 solution. How many gram of each metal will be deposited assuming only cathodic reaction in each cell.

Sol. The cathodic reaction in the cell are respectively.



1 mole 1 mole

108 g 1 F



1 mole 1 mole

63.5 g 2 F

and $\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$

1 mole 1 mole

56 g 3 F

As deposited =

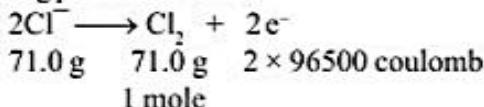
$$\text{Hence, } \text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$$

$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

$$\text{and } \text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$$

3. An 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.

Sol. The reaction taking place at anode is



$$Q = j \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

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

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

$$\text{Volume of Cl}_2 \text{ liberated at NTP} = 9.3264 \times 22.4 = 208.91 \text{ L}$$

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4. How long a current of 2A has to be passed through a solution of AgNO_3 to coat a metal surface of 80cm^2 with $5\mu\text{m}$ thick layer? Density of silver = 10.8g/cm^3 .

Ans. $t = 193 \text{ sec}$

$$\text{Sol. } I = \frac{M}{V} \Rightarrow 10.8 = \frac{M}{80 \times 5 \times 10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}$$

$$M = 43.2 \times 10^{-2} \text{ gm}$$

$$\text{Eq. of Ag} = \frac{I \cdot t}{96500}$$

$$\frac{43.2 \times 10^{-2}}{108} = \frac{2 \times t}{96500} = t = 193 \text{ sec}$$

Exercise

1. What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?

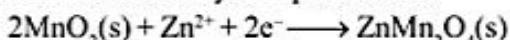
Ans. 7.55 ampere

2. A current of 2.68 ampere is passed for one hour through an aqueous solution of copper sulphate using copper electrodes. Calculate the change in mass of cathode and that of the anode. (at. mass of copper = 63.5).

Ans. 3.174 g

3. In a zinc manganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of MnO_2 , carbon, NH_4Cl and ZnCl_2 in aqueous base.

The cathodic reaction may be represented as



Let there be 8 g MnO_2 in the cathodic compartment. How many days will the dry cell continue to give a current of 4×10^{-3} ampere.

Ans. 25.675 day

CONDUCTANCE

Introduction

Both metallic and electrolytic conductors obey Ohm's law

i.e. $V = IR$

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm².

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho l} \quad \text{or} \quad C = K \frac{A}{l}$$

where C = conductance ohm⁻¹; K = specific conductance ohm⁻¹cm⁻¹.

Mho and siemens are other units of conductance

$$K = \frac{l}{A} C$$

Specific conductance = Cell constant × Conductance

$$k = G^* \times G$$

SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM³ OF AN ELECTROLYTE SOLUTION

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by Λ .

$$\Lambda = K \times V$$

$$(\Lambda = \text{ohm}^{-1} \text{cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{cm}^2)$$

Usually concentration of electrolyte solution is expressed as C gm equivalent per litre.

$$\text{Thus, } V = \frac{1000}{C}$$

$$\{\text{Volume having 1 gm equivalent electrolyte in the solution}\} \text{ Thus, } \Lambda = K \times \frac{1000}{C}$$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by Λ_m .

$$\Lambda_m = K \times V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole electrolyte per litre.

$$\text{Thus, } V = \frac{1000}{M}$$

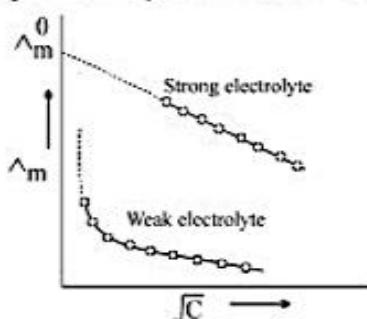
$$\text{Hence, } \Lambda_m = K \times \frac{1000}{M}$$

$$\text{Relation between } \Lambda \text{ and } \Lambda_m : \quad \Lambda_m = n \times \Lambda$$

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DETERMINATION OF λ_m^0 OR λ^0

A plot of λ_m vs \sqrt{C} as found experimentally is as shown below graphically.



The λ_m vs \sqrt{C} plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, λ_m^0 values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

λ_m values are then plotted against \sqrt{C} when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects λ_m axis is λ_m^0 of the strong electrolyte.

However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to λ_m axis. Hence extrapolation in this case is not possible. Thus, λ_0 of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.



Is electrolytic conductance depends on temperature ?

Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined λ_0 values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in λ_0 values in each case remains the same:

$$\lambda_m^0(\text{KCl}) - \lambda_m^0(\text{KF}) = \lambda_m^0(\text{NaCl}) - \lambda_m^0(\text{NaF})$$

He also determined λ_0 values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in λ_0 values in each case remains the same.

$$\lambda_m^0(\text{KF}) - \lambda_m^0(\text{NaF}) = \lambda_m^0(\text{KCl}) - \lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

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Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, MgSO₄ etc.

APPLICATION OF KOHLRAUSCH'S LAW

(1) Determination of λ_m^0 of a weak electrolyte:

In order to calculate λ_m^0 of a weak electrolyte say CH₃COOH, we determine experimentally λ_m^0 values of the following three strong electrolytes:

- (a) A strong electrolyte containing same cation as in the test electrolyte, say HCl
- (b) A strong electrolyte containing same anion as in the test electrolyte, say CH₃COONa
- (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

λ_m^0 of CH₃COOH is then given as:

$$\lambda_m^0(\text{CH}_3\text{COOH}) = \lambda_m^0(\text{HCl}) + \lambda_m^0(\text{CH}_3\text{COONa}) - \lambda_m^0(\text{NaCl})$$

Proof:

$$\lambda_m^0(\text{HCl}) = \lambda_{\text{H}}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \dots \dots \text{(i)}$$

$$\lambda_m^0(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots \dots \dots \text{(ii)}$$

$$\lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \dots \dots \text{(iii)}$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\lambda_m^0(\text{HCl}) + \lambda_m^0(\text{CH}_3\text{COONa}) - \lambda_m^0(\text{NaCl}) = \lambda_{(\text{H}^+)}^0 + \lambda_{(\text{CH}_3\text{COO}^-)}^0 = \lambda_0(\text{CH}_3\text{COOH})$$

(2) Determination of degree of dissociation (α):

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\lambda_m}{\lambda_m^0}$$

(3) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to λ_m^0 as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\lambda_m^0 = \frac{1000\kappa}{C},$$

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

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Illustration

1. 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.

Sol. Given $I = 2.1$ cm, $a = 4.2$ sq. cm, $R = 50$ ohm

$$\text{Specific conductance, } \kappa = \frac{l}{a} \cdot \frac{1}{R}$$

$$\text{or } \kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Equivalent conductivity} = \kappa \times V$$

V = the volume containing 1 g equivalent = 1000 ml

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

2. The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$, respectively at 25 °C. Calculate the equivalent conductance of acetic acid at infinite dilution.

Sol. According to Kohlrausch's law,

$$\Lambda_{\infty \text{CH}_3\text{COONa}} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} = 91.0 \quad \dots \dots \text{(i)}$$

$$\Lambda_{\infty \text{HCl}} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.16 \quad \dots \dots \text{(ii)}$$

$$\Lambda_{\infty \text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.45 \quad \dots \dots \text{(iii)}$$

Adding equations (i) and (ii) and subtracting (iii),

$$\begin{aligned} \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} \\ = 91.0 + 426.16 - 126.45 \end{aligned}$$

$$\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} = \Lambda_{\infty \text{CH}_3\text{COOH}} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

3. The specific conductivity of a saturated solution of silver chloride is 2.30×10^{-6} mho cm^{-1} at 25 °C. Calculate the solubility of silver chloride at 25 °C ;

if $\lambda_{\text{Ag}^+} = 61.9 \text{ mho cm}^2 \text{ mol}^{-1}$ and $\lambda_{\text{Cl}^-} = 76.3 \text{ mho cm}^2 \text{ mol}^{-1}$.

Sol. Let the solubility of AgCl be s gram mole per litre

$$\text{Dilution} = \frac{1000}{s}$$

$$\Lambda_{\infty \text{AgCl}} = \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-} = 61.9 + 76.3 = 138.2 \text{ mho cm}^2 \text{ mol}^{-1}$$

$$\text{Sp. conductivity} \times \text{dilution} = \Lambda_{\infty \text{AgCl}} = 138.2$$

$$2.30 \times 10^{-6} \times \frac{1000}{s} = 138.2$$

$$s = \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mole per litre} = 1.66 \times 10^{-5} \times 143.5 \text{ gL}^{-1} = 2.382 \times 10^{-3} \text{ gL}^{-1}$$

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Exercise

1. Specific conductance of a decinormal solution of KCl is $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of a cell containing the solution was found to be 56. What is the cell constant?
Ans. 0.6272 cm^{-1}
2. The specific conductivity of 0.02 M 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 ohms. The resistance of 0.01 M CuSO_4 solution at 25°C measured with the same cell was 8331 ohms. Calculate the molar conductivity of the copper sulphate solution.
Ans. $8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$
3. A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of 4.5 cm^2 has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.
Ans. $30.56 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
4. 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.
Ans. 0.85

