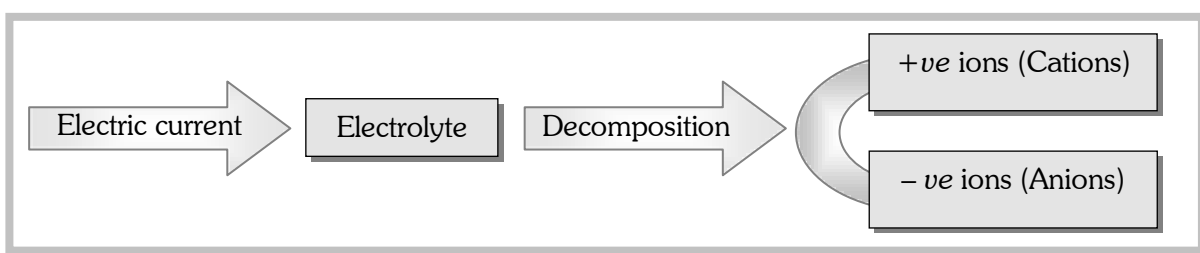


Electrochemistry

Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions i.e., how chemical energy produced in a redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous. Chemical changes involving production or consumption of electricity are called electrochemical changes.

Electrolytes and Electrolysis.

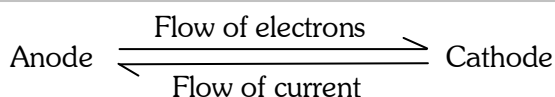
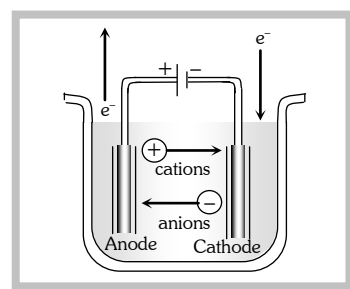
(1) **Definition** : “The substances whose aqueous solution undergo decomposition into ions when electric current is passed through them are known as **electrolytes** and the whole process is known as **electrolysis** or **electrolytic decomposition**.”



Solutions of acids, bases, salts in water and fused salts etc. are the examples of electrolytes. Electrolytes may be **weak** or **strong**. Solutions of cane sugar, glycerine, alcohol etc., are examples of **non-electrolytes**.

(2) **Electrolytic cell or Voltameter** : The device in which the process of electrolysis or electrolytic decomposition is carried out is known as **electrolytic cell** or **voltameter**. Following are the important characteristics of voltameter,

- (i) Voltameter consist of a vessel, two electrodes and electrolytic solution.
- (ii) Voltameter convert **electrical energy into chemical energy** i.e., electrical energy is supplied to the electrolytic solution to bring about the redox reaction (i.e., electrolysis) which is **non-spontaneous** and takes place only when electrical energy is supplied.
- (iii) In voltameter, both the electrodes are suspended in only one of the electrolytic solution or melt of the electrolyte in the same vessel.
- (iv) The electrodes taken in voltameter may be of the same or different materials.
- (v) The electrode on which oxidation takes place is called **anode** (or +ve pole) and the electrode on which reduction takes place is called **cathode** (or -ve pole)
- (vi) During electrolysis in voltameter **cations are discharged on cathode** and **anions on anode**.
- (vii) In voltameter, outside the **electrolyte** electrons flow from **anode to cathode** and **current** flow from **cathode to anode**.
- (viii) For voltameter, $E_{\text{cell}} = -ve$ and $\Delta G = +ve$.



(3) Mechanism of electrolysis

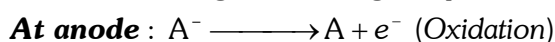
(i) The net chemical change that takes place in the cell is called the **cell reaction**, which is non-spontaneous in case of electrolytic cell.

Electrochemistry

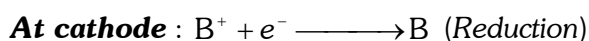
(ii) The mechanism of electrolysis can be easily explained on the basis of **ionisation theory** according to which, the electrolytes are present in the form of ions in solution and the function of electricity is only to direct these ions to their respective electrodes.

(iii) During electrolysis cations move towards the cathode (*-vely* charged) while anions move towards the anode (*+vely* charged).

(iv) The anions on reaching the anode give up their electrons and converted into the neutral atoms.



