

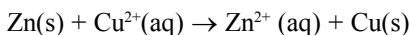
ELECTROCHEMISTRY

3.2 Galvanic Cell :

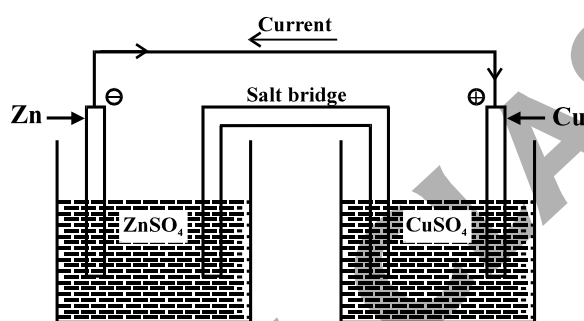
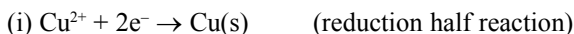
Q. What are galvanic cells ? Explain with example.

Solution : A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

For e.g., Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.



This reaction is a combination of two half reactions whose addition gives the overall cell reaction :



Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts

These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called half-cells or redox couples. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

Q. Define electrode potential ?

Solution : At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called electrode potential.

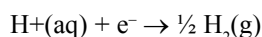
Q. What is Cell Potential ?

Solution : The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (emf) of the cell when no current is drawn through the cell.

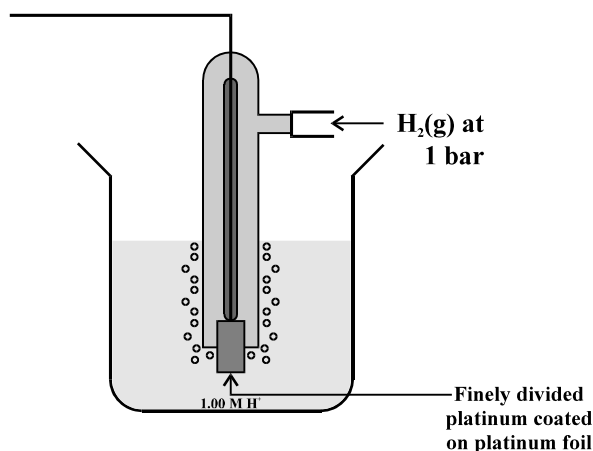
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Q. Explain standard hydrogen electrode with neat diagram.

Solution : A half-cell called standard hydrogen electrode represented by $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$, is assigned a zero potential at all temperatures corresponding to the reaction



The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity.



This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

Q. Why platinum or gold are used as electrodes.

Solution : Metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used in the following half-cells :

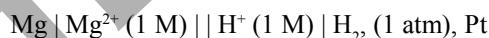
Hydrogen electrode : $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq})$

With half-cell reaction : $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2(\text{g})$

Bromine electrode : $\text{Pt(s)} \mid \text{Br}_2(\text{aq}) \mid \text{Br}^-(\text{aq})$

Q. How would you determine the standard electrode potential of the system $\text{Mg}^{2+} \mid \text{Mg}$?

Solution : A cell consisting of $\text{Mg} \mid \text{MgSO}_4 (1 \text{ M})$ as one electrode (by dipping a magnesium wire in 1 M MgSO_4 solution) and standard hydrogen electrode $\text{Pt, H}_2 (1 \text{ atm}) \mid \text{H}^+ (1 \text{ M})$ as the second electrode is set up and emf of the cell and the direction of deflection in voltmeter and noted. The direction of deflection shows that electrons flow from magnesium electrode to hydrogen electrode, i.e., oxidation takes place on magnesium electrode and reduction on hydrogen electrode. The cell may be represented as follows :



$$\text{or } E_{\text{cell}}^0 = E_{\text{H}^+ / \frac{1}{2}\text{H}_2}^0 - E_{\text{Mg}^{2+} / \text{Mg}}^0$$