ELECTROCHEMICAL SERIES

S.No.	Reduction half cell reaction	E° in volts at 25°C
1.	$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+ 2.65
2.	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \longrightarrow 2\text{SO}_4^{2-}$	+ 2.01
3.	$\text{Co}^{3+} + \text{e}^- \longrightarrow \text{Co}^{2+}$	+ 1.82
4.	$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+ 1.65
5.	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.52
6.	$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	+ 1.50
7.	$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+ 1.36
8.	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
9.	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+ 1.229
10.	$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+ 1.07
11.	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{NO} + 2\text{H}_2\text{O}$	+ 0.96
12.	$2\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}$	+ 0.92
13.	$\text{Cu}^{2+} + \text{I}^- + \text{e}^- \longrightarrow \text{CuI}$	+ 0.86
14.	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+ 0.799
15.	$\text{Hg}_2^{2+} + 2\text{e}^- \longrightarrow 2\text{Hg}$	+ 0.79
16.	$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+ 0.77
17.	$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+ 0.535

S.No.	Reduction half cell reaction	E° in volts at 25°C
18.	$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+0.53
19.	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34
20.	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27
21.	$\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$	+0.222
22.	$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	+0.15
23.	$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$	+0.13
24.	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
25.	$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$	-0.036
26.	$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	-0.126
27.	$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.14
28.	$\text{AgI} + \text{e}^- \longrightarrow \text{Ag} + \text{I}^-$	-0.151
29.	$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	-0.25
30.	$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	-0.28
31.	$\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}$	-0.403
32.	$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	-0.41
33.	$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	-0.44
34.	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	-0.74
35.	$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.762
36.	$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$	-0.828
37.	$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	-1.18
38.	$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	-1.66
39.	$\text{H}_2 + 2\text{e}^- \longrightarrow 2\text{H}^-$	-2.25
40.	$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.37
41.	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	-2.71
42.	$\text{Ca}^{2+} + \text{e}^- \longrightarrow \text{Ca}$	-2.87
43.	$\text{Ba}^{2+} + 2\text{e}^- \longrightarrow \text{Ba}$	-2.90
44.	$\text{Cs}^+ + \text{e}^- \longrightarrow \text{Cs}$	-2.92
45.	$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	-2.93
46.	$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.03

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SOLVED EXAMPLES

OBJECTIVE

- Q.1** On passing C amperes of current through an electrolyte solution for t seconds, m gram of metal deposits on the cathode. The equivalent weight of the metal is

$$(A) \frac{Ct}{m \times 96500} \quad (B) \frac{Cm}{t \times 96500} \quad (C) \frac{96500 \times m}{C \times t} \quad (D) \frac{C \times t \times 96500}{m}$$

Ans. (C)

- Sol.** 1 Faraday, that is, 96500 coulombs deposits 1 gm equivalent of the substance. Now C × t amount of electricity deposits 'm' gm of substance

$$\therefore \text{96500 C amount of electricity deposits} = \frac{96500 \times m}{C \cdot t} = \text{equivalent weight}$$

- Q.2** One coulomb is equal to

- | | |
|--------------------------|---|
| (A) 96500 Faraday | (B) charge on 6.24×10^{18} electrons |
| (C) charge on 1 electron | (D) none of the above |

Ans. (B)

- Sol.** Charge on 6.023×10^{23} electrons = 96500 C

$$\text{So, 1 coulomb would be the charge on } \frac{6.023 \times 10^{23}}{96500} = 6.24 \times 10^{18} \text{ electrons.}$$

- Q.3** If three Faradays (F) of electricity is passed through the solutions of AgNO_3 , CuSO_4 and AuCl_3 , the molar ratio of the cations deposited at the cathode is

- | | | | |
|---------------|---------------|---------------|---------------|
| (A) 1 : 1 : 1 | (B) 1 : 2 : 3 | (C) 3 : 2 : 1 | (D) 6 : 3 : 2 |
|---------------|---------------|---------------|---------------|

Ans. (D)

- Sol.** Since $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$, $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, $\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$, three Faradays of electricity will deposit 3 moles of Ag, 1.5 moles of copper, and 1 mole of gold. Therefore, the molar ratio is 3 : 1.5 : 1 or 6 : 3 : 2.

- Q.4** During electrolysis of a concentrated aqueous solution of NaCl, the product at the cathode is

- | | | | |
|--------|-------------------|------------------|------------------|
| (A) Na | (B) Cl_2 | (C) O_2 | (D) H_2 |
|--------|-------------------|------------------|------------------|

Ans. (B)

- Sol.** Chlorine gas is produced as chloride ions need a less voltage for oxidation to chlorine than needed by H_2O for oxidation to O_2 (This extra voltage needed by water is called over voltage).