On the other hand cations on reaching the cathode take up electrons supplied by battery and converted to the neutral atoms.



This overall change is known as **primary change** and products formed is known as **primary products**.

(v) The primary products may be collected as such or they undergo further change to form molecules or compounds. These are called **secondary products** and the change is known as **secondary change**.

(vi) The products of electrolysis depend upon,

- Nature of electrolyte,
- Concentration of electrolyte,
- Charge density flown during electrolysis,
- Nature of electrodes used,

• Electrodes which do not take part in chemical change involved in a cell are known as **Inert electrode**. eg. Graphite, Platinum.

• Electrodes which take part in chemical change involved in a cell known as **active electrode**. eg. Hg, Au, Cu, Fe, Zn and Ni electrode etc.

(e) **Over voltage** : For metal ions to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the *standard electrode potential* (E^0). This extra voltage required is called **over voltage or bubble voltage**.

(vii) The deposition of different ions at the electrodes takes place only for the time of electricity is passed and stops as soon as electricity is switched off.

Note : * The electrolyte as a whole remains neutral during the process of electrolysis as equal number of charges are neutralised at the electrodes.

* If the cathode is pulled out from the electrolytic solution of the cell then there will be no passage of current and ions will show simply diffusion and state moving randomly.

* If electrode is active at cathode, metal goes on depositing on cathode and at anode metal is dissolved.

(4) Preferential discharge theory

(i) According to this theory "If more than one type of ion is attracted towards a particular electrode, then the ion is discharged one which requires least energy or ions with lower discharge potential or which occur low in the electrochemical series".

(ii) The potential at which the ion is discharged or deposited on the appropriate electrode is termed the **discharge or deposition potential**, (D.P.). The values of discharge potential are different for different ions.

(iii) The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below,

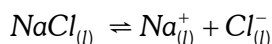
For cations : $Li^{+}, K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, H^{+}, Cu^{2+}, Hg^{2+}, Ag^{+}, Au^{3+}$.

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For anions : $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$.

(5) **Electrolysis and electrode processes :** The chemical reactions which take place at the surface of electrode are called **electrode reactions or electrode processes**. Various types of electrode reactions are described below,

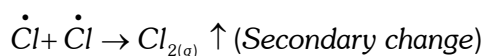
(i) **Electrolysis of molten sodium chloride :** Molten sodium chloride contains Na^+ and Cl^- ions.



On passing electricity, Na^+ ions move towards cathode while Cl^- ions move towards anode. On reaching cathode and anode following reactions occur.

At cathode : $Na_{(l)}^+ + e^- \rightarrow Na_{(l)} \downarrow$ (Reduction, primary change)

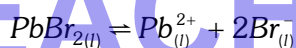
At anode : $Cl_{(l)}^- - e^- \rightarrow \dot{Cl}$ (Oxidation, primary change)



Overall reaction : $2Na_{(l)}^+ + 2Cl_{(l)}^- \xrightarrow{\text{Electrolysis}} 2Na_{(l)} + Cl_{2(g)}$

The sodium obtained at the cathode is in the molten state.

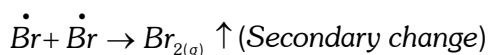
(ii) **Electrolysis of molten lead bromide :** Molten lead bromide contains Pb^{2+} and Br^- ions.



On passing electricity, Pb^{2+} ions move towards cathode while Br^- ions move towards anode. On reaching cathode and anode following reactions occur,

At cathode : $Pb_{(l)}^{2+} + 2e^- \rightarrow Pb_{(l)} \downarrow$ (Reduction, primary change)

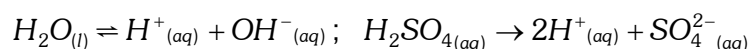
At anode : $Br_{(l)}^- - e^- \rightarrow \dot{Br}$ (Oxidation, primary change)



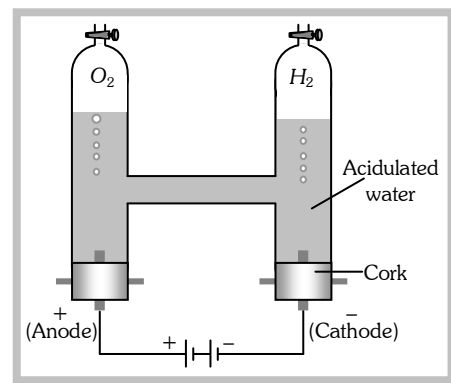
Overall reaction : $Pb_{(l)}^{2+} + 2Br_{(l)}^- \xrightarrow{\text{Electrolysis}} Pb_{(l)} + Br_{2(g)}$

The lead obtained at the cathode is in the molten state.