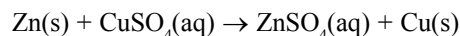
$$\text{Put } E_{\text{H}^+ / \frac{1}{2}\text{H}_2}^0 = 0$$

$$\text{Hence, } E_{\text{Mg}^{2+} / \text{Mg}}^0 = -E_{\text{cell}}^0$$

Q. Can you store copper sulphate solution in a zinc pot ?

Solution : $E_{\text{Zn}^{2+} / \text{Zn}}^0 = -0.76 \text{ V}$, $E_{\text{Cu}^{2+} / \text{Cu}}^0 = 0.34 \text{ V}$

To check whether zinc reacts with CuSO_4 solution, we shall see whether the following reaction takes place or not :



The cell may be represented as : $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

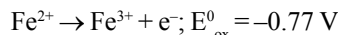
$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+} / \text{Cu}}^0 - E_{\text{Zn}^{2+} / \text{Zn}}^0 = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

As E_{cell}^0 is positive, the reaction takes place and we cannot store copper sulphate solution in zinc pot.

Q. Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous

ions under suitable conditions.

Solution : Oxidation of ferrous ions means the following reaction should occur :



Only those substances can oxidise Fe^{2+} to Fe^{3+} which are stronger oxidising agents and have positive reduction potentials greater than 0.77 V so that emf of the cell reaction is positive. Elements lying below $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the electrochemical series, e.g., Br_2 , Cl_2 and F_2 will satisfy this requirement.

3.3 Nernst Equation :

Q. Explain the Nernst equation.

Solution : Nernst showed that for the electrode reaction : $\text{Mn}^{+}(\text{aq}) + n\text{e}^{-} \rightarrow \text{M}(\text{s})$, the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by :

$$E_{(\text{M}^{n+}/\text{M})} = E_{(\text{M}^{n+}/\text{M})}^{\circ} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

but concentration of solid M is taken as unity.

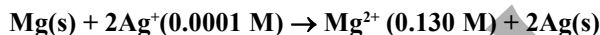
$E_{(\text{M}^{n+}/\text{M})}^{\circ}$ standard electrode potential, R is gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), F is Faraday constant (96487 C mol^{-1}), T is temperature in kelvin and $[\text{M}^{n+}]$ is the concentration of the species, M^{n+} .

Q. Write the Nernst equation for the following cell reaction $\text{Ni}(\text{s}) | \text{Ni}^{2+}(\text{aq}) || \text{Ag}^{+}(\text{aq}) | \text{Ag}(\text{s})$.

Solution : The cell reaction is $\text{Ni}(\text{s}) + 2\text{Ag}^{+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$. The Nernst equation can be written

$$\text{as } E_{(\text{cell})} = E_{(\text{cell})}^{\circ} - \frac{RT}{2F} \ln \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}.$$

Q. Represent the cell in which the following reaction takes place



Calculate its $E_{(\text{cell})}$ if $E_{(\text{cell})}^{\circ} = 3.17 \text{ V}$. [NCERT Solved Example 3.1]

Solution : 2.96 V

Q. What is the condition for equilibrium in a galvanic cell reaction. What is the relation between K_c and $E_{(\text{cell})}^{\circ}$?

$$\text{Solution : } E_{(\text{cell})} = 0, E_{(\text{cell})}^{\circ} = \frac{2.303RT}{nF} \log K_c.$$

Q. Calculate the equilibrium constant of the reaction :



$E_{(\text{cell})}^{\circ} = 0.46 \text{ V}$ [NCERT Solved Example 3.2]

Solution : $K_c = 3.92 \times 10^{15}$

Q. How is the electrical work is determined in a galvanic cell ?

Solution : Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_r G = -nFE_{(\text{cell})}$$

Q. Among $E_{(\text{cell})}$, $\Delta_r G$ which is intensive and extensive property.

Solution : It may be remembered that $E_{(\text{cell})}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n.

Q. What is relation between $\Delta_r G^{\circ}$ and K_c .

Solution : $\Delta_r G^{\circ} = -RT \ln K_c$.