- Q.5** Two Pt electrodes fitted in a conductance cell are 1.5 cm apart and the cross-sectional area of each electrode is 0.75 cm^2 . The cell constant is

- | | | | |
|----------|------------|---------------------------|---------------------------|
| (A) 1.25 | (B) 0.5 cm | (C) 2.0 cm^{-1} | (D) 0.2 cm^{-1} |
|----------|------------|---------------------------|---------------------------|

Ans. (C)

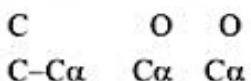
$$\text{Sol. Cell constant} = \frac{\ell}{a} = \frac{1.5}{0.75} = 2.0 \text{ cm}^{-1}$$

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- Q.6** The ionisation constant of a weak electrolyte is 25×10^{-6} and the equivalent conductance of its 0.01 M solution is $19.6 \text{ S cm}^2 \text{ eq}^{-1}$. The equivalent conductance at infinite dilution of the electrolyte in $\text{S cm}^2 \text{ eq}^{-1}$ is

(A) 250 (B) 196 (C) 392 (D) 384

Ans. (C)



$$\text{Or } K = C\alpha^2 \quad \text{Or } 25 \times 10^{-6} = 10^{-2}, \alpha^2$$

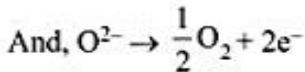
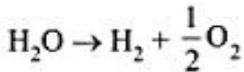
$$\text{Or } \alpha = 5 \times 10^{-2} \text{ Also } \alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{19.6}{\lambda_\infty} \text{ or } \lambda_\infty = \frac{19.6}{5 \times 10^{-2}} = 392 \text{ S cm}^2 \text{ eq}^{-1}$$

- Q.7** How many c.c. of oxygen is released by a current of 2 A flowing for 3 minutes and 13 seconds in acidulated water?

(A) 11.2 c.c. (B) 33.6 c.c. (C) 44.8 c.c. (D) 22.4 c.c.

Ans. (D)

Sol. $Q = 2 \times 193 = 386 \text{ C}$



2 mole of electrons = 2×96500 C give 1/2 mole of oxygen i.e., $11,200 \text{ cm}^3$.

So, 386 C will give $\frac{386 \times 11,200}{2 \times 96,500} = 22.4$ c.c. of oxygen.

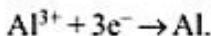
- Q.8** The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 10.0 g of Al? (Al = 27, Mg = 24)

(A) Rs.10.0 (B) Rs. 27.0 (C) Rs. 44.44 (D) Rs. 66.67

Ans. (D)

Sol. $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$

$$\text{Quantity of electricity required to deposit 1.0 g of Mg} = \frac{2 \times 96500}{24}$$



$$\text{Quantity of electricity required to deposit } 10.0 \text{ g of Al} = \frac{3 \times 96500}{27} \times 10$$

$$\text{Cost} = \frac{3 \times 96500}{27} \times \frac{10 \times 5 \times 24}{2 \times 96500} = \text{Rs. } 66.67$$

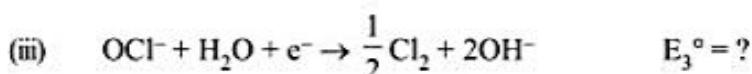
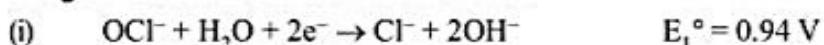
Q.9 The standard electrode potential (E°) for OCl^-/Cl^- and $\text{Cl}^-/\frac{1}{2}\text{Cl}_2$ respectively are 0.94 V and -1.36 V.

The E° value for $\text{OCl}^-/\frac{1}{2}\text{Cl}_2$ will be

- (A) -0.42 V (B) -2.20 V (C) 0.52 V (D) 1.04 V

Ans. (C)

Sol. The given half cell reactions can be written as



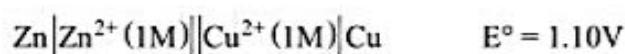
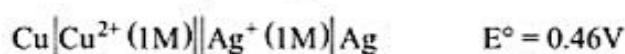
Now consider free energies ($\Delta G^\circ = -nE^\circ F$)

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

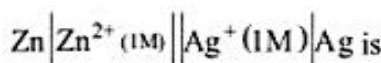
$$-1 \times F \times E_3^\circ = -2 \times F(0.94) - 1 \times F(-1.36)$$

$$E_3^\circ = 2 \times 0.94 - 1.36 = 0.52 \text{ V}$$

Q.10 The e.m.f of the following cells is given



The e.m.f of the cell



- (A) 1.56 V (B) 0.64 V (C) -1.56 V (D) 2.02 V

Ans. (A)

$$\text{(i)} \quad E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.46 \text{ V}$$

$$\text{(ii)} \quad E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ = 1.10 \text{ V}$$