(iii) **Electrolysis of water :** Water is only weakly ionized so it is bad conductor of electricity but the presence of an acid (H_2SO_4) increases the degree of ionization of water. Thus, in solution, we have three ions, i.e., H^+ , OH^- and SO_4^{2-} produced as follows,



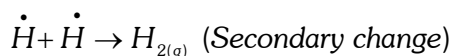
When electric current is passed through acidified water, H^+ ions move towards cathode, OH^- and SO_4^{2-} ions move towards anode. Now since the discharge potential of OH^- ions is much lower than that of SO_4^{2-} ions,



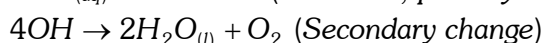
Electrochemistry

therefore, OH^- ions are discharged at anode while SO_4^{2-} ions remain in solution. Similarly, H^+ ions are discharged at the cathode. The reactions, occurring at the two electrodes may be written as follows,

At cathode : $\text{H}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{H}$. (Reduction, primary change)

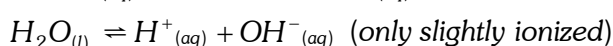
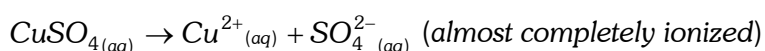


At anode : $\text{OH}^-_{(\text{aq})} + \text{e}^- \rightarrow \text{OH}$ (Oxidation, primary change)



Overall reaction : $4\text{H}^+_{(\text{aq})} + 4\text{OH}^-_{(\text{aq})} \rightarrow 2\text{H}_{2(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} + \text{O}_{2(\text{g})}$.

(iv) **Electrolysis of aqueous copper sulphate solution using inert electrodes :** Copper sulphate and water ionize as under,



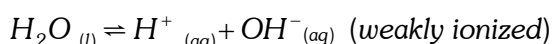
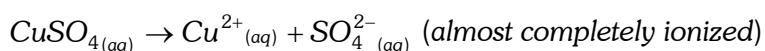
On passing electricity, $\text{Cu}^{2+}_{(\text{aq})}$ and $\text{H}^+_{(\text{aq})}$ move towards the cathode while SO_4^{2-} ions and OH^- ions move towards the anode. Now since the discharge potential of Cu^{2+} ions is lower than that of H^+ ions, therefore, Cu^{2+} ions are discharged at cathode. Similarly, OH^- ions are discharged at the anode. the reactions, occurring at the two electrodes may be written as follows,

At cathode : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (Reduction, primary change)

At anode : $4\text{OH}^- - 4\text{e}^- \rightarrow 4\text{OH}$ (Oxidation, primary change)



(v) **Electrolysis of an aqueous solution of copper sulphate using copper electrode :** Copper sulphate and water ionize as under:



On passing electricity, Cu^{2+} and H^+ move towards cathode while OH^- and SO_4^{2-} ions move towards anode. Now since the discharge potential of Cu^{2+} ions is lower than that of H^+ ions, therefore, Cu^{2+} ions are discharged in preference to H^+ ions at cathode. **Unlike electrolysis of CuSO_4 using platinum electrodes**, no ions are liberated here, instead, anode itself undergoes oxidation (i.e., loses electrons) to form Cu^{2+} ions which go into the solution. This is due to the reason that Cu is more easily oxidised than both OH^- and SO_4^{2-} ions. The reactions, occurring at the two electrodes may be written as follows,

At cathode : $\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Cu}_{(\text{s})}$ (Reduction, primary change).

At anode : $\text{Cu}_{(\text{s})} \rightarrow \text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^-$ (Oxidation, primary change).