Q. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the

reaction : $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$. [NCERT Solved Example 3.3]

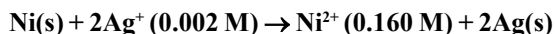
Solution : $-21.227 \text{ kJ mol}^{-1}$

Q. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

[NCERT Solved Example 3.4]

Solution : -0.591 V

Q. Calculate the emf of the cell in which the following reaction takes place :



Given that $E_{\text{cell}}^0 = 1.05 \text{ V}$

Solution : 0.91 V

Q. The cell in which the following reaction occurs :

$2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$ has $E_{\text{cell}}^0 = 0.236 \text{ V}$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Solution : $\Delta_r G^0 = -45.55 \text{ kJ mol}^{-1}$, $K_c = 9.616 \times 10^7$.

3.4 Conductance of Electrolytic Solutions :

Q. Give the relation between electrical resistance of any object with length l and area of cross-section A of object.

Solution : The electrical resistance of any object is directly proportional to its length l and inversely proportional to its area of cross section, A . That is,

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A}$$

The constant of proportionality, ρ (Greek, rho), is called resistivity (specific resistance). Its SI units are ohm metre (Ωm).

Q. Define resistivity.

Solution : The resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2 .

Q. Define conductance and give its SI units.

Solution : The inverse of resistance, R , is called conductance, G , and we have the relation :

$$G = \frac{1}{R} = \frac{A}{\rho l} = k \frac{A}{l}$$

The SI unit of conductance is siemens, represented by the symbol S and is equal to ohm^{-1} (also known as mho) or Ω^{-1} .

Q. Define conductivity along with its unit.

Solution : The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol, k (Greek, kappa). The SI units of conductivity are $S \text{ m}^{-1}$. Conductivity of a material in $S \text{ m}^{-1}$ is its conductance when it is 1 m long and its area of cross section is 1 m^2 .

Q. What are conductors, semiconductors, insulators and superconductors. Give examples also.

Solution : Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers are also electronically conducting. Substances like glass, ceramics, etc., having very low conductivity are known as insulators. Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called semiconductors and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.

Q. What is electrical conductance and on what factors it depends ?

Solution : Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on

- (i) the nature and structure of the metal
- (ii) the number of valence electrons per atom
- (iii) temperature (it decreases with increase of temperature)

Q. What is electrolytic or ionic conductance and on what factors it depends ?

Solution : Even very pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7}$ M) which lend it very low conductivity (3.5×10^{-5} S m^{-1}). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases. The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on :

- (i) the nature of the electrolyte added
- (ii) size of the ions produced and their solvation
- (iii) the nature of the solvent and its viscosity
- (iv) concentration of the electrolyte
- (v) temperature (it increases with the increase of temperature).

Q. Conductivity of different ions having different charge is different or same in same solvent.

Solution : The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient.

Q. What is the relation between molar conductivity Λ_m with conductivity (k) and C (mol m^{-3}) what are units of Λ_m .

Solution : Molar conductivity = $\Lambda_m = \frac{k}{C}$.

In the above equation, if k is expressed in S m^{-1} and the concentration, c in mol m^{-3} then the units of Λ_m are in S m^2 mol $^{-1}$.

Q. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω . If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω , calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m. [NCERT Solved Example 3.4]

Solution : 124 S cm^2 mol $^{-1}$

Q. The electrical resistance of a column of 0.005 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

[NCERT Solved Example 3.5]

Solution : 87.135 Ω cm, 0.01148 S cm^{-1} , 229.6 S cm^2 mol $^{-1}$.

Q. What is effect of dilution on conductivity of weak electrolyte and strong electrolyte ?

Solution : Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.

Q. Define molar conductivity.

Solution : Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and

distance of unit length. Therefore, $\Lambda_m = \frac{kA}{l} = k$.

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte) $\Lambda_m = kV$.

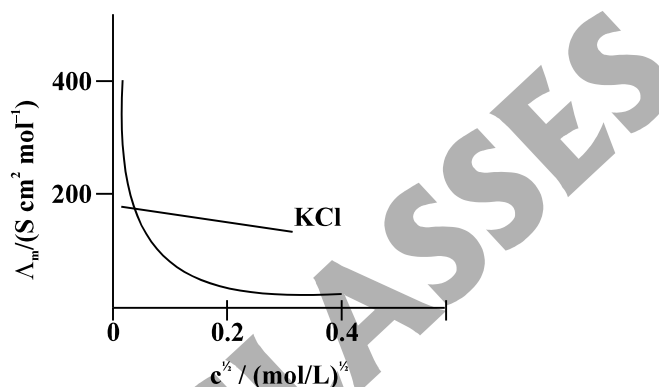
Q. What is the effect of increase of concentration on molar conductivity ?