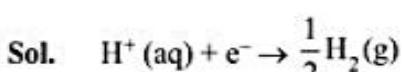
On adding (i) and (ii)

$$E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ = 1.56 \text{ V}$$

Q.11 A hydrogen electrode is dipped in a solution of $\text{pH} = 3.0$ at 25°C . The potential of the cell will be

- (A) 0.177 V (B) 0.087 V (C) -0.177 V (D) 0.059 V

Ans. (C)



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$$E = E^\circ - \frac{0.059}{n} \log \left(\frac{1}{[H^+]} \right) = 0 - \frac{0.059}{1} \cdot pH$$

$$\text{Or } E = -0.059 \times 3 = -0.177$$

O.12 In the cell



$E_{\text{cell}} - E^{\circ}_{\text{cell}} = 0.0591 \text{ V}$. The ratio of C_1/C_2 at 298 K is

Ans. (C)

$$\text{Sol: } \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$$

$$E_{\text{cell}} - E_{\text{cell}}^{\circ} = -\frac{0.0591}{2} \log \frac{C_1}{C_2}$$

$$\text{Or } 0.0591 = -\frac{0.0591}{2} \log \frac{C_1}{C_2} \quad \text{Or } \log \left(\frac{C_1}{C_2} \right) = -2 \text{ or } \frac{C_1}{C_2} = \text{antilog } -2 = 10^{-2}$$

Q.13 The solution of nickel sulphate, in which a nickel rod is dipped, has been diluted 10 times. The potential of the nickel electrode

- (A) decreases by 60 mV (B) increases by 30 mV (C) decreases by 30 mV (D) increases by 60 mV

Ans. (C)

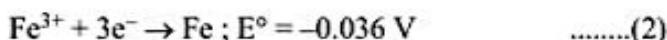
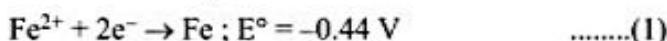
Sol. $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$

$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{x}$$

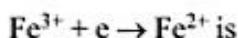
$$\text{After dilution } E = E^\circ - \frac{0.059}{2} \log \frac{10}{x}$$

Therefore, the potential decreases by $\frac{0.059}{2} \log 10 = 0.0295$ V or 0.03 V or 30.0 mV.

Q.14 Given standard electrode potentials

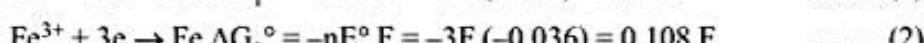


The standard electrode potential E° for

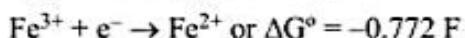


- (A) -0.476 V (B) -0.404 V (C) 0.404 V (D) +0.772 V

Ans. (D)



On subtracting (1) from (2)

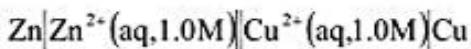


$$\text{Or } \Delta G^\circ = -nE^\circ F = -0.772 \text{ F}$$

$$\text{Or } E^\circ = \frac{0.772}{1} = 0.772 \text{ V}$$

SUBJECTIVE

Q.15 Consider the cell



The standard reduction potentials are 0.350 V for $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}$ and
 -0.763 V for $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}$

- (a) What is the cell reaction?
- (b) Calculate the e.m.f of the cell.
- (c) Is the cell reaction spontaneous?

Sol. Anodic reaction: $\text{Zn} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

Cathodic reaction: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}$

Overall reaction: $\text{Zn} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+} + \text{Cu}$

$$\text{e.m.f of the cell } E_{\text{Cell}}^\circ = E_R^\circ - E_L^\circ = 0.350 - (-0.763) = 1.113 \text{ V}$$

Since E_{Cell}° is positive, the ΔG of the reaction ($= -nEF$) will be negative and so the reaction is spontaneous.

Q.16 Calculate the electrode potential of a copper wire dipped in 0.1 M CuSO_4 solution at 25°C. The standard electrode potential of copper is 0.34 V.

Sol. The electrode reaction is $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$.

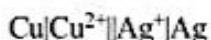
$$\text{By using Nernst equation, } E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$\text{Or } E = 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1} = 0.34 - 0.02955 \\ = 0.31045 \text{ V}$$

Q.17 The standard reduction potential of $\text{Cu}^{2+}|\text{Cu}$ and $\text{Ag}^+|\text{Ag}$ electrodes are 0.337 V and 0.799 V respectively. Construct a working cell with positive e.m.f. If the concentration of Cu^{2+} ions is 0.01 M, then for what concentration of Ag^+ will the e.m.f of the cell be zero at 25°C?