Products of electrolysis of some electrolytes

Electrolyte	Electrode	Product at cathode	Product at anode
Aqueous NaOH	Pt or Graphite	H_2	O_2
Fused NaOH	Pt or Graphite	Na	O_2
Aqueous NaCl	Pt or Graphite	H_2	Cl_2
Fused NaCl	Pt or Graphite	Na	Cl_2
Aqueous CuCl_2	Pt or Graphite	Cu	Cl_2
Aqueous CuCl_2	Cu electrode	Cu	Cu oxidised to Cu^{2+} ions
Aqueous CuSO_4	Pt or Graphite	Cu	O_2

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Aqueous CuSO_4	Cu electrode	Cu	Cu oxidised to Cu^{2+} ions
Dilute H_2SO_4	Pt electrode	H_2	O_2
Conc. H_2SO_4	Pt electrode	H_2	Peroxodisulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$)
Aqueous AgNO_3	Pt electrode	Ag	O_2
Aqueous AgNO_3	Ag electrode	Ag	Ag oxidised to Ag^+ ions
Acidified water	Pt electrode	H_2	O_2
Fused PbBr_2	Pt electrode	Pb	Br_2

Note : ✱ Alkali metals, alkaline earth metals and other metals having E^0 lower than hydrogen can not be obtained during electrolysis of their aqueous salt solutions because of their strong electropositive nature.

✱ The electrolysis of aqueous solution of electrolytes is some what more complex because of the ability of water to be oxidised as well as reduced.

(6) Application of electrolysis: Electrolysis has wide applications in industries. Some of the important applications are, as follows,

(i) Production of hydrogen by electrolysis of water.

(ii) Manufacture of heavy water (D_2O).

(iii) **Electrometallurgy :** The metals like Na , K , Mg , Al , etc., are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$\text{NaCl} + \text{CaCl}_2 + \text{KF}$	Na
$\text{CaCl}_2 + \text{CaF}_2$	Ca
$\text{Al}_2\text{O}_3 + \text{cryolite}$	Al
$\text{MgCl}_2 + \text{NaCl} + \text{CaCl}_2$	Mg
NaOH	Na
$\text{KCl} + \text{CaCl}_2$	K

(iv) **Manufacture of non-metals :** Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(v) **Electro-refining of metals :** It involves the deposition of pure metal at cathode from a solution containing the metal ions. Ag , Cu etc. are refined by this method.

(vi) **Electrosynthesis :** This method is used to producing substances through non-spontaneous reactions carried out by electrolysis. Compounds like NaOH , KOH , Na_2CO_3 , KClO_3 , white lead, KMnO_4 etc. are synthesised by this method.

(vii) **Electroplating :** The process of coating an inferior metal with a superior metal by electrolysis is known as *electroplating*. The aim of electroplating is, to prevent the inferior metal from corrosion and to make it more attractive in appearance. The object to be plated is made the cathode of an electrolytic cell that contains a solution of ions of the metal to be deposited.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$\text{CuSO}_4 + \text{dilute } \text{H}_2\text{SO}_4$
With silver	Ag	Object	$\text{K}[\text{Ag}(\text{CN})_2]$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$\text{K}[\text{Au}(\text{CN})_2]$

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With zinc	Zn	Iron objects	ZnSO ₄
With tin	Sn	Iron objects	SnSO ₄

Thickness of coated layer : Let the dimensions of metal sheet to be coated be ($a \text{ cm} \times b \text{ cm}$).

Thickness of coated layer = $c \text{ cm}$

Volume of coated layer = $(a \times b \times c) \text{ cm}^3$

Mass of the deposited substance = Volume \times density = $(a \times b \times c) \times d \text{ g}$

$$\therefore (a \times b \times c) \times d = \frac{I \times t \times E}{96500}$$

Using above relation we may calculate the thickness of coated layer.

Note : Sometimes radius of deposited metal atom is given instead of density.

For example, radius of silver atom = 10^{-8} cm ; Atomic mass of Ag = 108

$$\text{Mass of single silver atom} = \frac{108}{6.023 \times 10^{23}} \text{ g}$$

$$\text{Volume of single atom} = \frac{4}{3} \times \pi R^3 = \frac{4}{3} \times 3.14 \times (10^{-8})^3 \text{ cm}^3$$

$$\text{Density of Ag} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}} = \frac{108 / 6.023 \times 10^{23}}{\frac{4}{3} \times 3.14 \times (10^{-8})^3} = 42.82 \text{ g / cm}^3$$

Faraday's laws of electrolysis.

The laws which govern the deposition of substances (In the form of ions) on electrodes during the process of electrolysis is called **Faraday's laws of electrolysis**. These laws given by **Michael Faraday in 1833**.