Solution : Molar conductivity increases with decrease in concentration. For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation : $\Lambda_m = \Lambda_m^0 - Ac^{1/2}$.

It can be seen that if we plot Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal to Λ_m^0 and slope equal to $-A$. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution.

Q. Show graphically variation of molar conductivity with concentration for weak electrolyte and strong electrolyte.

Solution :



Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

Q. What is relation between Δ_m , Δ_m^0 and C (concentration) for strong electrolyte ?

Solution : $\Lambda_m = \Lambda_m^0 - Ac^{1/2}$

Q. The molar conductivity of KCl solutions at different concentrations at 298 K are given below :

$c/\text{mol L}^{-1}$	$\Lambda_m/\text{S cm}^2 \text{ mol}^{-1}$
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between Λ_m and $c^{1/2}$ is a straight line. Determine the values of Λ_m^0 and A for KCl. [NCERT Solved Example 3.6]

Solution : $\Lambda_m^0 = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$, $A = -\text{slope} = 87.46 \text{ S cm}^2 \text{ mol}^{-1} / (\text{mol/L}^{-1})^{1/2}$.

Q. Define Kohlrausch law of independent migration of ions.

Solution : The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if $\lambda_{\text{Na}^+}^0$ and $\lambda_{\text{Cl}^-}^0$ are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation : $\Lambda_{\text{m}(\text{NaCl})}^0 = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0$.

Q. What is effect of dilution on Δ_m .

Solution : Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte.

Q. Why Λ_m^0 cannot be calculated for weak electrolyte graphically.

Solution : In such cases Λ_m increases steeply on dilution, especially near lower concentrations. Therefore, Λ_m cannot be obtained by extrapolation of Λ_m to zero concentration. At infinite dilution (i.e., concentration $c \rightarrow$ zero) electrolyte dissociates completely ($\alpha = 1$), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore Λ_m^0 for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions.

Q. What is the relation between α , Λ_m^c and Λ_m^0 for weak electrolyte. Also write expression of k_a for acetic acid.

Solution : At any concentration c , if α is the degree of dissociation then it can be approximated to the ratio

of molar conductivity Λ_m at the concentration c to limiting molar conductivity, Λ_m^0 . Thus we have: $\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$.

But we know that for a weak electrolyte like acetic acid (Class XI, Unit 7),

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^0 \left(1 - \frac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^0 (\Lambda_m^0 - \Lambda_m)}$$

Q. Calculate Λ_m^0 for CaCl_2 and MgSO_4 ($\lambda_{\text{Ca}^{2+}}^0 = 119.0$, $\lambda_{\text{Cl}^-}^0 = 76.3$, $\lambda_{\text{Mg}^{2+}}^0 = 106.0$, $\lambda_{\text{SO}_4^{2-}}^0 = 160.0$)

[NCERT Solved Example 3.8]

Solution : 271.6 S cm² mol⁻¹, 266 S cm² mol⁻¹.

Q. Λ_m^0 for NaCl, HCl and NaAc are 126.4, 425.4, 425.9 and 91.0 S cm² mol⁻¹ respectively. Calculate Λ_m^0 for HAc. [NCERT Solved Example 3.8]

Solution : 390.5 S cm² mol⁻¹

Q. The conductivity of 0.001028 mol L⁻¹ acetic acid is 4.95×10^{-5} S cm⁻¹. Calculate its dissociation constant if Λ_m^0 for acetic acid is 390.5 S cm² mol⁻¹. [NCERT Solved Example 3.9]

Solution : 48.15 S cm³ mol⁻¹, 0.1233, 1.78×10^{-5} mol L⁻¹.

Q. Why does the conductivity of a solution decrease with dilution ?

Solution : Conductivity of a solution is the conductance of ions present in a unit volume of the solution. On dilution, the number of ions per unit volume decreases. Hence, the conductivity decreases.