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Sol. Since the reduction potential of silver electrode $E_{\text{Ag}^+/\text{Ag}}^\circ$ is higher than copper electrode, the half cell Ag^+/Ag will constitute the cathode of the cell and the cell is



The cell reaction is $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$ and the standard e.m.f

$$E^\circ = 0.799 - 0.337 = 0.462 \text{ V.}$$

The Nernst equation for the cell is

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

$$\text{Or } E_{\text{cell}} = 0 = 0.462 - \frac{0.0591}{2} \log \frac{[0.01]}{[\text{Ag}^+]^2}$$

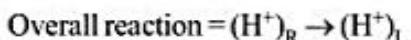
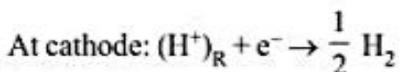
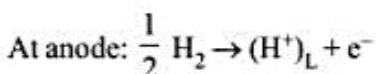
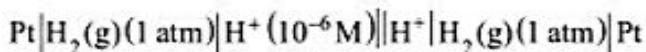
$$\text{Or } \log \frac{[0.01]}{[\text{Ag}^+]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\text{Or } 2 \log [\text{Ag}^+] = \log [0.01] - 15.6345 = \frac{-2 - 15.6345}{2} = -8.8173$$

$$\text{Or } [\text{Ag}^+] = 1.523 \times 10^{-9} \text{ M}$$

Q.18 A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The e.m.f of the cell is 0.118 V at 25°C . Calculate the concentration of hydrogen ions at the positive electrode.

Sol. The cell is



$$\text{The cell potential is } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \log \frac{(\text{H}^+)_L}{(\text{H}^+)_R}$$

$$\text{Or } 0.118 \text{ V} = 0 - \frac{0.059}{1} \log \frac{10^{-6}}{[\text{H}^+]} \quad \text{Or } [\text{H}^+] = 10^{-4} \text{ M}$$

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- Q.19** Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until equilibrium is reached. If the standard reduction potential of Zn²⁺/Zn and Ni²⁺/Ni are -0.75 V and -0.24 V respectively, calculate the concentration of Ni²⁺ in the solution at equilibrium.

Sol. The cell reaction is $Zn + Ni^{2+} \rightarrow Zn^{2+} + Ni$.

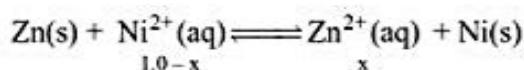
E° , the standard e.m.f, is $-0.24 - (-0.75) = 0.51$ V.

The equilibrium constant of the reaction K is [$\Delta G^\circ = -nE^\circ F = -RT \ln K$], given by the expression

$$\log K = \frac{nE^\circ F}{2.303 RT} = \frac{(2 \times 96500 \text{ C mol}^{-1})(0.51)}{(2.303)(8.314 \text{ J K}^{-1})(298)}$$

$$\text{Or } K = 1.78 \times 10^{-17}$$

Let 'x' be the concentration of Zn²⁺ ions. Then



$$K = 1.78 \times 10^{-17} = \frac{[Zn^{2+}]}{[Ni^{2+}]} = \frac{x}{(1.0-x)} \text{ or } K(1.0-x) = x$$

$$\therefore x = \frac{K(1.0)}{1+K} \simeq 1.0 \text{ M}$$

$$[Ni^{2+}] = \frac{[Zn^{2+}]}{K} = \frac{1.0 \text{ M}}{1.78 \times 10^{-17}} = 5.6 \times 10^{-18} \text{ M}$$

- Q.20** How many coulombs of electricity are required for the following reactions?

(i) 1.0 mol of Cu²⁺ to Cu and

(ii) 1.0 mol of KMnO₄ to MnSO₄

Sol. (i) The reaction is $Cu^{2+} + 2e^- \rightarrow Cu$ and for this the quantity of electricity required is 2 Faradays, as two mole of electrons are involved. Therefore, $2 \times 96500 = 193000$ coulombs of electricity is required.

(ii) For the reaction MnO₄⁻ to Mn²⁺, 5 moles of electrons are involved $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$ and for this the quantity of electricity required is $5 \times 96500 = 482500$ coulombs.

- Q.21** How long a current of 3 A has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm² with a 0.005 mm thick layer. Density of silver is 10.5 g cm⁻³.