(1) Faraday's first law : It states that,

"The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

$$\text{i.e., } W \propto Q$$

Where, W = Mass of ions liberated in gm,

Q = Quantity of electricity passed in Coulombs = Current in Amperes (I) \times Time in second (t)

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

In case current efficiency (η) is given, then

$$W = Z \times I \times t \times \frac{\eta}{100}$$

where, Z = constant, known as **electrochemical equivalent** (ECE) of the ion deposited.

When a current of 1 Ampere is passed for 1 second (i.e., $Q = 1$), then, $W = Z$

Thus, **electrochemical equivalent** (ECE) may be defined as "the mass of the ion deposited by passing a current of one Ampere for one second (i.e., by passing Coulomb of electricity)". Its unit is gram per Coulomb. The ECE values of some common elements are,

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Element	Hydrogen	Oxygen	Copper	Silver	Iodine	Mercury
$Z, g\ C^{-1}$	1.045×10^{-5}	8.29×10^{-5}	3.294×10^{-4}	1.18×10^{-3}	1.315×10^{-3}	1.039×10^{-3}

Note : * Coulomb is the smallest unit of electricity.

* 96500 Coulombs = 6.023×10^{23} electrons.

* 1 Coulomb = $\frac{6.023 \times 10^{23}}{96500} = 6.28 \times 10^{18}$ electrons, or 1 electronic charge = 1.6×10^{-19} Coulomb.

(2) Faraday's second law : It states that,

“When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights).” i.e.,

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \quad \text{or} \quad \frac{Z_1 It}{Z_2 It} = \frac{E_1}{E_2} \quad \text{or} \quad \frac{Z_1}{Z_2} = \frac{E_1}{E_2} \quad (\because W = Zit)$$

Thus the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight (E), i.e.,

$$E \propto Z \quad \text{or} \quad E = FZ \quad \text{or} \quad E = 96500 \times Z$$

where, F = Faraday constant = $96500\ C\ mol^{-1}$

So, 1 Faraday = $1F$ = Electrical charge carried out by one mole of electrons.

$1F$ = Charge on an electron \times Avogadro's number.

$1F = e^- \times N = (1.602 \times 10^{-19}\ C) \times (6.023 \times 10^{23}\ mol^{-1})$.

Number of Faraday = $\frac{\text{Number of electrons passed}}{6.023 \times 10^{23}}$

(3) Faraday's law for gaseous electrolytic product : For the gases, we use

$$V = \frac{It V_e}{96500}$$

where, V = Volume of gas evolved at S.T.P. at an electrode

V_e = Equivalent volume = Volume of gas evolved at an electrode at S.T.P. by 1 Faraday charge

Examples : (a) O_2 : $M = 32, E = 8$; $32\ g\ O_2 \equiv 22.4\ L$ at S.T.P. [M = Molecular mass, E = Equivalent mass]

$8\ g\ O_2 \equiv 5.6\ L$ at S.T.P.; Thus V_e of $O_2 = 5.6\ L$.

(b) H_2 : $M = 2, E = 1$; $2\ g\ H_2 \equiv 22.4\ L$ at S.T.P.

$1\ g\ H_2 \equiv 11.2\ L$ at S.T.P.

Thus V_e of $H_2 = 11.2\ L$.

(c) Cl_2 : $M = 71, E = 35.5$; $71\ g\ Cl_2 \equiv 22.4\ L$ at S.T.P.

$35.5\ g\ Cl_2 \equiv 11.2\ L$ at S.T.P.

Thus V_e of $Cl_2 = 11.2\ L$.

(4) Quantitative aspects of electrolysis : We know that, one Faraday ($1F$) of electricity is equal to the charge carried by one mole (6.023×10^{23}) of electrons. So, in any reaction, if one mole of electrons are involved, then that reaction would consume or produce $1F$ of electricity. Since $1F$ is equal to 96,500 Coulombs, hence 96,500 Coulombs of electricity would cause a reaction involving one mole of electrons.

If in any reaction, n moles of electrons are involved, then the total electricity (Q) involved in the reaction is given by, $Q = nF = n \times 96,500\ C$

Thus, the amount of electricity involved in any reaction is related to,

- The number of moles of electrons involved in the reaction,
- The amount of any substance involved in the reaction.