Q. Suggest a way to determine the Λ_m^0 value of water.

Solution : $\Lambda_m^0(\text{H}_2\text{O}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaCl})$

Q. The molar conductivity of 0.025 mol L⁻¹ methanoic acid is 46.1 S cm² mol⁻¹. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(\text{H}^+) = 349.6$ S cm² mol⁻¹ and $\lambda^0(\text{HCOO}^-) = 54.6$ S cm² mol⁻¹.

Solution : 0.114

3.5 Electrolytic Cells and Electrolysis :

Q. What are electrolytic cells. Explain with example ?

Solution : In an electrolytic cell external source of voltage is used to bring about a chemical reaction. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction takes place : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$.

Copper metal is deposited on the cathode. At the anode, copper is converted into Cu^{2+} ions by the reaction : $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{s}) + 2\text{e}^-$.

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity.

Q. Define Faraday's laws of electrolysis.

Solution : (i) First Law : The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

(ii) Second Law : The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

Q. A solution of CuSO_4 is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

Solution : 0.2938 g

Q. Define Faraday.

Solution : We, know that charge on one electron is equal to $1.6021 \times 10^{-19}\text{C}$. Therefore, the charge on one mole of electrons is equal to :

$$N_A \times 1.6021 \times 10^{-19} \quad C = 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.6021 \times 10^{-19}$$

$$C = 96487 \text{ C mol}^{-1}$$

This quantity of electricity is called Faraday and is represented by the symbol F.

For approximate calculations we use $1F \cong 96500 \text{ C mol}^{-1}$.

Q. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire ?

Solution : 2.246×10^{22} electrons.

Q. Suggest a list of metals that are extracted electrolytically.

Solution : Sodium, Calcium and Aluminium

Q. Consider the reaction : $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

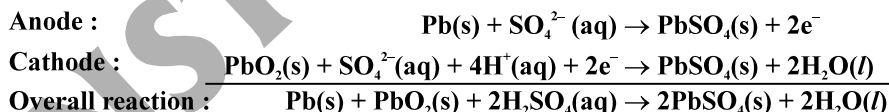
What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$?

Solution : 579000 C

3.6 Batteries :

Q. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Solution : A lead storage battery comprises anode of lead, cathode of a grid of lead packed with lead dioxide (PbO_2) and 38% solution of sulphuric acid as electrode. The following reactions take place in lead storage battery when it is working.



On charging the battery, the reverse reaction takes place, i.e., PbSO_4 deposited on the electrodes is converted back into Pb and PbO_2 and H_2SO_4 gets regenerated.

Q. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Solution : Methane, carbon monoxide and methanol.

Q. How does fuel cell operate ?

Solution : Chemical energy of fuel is converted into electrical energy.

Q. Which type of metal can be used in cathodic protection of iron against rusting ?

Solution : A metal which is more reactive (higher on the electrochemical series) than iron is used.

Q. How does cathodic protection of iron operate ?

Solution : More reactive metal acts as anode i.e., loses electrons. Thus, it prevents the oxidation of iron.

Q. Why does an alkaline medium inhibit the rusting of iron ?

Solution : Rusting takes place in a presence of H^+ . Alkali neutralises hydrogen ions.

Q. Name any two metals which can be used for cathodic protection of iron.

Solution : Zinc and magnesium.

Q. What is the function of platinised platinum in standard hydrogen electrode ?

Solution : 1. It acts as inert metal for electrical contact.

2. With platinised platinum, H_2 gas gets absorbed on the surface.

Q. What is primary cells ?

Solution : Cells which are not rechargeable are primary cells i.e., the products cannot be converted into reactants.

Q. Write the reactions taking place at positive and negative terminals in lead acid accumulator.

Solution : At anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

At cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + H_2O(l)$

Q. What are secondary cells ?

Solution : Cells which are rechargeable are called secondary cells i.e., products can be converted into reactants.

Q. Write electrode reactions taking place in Ni – Cd cell ? Is it primary or secondary cell ?

Solution : At anode : $Cd + 2OH^- \rightarrow CdO + H_2O + 2e^-$

At cathode : $Ni(OH)_3 + e^- \rightarrow Ni(OH)_2 + OH^-$

It is secondary cell.