Sol. Volume of metal to be deposited = $(80 \text{ cm}^2)(0.0005 \text{ cm}) = 0.04 \text{ cm}^3$

Mass of metal to be deposited = $(10.5)(0.04) = 0.42 \text{ gm}$

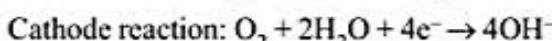
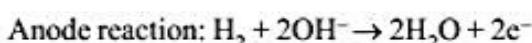
Amount of silver to be deposited = $\frac{0.42}{108.0} = 3.889 \times 10^{-3} \text{ moles}$

Amount of electricity necessary = $3.889 \times 10^{-3} \times 96500 \text{ C mol}^{-1} = 375.27 \text{ C}$

Time for which 3 A current is to be passed = $\frac{375.27}{3} = 125.09 \text{ sec.}$

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- Q.22** In a fuel cell, hydrogen and oxygen react to produce electricity. In the process, hydrogen gets oxidised at the anode and oxygen gets reduced at the cathode. If 67.2 L of H₂ at STP reacts in 15 minutes, what is the average current produced? If the entire current is used for electro-deposition of copper from copper (II) in solution, what mass of copper is deposited?



Sol. Amount of hydrogen oxidised = $\frac{67.2}{22.4} = 3 \text{ moles}$

Amount of electrons produced = $2 \times 3 \text{ moles of electrons}$

Electricity produced = $2 \times 3 \times 96500 \text{ C}$

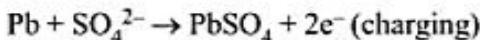
Current produced = $2 \times 3 \times 96500 / 15 \times 60 = 643.33 \text{ A}$

1.0 mole of copper gets deposited by the absorption of 2 moles of electrons

Amount of Cu deposited = 3 moles

Or, mass of Cu deposited = $3 \times 63.5 = 190.5 \text{ gm}$

- Q.23** During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 g m L⁻¹ to 1.139 g m L⁻¹. Sulphuric acid of density 1.294 g mL⁻¹ is 39% H₂SO₄ by mass and that of density 1.139 g mL⁻¹ is 20% H₂SO₄ by mass. The battery holds 3.5 L of acid and the volume remains practically constant during the discharge. Calculate the number of ampere hour for which the battery has been used. The reactions are



Sol. Mass of H₂SO₄ (initially) = $3.5 \times 10^3 \times 1.294 = 4529 \text{ gm}$

$$\text{Actual mass of H}_2\text{SO}_4 = \frac{39}{100} \times 4529 = 1766.3 \text{ gm}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ in the end} = 1.139 \times 3.5 \times 10^3 = 3986.5 \text{ gm}$$

$$\text{Actual mass of H}_2\text{SO}_4 = \frac{20}{100} \times 3986.5 = 797.3 \text{ gm}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ consumed} = 1766.3 - 797.3 = 969.0 \text{ gm}$$

$$\text{Moles of H}_2\text{SO}_4 \text{ consumed} = \frac{969}{98} = 9.888 \text{ moles}$$

Amount of H⁺ consumed = $2 \times 9.888 \text{ moles}$ (since H₂SO₄ has 2H⁺). In the discharge reaction, 4 moles of H⁺ are consumed per 2 moles of electrons. Therefore, electrons discharged $(2 \times 9.888) \times 2/4 = 9.888 \text{ moles of electrons}$. So, the amount of electricity discharged = $9.888 \text{ moles} \times 96,500 \text{ C} = 954192 \text{ C}$.

Battery has been used for = $954192/60 \times 60 = 265.05 \text{ ampere hours}$.

- Q.24** 19.0 grams of molten SnCl₂ is electrolysed for some time by using inert electrodes, until 0.119 g of Sn is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of masses of SnCl₂ and SnCl₄ after electrolysis.

Sol. Cathode: $\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$; Anode: $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$

Since 0.119 g of Sn is deposited at cathode then 0.119 g of Sn^{4+} must have formed at anode (see the electrode reactions). So, a total of 2×0.119 g of Sn^{2+} are lost from the solution.

$$\begin{aligned}\text{Mass of remaining } \text{SnCl}_2 &= 19 \text{ g} - \frac{M_{\text{SnCl}_2}}{M_{\text{Sn}}} \times m_{\text{Sn}} \\ &= 19 - \frac{189.6}{119} \times 2 \times 0.119 = (19 - 0.379) = 18.621 \text{ g}\end{aligned}$$

$$\text{Mass of } \text{SnCl}_4 \text{ formed} = \frac{M_{\text{SnCl}_4}}{M_{\text{Sn}}} \times m_{\text{Sn}} = \frac{260.2}{119} \times 0.119 = 0.26 \text{ g}$$

$$\frac{m(\text{SnCl}_2)}{m(\text{SnCl}_4)} = \frac{18.621}{0.260} = \frac{71.62}{1}$$

- Q.25** How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8 hours at a current of 8.46 amperes. What is the area of the tray if the thickness of the silver plating is 0.00254 cm? The density of silver is 10.5 g/cm³.

$$\text{Sol. } m = \frac{It}{F} \cdot \frac{M}{z} = \frac{(8.46)(8 \times 60 \times 60)(107.8)}{(96500 \text{ C mol}^{-1})} = 272.18 \text{ g}$$

$$\text{Volume of silver plated out } V = \frac{m}{\rho} = \frac{272.18}{10.5} = 25.92 \text{ cm}^3$$

$$\text{Area of tray plated} = \frac{25.92}{0.00254} = 10204.7 \text{ cm}^2$$

- Q.26** One of the methods of preparation of per disulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $\text{H}_2\text{S}_2\text{O}_8$ formed?