Q. Define corrosion.

Solution : It is a process in which the metal reacts with substances present in air to form compounds on the surface. For example, $Fe_2O_3 \cdot xH_2O$ is formed at the surface of Fe.

Q. What is galvanisation ?

Solution : Coating zinc over iron is called galvanisation.

Q. What are fuel cells ? Write the electrode reactions of a fuel cell which uses the reaction of hydrogen with oxygen.

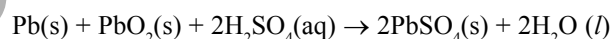
Solution : Those cells in which chemical energy of fuel is converted into electrical energy are called fuel cells.

Q. What are fuel cells ? How do they resemble and differ from galvanic cells ?

Solution : Fuel cells are those cells in which chemical energy of fuel is converted into electrical energy. In both cells, chemical energy is converted into electrical energy. The efficiency of fuel cell is higher than that of galvanic cell. Fuel cells are non-polluting.

Q. Write the cell reactions which occur in lead storage battery (i) when the battery is in use and (ii) when the battery is on charging.

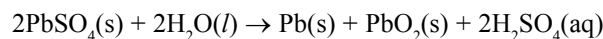
Solution : (i) When the battery is in use



At anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

At cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

(ii) When the battery is on charging



Q. Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for the cell.

Solution : It consists of zinc mercury amalgam as anode, a paste of HgO and carbon as cathode.

The electrolyte is paste of KOH and ZnO.

Electrode reactions are given as under :

At anode : $Zn(\text{amalgam}) + 2OH^- \rightarrow ZnO(s) + H_2O(l) + 2e^-$

At cathode : $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

Net reaction : $Zn(\text{amalgam}) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

Q. State two advantages of $H_2 - O_2$ fuel cell over ordinary cells.

- Solution :** (i) It does not create efficiency.
 (ii) It has much higher efficiency.

Q. What is corrosion ? Describe the role of zinc in cathodic protection of iron. Can we use tin in place of zinc for this purpose ? Give reason.

Solution : Corrosion is a process in which metal reacts with substances present in atmospheric to form compounds at its surface.

Role of Zinc.

Zn acts as anode. It loses electrons in preference to iron because it is more reactive than Fe.



If any Fe^{2+} ions are formed, they gain electrons to form iron back



Tin cannot be used to protect iron because it is less reactive than Fe.

Q. Draw a neat diagram of $\text{H}_2 - \text{O}_2$ fuel cell.

- (i) Indicate anode and cathode of the cell.
 (ii) What is the overall reaction taking place in the cell ?

NCERT EXERCISE

3.1 Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn.

3.2 Given the standard electrode potentials,

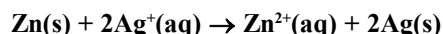
$$\text{K}^+/\text{K} = -2.93 \text{ V}, \text{Ag}^+/\text{Ag} = 0.80 \text{ V},$$

$$\text{Hg}^{2+}/\text{Hg} = 0.79 \text{ V},$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}, \text{Cr}^{3+}/\text{Cr} = -0.74 \text{ V}$$

Arrange these metals in their increasing order of reducing power.

3.3 Depict the galvanic cell in which the reaction :



takes place. Further, show :

- (i) Which of the electrodes is negatively charged ?
 (ii) The carriers of the current in the cell.
 (iii) Individual reaction at each electrode.
- 3.4 Calculate the standard cell potentials of galvanic cell in which the following reactions takes place :
- (i) $2\text{Cr(s)} + 3\text{Cd}^{2+}(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Cd}$
 (ii) $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag(s)}$

given $E_{\text{Cr}^{3+}, \text{Cr}}^0 = -0.74 \text{ V}, E_{\text{Cd}^{2+}, \text{Cd}}^0 = -0.04 \text{ V}, E_{\text{Ag}^+, \text{Ag}}^0 = 0.80 \text{ V}, E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 = 0.77 \text{ V}.$

Calculate the ΔG^0 and equilibrium constant of the reactions.

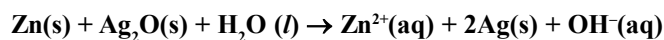
3.5 Write the Nerst equation and emf of the following cells at 298 K :

- (i) $\text{Mg (s)} \mid \text{Mg}^{2+} (0.001 \text{ M}) \parallel \text{Cu}^{2+} (0.0001 \text{ M}) \mid \text{Cu (s)}$
 (ii) $\text{Fe(s)} \mid \text{Fe}^{2+} (0.001 \text{ M}) \parallel \text{H}^+ (1 \text{ M}) \mid \text{H}_2(\text{g}) (1 \text{ bar}) \mid \text{Pt (s)}$
 (iii) $\text{Sn(s)} \mid \text{Sn}^{2+} (0.050 \text{ M}) \parallel \text{H}^+ (0.020 \text{ M}) \mid \text{H}_2(\text{g}) (1 \text{ bar}) \mid \text{Pt (s)}$
 (iv) $\text{Pt(s)} \mid \text{Br}_2(\text{l}) \mid \text{Br}^- (0.010 \text{ M}) \parallel \text{H}^+ (0.030 \text{ M}) \mid \text{H}_2(\text{g}) (1\text{bar}) \mid \text{Pt(s)}$

Given : $E_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.37 \text{ V}$, $E_{\text{Cu}^{2+},\text{Cu}}^0 = +0.34 \text{ V}$, $E_{\text{Fe}^{2+},\text{Fe}}^0 = -0.44 \text{ V}$,

$E_{\text{Sn}^{2+}/\text{Sn}}^0 = -0.14 \text{ V}$, $E_{\text{Br}_2,\text{Br}^-}^0 = +1.08 \text{ V}$

3.6 In the button cells widely used in watches and other devices, the following reaction takes place :



Determine E^0 and ΔG^0 for the reaction. $E_{\text{Zn}/\text{Zn}^{2+}}^0 = 0.76\text{V}$, $E_{\text{Ag}/\text{Ag}^+}^0 = -0.8\text{V}$

3.7 Define conductivity and molar conductivity for solution for an electrolyte. Discuss their variation with concentration.

3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity.

3.9 The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 15000Ω . What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$.

3.10 The conductivity of sodium chloride at 298 K has been determined at different concentrations and the result are given below :

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa/\text{S m}^{-1}$	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{1/2}$. Find the value of Λ_m^0 .

3.11 Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m^∞ for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant ?

3.12 How much charge is required for the following reductions :

- (i) 1 mol of Al^{3+} to Al ?
 (ii) 1 mol of Cu^{2+} to Cu ?
 (iii) 1 mol of MnO_4^- to Mn^{2+} ?

3.13 How much electricity in terms of Faraday is required to produce

- (i) 20.0 g of Ca from molten CaCl_2 ?
 (ii) 40.0 g of Al from molten Al_2O_3 ?

[At. Wt. Ca = 40, Al = 27]

3.14 How much electricity is required in coulomb for the oxidation of

- (a) 1 mol of H_2O to O_2 ?
 (b) 1 mol of FeO to Fe_2O_3 ?

3.15 A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 0.5 ampere for 20 minutes. What mass of Ni is deposited at the cathode ?

3.16 Three electrolytic cells A, B, C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 1.50 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow ? What mass of copper and zinc were deposited ?

[At. wt. Cu = 63.5, Zn = 65.3, Ag = 108]

3.17 Using the standard electrode potentials, predict if the reaction between the following is feasible :

- (a) $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^{-}(\text{aq})$ (b) $\text{Ag}^{+}(\text{aq})$ and $\text{Cu}(\text{s})$
 (c) $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^{-}(\text{aq})$ (d) $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$
 (e) $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$

Given standard electrode potentials :

$$E_{1/2\text{I}_2, \text{I}^{-}}^0 = 0.541 \text{ V}, \quad E_{\text{Cu}^{2+}, \text{Cu}}^0 = 0.34 \text{ V}$$

$$E_{1/2\text{Br}_2, \text{Br}^{-}}^0 = 1.09 \text{ V}, \quad E_{\text{Ag}^{+}, \text{Ag}}^0 = 0.80 \text{ V}$$

$$E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 = 0.77 \text{ V}$$

3.18 Predict the products of electrolysis in each of the following :

- (i) An aqueous solution of AgNO_3 with silver electrodes
 (ii) An aqueous solution of AgNO_3 with platinum electrodes
 (iii) A dilute solution of H_2SO_4 with platinum electrodes
 (iv) An aqueous solution of CuCl_2 with platinum electrodes