Ans. 43.49g

Sol. Equivalent in oxidation process = Equivalent in reduction process

Equivalent of $[\text{H}_2\text{S}_2\text{O}_8 + \text{O}_2]$ = Equivalent of H_2

$$n_{\text{H}_2\text{S}_2\text{O}_8} \times 2 + \frac{2.35}{22.4} \times 4 = \frac{9.722}{22.4} \times 2$$

$$n_{\text{H}_2\text{S}_2\text{O}_8} \times 2 + 0.4196 = 0.868$$

$$n_{\text{H}_2\text{S}_2\text{O}_8} = 0.2242 \text{ mol}$$

$$\text{wt. of } \text{H}_2\text{S}_2\text{O}_8 = 0.2242 \times 194 = 43.49 \text{ gm}$$

- Q.27** A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the K^+ ion move in 2 hours at $25^\circ C$? Ionic conductance of K^+ ion at infinite dilution at $25^\circ C$ is $73.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

Ans. 3.29 cm

Sol. $\lambda = \mu F$

$$\mu = \frac{\text{velocity}}{\text{Potential gradient}} = \frac{\lambda}{F}$$

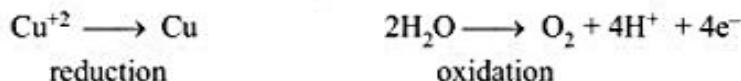
$$\frac{\text{distance} / 2 \times 3600}{6/10} = \frac{73.52}{96500}$$

$$\text{distance} = \frac{73.52}{96500} \times \frac{6}{10} \times 2 \times 3600 = 3.29 \text{ cm}$$

- Q.28** 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 the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

Ans. $V(O_2) = 99.68 \text{ mL}$, $V(H_2) = 58.49 \text{ mL}$, Total vol. = 158.17 mL

Sol. solution of Cu salt electrolysed



Initially Equivalent of Cu^{+2} = Equivalent of O_2

$$\frac{0.4}{63.5} \times 2 = n_{O_2} \times 4$$

$$n_{O_2} \text{ released at anode} = 3.14 \times 10^{-3}$$

charge transfer in next seven minutes

$$q = It = \frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$$

eq. of H_2 released

$$\text{due to further reduction} = 5.22 \times 10^{-3} \Rightarrow n_{H_2} = 2.61 \times 10^{-3}$$

eq. of O_2 released

$$\text{due to further oxidation} = 5.22 \times 10^{-3} \Rightarrow n_{O_2} = 1.3 \times 10^{-3}$$

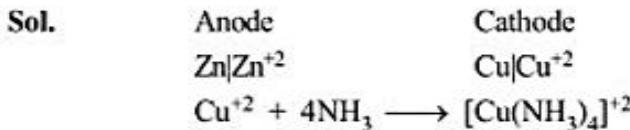
$$\begin{aligned} \text{Total volume of } H_2 \text{ released} &= 2.61 \times 10^{-3} \times 22.4 \times 100 \text{ ml} \\ &= 58.49 \text{ ml} \end{aligned}$$

$$\begin{aligned} \text{Total volume of } O_2 \text{ released} &= (3.14 \times 10^{-3} + 1.3 \times 10^{-3}) \times 22400 \text{ ml} \\ &= 99.68 \text{ ml} \end{aligned}$$

$$\text{Total volume } 58.49 + 99.68 = 158.17 \text{ mL}$$

- Q.29** Estimate the cell potential of a Daniel cell having 1 M Zn^{2+} & originally having 1 M Cu^{2+} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2 M.
 K_f for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, E^0 for the reaction,
 $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ is 1.1 V.

Ans. $E^0 = 0.610V$



Initially 1 M

finally x 2M 1M

$$1 \times 10^{12} = \frac{1}{x(2)^4}$$

$$x = 6.25 \times 10^{-14}$$

for reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$$\begin{aligned} E &= E^o - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \\ &= 1.1 - \frac{0.059}{2} \log \frac{1}{6.25 \times 10^{-14}} \\ &= 1.1 - (0.3895) = 0.610 V \end{aligned}$$

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