ANSWERS

3.1 Mg, Al, Zn, Fe, Cu, Ag

3.2 $\text{Ag} < \text{Hg} < \text{Cr} < \text{Mg} < \text{K}$

3.4 3.192×10^{34} , $-2.895 \text{ kJ mol}^{-1}$, 3.22

3.5 (i) 2.68 V (ii) 0.523 V (iii) 0.078 V (iv) -1.288 V

3.6 $+1.56 \text{ V}$, $-301.080 \text{ kJ mol}^{-1}$

3.8 $124 \text{ S cm}^2 \text{ mol}^{-1}$

3.9 0.219 cm^{-1}

3.11 1.86×10^{-5}

3.12 (i) 3F (ii) 2F (iii) 5F

3.13 (i) 1 F (ii) 4.44 F

3.14 (i) 2 F (ii) 1 F

3.15 1.825 g of Ni

3.16 863.7 s, 0.426 g Cu, 0.438 g Zn

ADDITIONAL QUESTIONS AND PROBLEMS

- Q. Explain why electrolysis of aqueous solution of NaCl gives H₂ at cathode and Cl₂ at anode. Write overall reaction.

[Given $E^0_{\text{Na}^+/\text{Na}} = -2.71\text{V}$; $E^0_{\text{Cl}_2/2\text{Cl}^-} = 1.36\text{V}$ and $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}(\text{l})$; $E^0 = 1.23\text{V}$].

- Q. Calculate the cell emf and ΔG for the cell reaction at 25°C for the cell



E^0 values at 25°C :

$$E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V} \text{ and } E^0_{\text{Cd}^{2+}/\text{Cd}} = -0.403\text{V};$$

$$F = 96,500\text{ C}, R = 8.314\text{ JK}^{-1}\text{ mol}^{-1}.$$

- Q. Calculate the standard electrode potential of Ni²⁺ | Ni electrode if the cell potential of the cell Ni | Ni²⁺ (0.01 M) || Cu²⁺ (0.1 M) | Cu is 0.59 V at 25°C.

[Given $E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$].

- Q. Blue colour of copper sulphate solution is slowly discharged (disappears) when an iron rod is dipped into it. Explain this by calculating ΔG^0 with the help of the following data :

$$[E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}; E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V} \text{ and } 1\text{ F} = 96500\text{ C mol}^{-1}]$$

- Q. (a) Calculate the electrode potential of silver electrode dipped in a 0.1 M solution of silver nitrate at 298 K assuming silver nitrate to be completely dissociated. The standard electrode potential of Ag⁺/Ag is 0.80 V at 298 K.

(b) At what concentration of silver ions will this electrode have a potential of zero volt ?

- Q. The emf of the cell

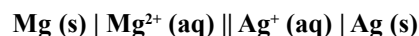


has been found to be 0.3305 V at 298 K. Calculate the value of M₁.

$$\text{Given : } E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}, E^0_{\text{Cd}^{2+}/\text{Cd}} = -0.40\text{V}.$$

- Q. Why does the molar conductance increase on diluting the solution of a weak electrolyte ? Electrolytic conductivity of 0.30 M solution of KCl at 298 K is $3.72 \times 10^{-2}\text{ S cm}^{-1}$. Calculate its molar conductivity.

- Q. (a) State the factors that influence the value of cell potential of the following cell :



(b) Write Nernst equation to calculate the cell potential of the above cell.

- Q. (i) Account for the following :

(a) Alkaline medium inhibits the rusting of iron.

(b) Iron does not rust even if the zinc coating is broken in a galvanised iron pipe.

(ii) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, $E^0 = +0.34\text{V}$

$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$, $E^0 = +0.80\text{V}$

(a) Construct a galvanic cell using the above data.

(b) For what concentration of Ag⁺ ions will the emf of the cell be at 25°C, if the concentration of Cu²⁺ is 0.01 M ?