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Therefore, 1 Faraday or 96,500 C or 1 mole of electrons will reduce,

- (a) 1 mole of monovalent cation, (b) $\frac{1}{2}$ mole of divalent cation,
 (c) $\frac{1}{3}$ mole of trivalent cation, (d) $\frac{1}{n}$ mole of n valent cations.

Example : 1 By passing 0.1 Faraday of electricity through fused sodium chloride, the amount of chlorine liberated is [Tamil Nadu CET 2002]

- (a) 35.45 g (b) 70.9 g (c) 3.55 g (d) 17.77 g

Solution: (c) $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ i.e., 1Faraday liberate $Cl_2 = \frac{1}{2} \text{ mol} = \frac{1}{2} \times 71 = 35.5$ (\therefore wt. of $Cl = 35.5$)
 \therefore 0.1Faraday will liberate $Cl_2 = 35.5 \times 0.1 = 3.55 \text{ g}$.

Example : 2 Silver is monovalent and has atomic mass of 108. Copper is divalent and has an atomic mass of 63.6. The same electric current is passed for the same length of time through a silver coulometer and a copper coulometer. If 27.0 g of silver is deposited, then the corresponding amount of copper deposited is [Kerala CEE 2002]

- (a) 63.60 g (b) 31.80 g (c) 15.90 g (d) 7.95 g

Solution: (d) $\frac{\text{Wt. of Cu deposited}}{\text{Wt. of Ag deposited}} = \frac{\text{Eq. Wt. of Cu}}{\text{Eq. Wt. of Ag}}; \frac{\text{Wt. of Cu deposited}}{27.0 \text{ g}} = \frac{63.6/2}{108}$
 $\text{Wt. of Cu deposited} = \frac{63.6/2}{108} \times 27.0 \text{ g} = 7.95 \text{ g}$.

Example : 3 How much charge must be supplied to a cell for the electrolytic production of 245 g $NaClO_4$ from $NaClO_3$? Because of a side reaction, the anode efficiency for the desired reaction is 60%
 (a) $6.43 \times 10^5 \text{ C}$ (b) 6.67 F (c) $6.43 \times 10^6 \text{ C}$ (d) 66.67 F

Solution: (a,b) $ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$

$$\text{Eq. wt. of } NaClO_4 = \frac{23 + 35 + 64}{2} = 61.25$$

$$\text{No. of equivalents of } NaClO_4 = \frac{245}{61.25} = 4 \equiv 4.0 \text{ F}$$

The anode efficiency is 60%

$$\text{No. of Faradays} = \frac{4.0}{60} \times 100 = 6.67 \text{ F}$$

$$6.67 \text{ F} = 6.67 \times 9.65 \times 10^4 \text{ C} = 6.43 \times 10^5 \text{ C}.$$

Example : 4 When 9.65 Coulombs of electricity is passed through a solution of silver nitrate (At. wt. of Ag = 107.87 taking as 108) the amount of silver deposited is [EAMCET 1992]

- (a) 10.8 mg (b) 5.4 mg (c) 16.2 mg (d) 21.2 mg

Solution: (a) $W = \frac{E \text{lt}}{96500} = \frac{108 \times 9.65}{96500} = 0.0108 \text{ g} = 10.8 \text{ mg}$.

Example : 5 Three faradays of electricity are passed through molten Al_2O_3 , aqueous solution of $CuSO_4$ and molten $NaCl$ taken in different electrolytic cells. The amount of Al Cu and Na deposited at the cathodes will be in the ratio of [BHU 1990]

- (a) 1mole : 2mole : 3mole (b) 3mole : 2mole : 1mole
 (c) 1mole : 1.5mole : 3mole (d) 1.5mole : 2mole : 3mole

Solution: (c) Eq. of Al = Eq. of Cu = Eq. of Na, or $\frac{1}{3}$ mole Al = $\frac{1}{2}$ mole Cu = 1 mole Na
 or 2 : 3 : 6 or 1 : 1.5 : 3 mole ratio.

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Example : 6 When electricity is passed through the solution of $AlCl_3$, 13.5 gm of Al are deposited. The number of Faraday must be [NCERT 1974; MP PET 1992; PM PMT 1994]

- (a) 0.50 (b) 1.00 (c) 1.50 (d) 2.00

Solution (c) Eq. of Al = $\frac{13.5}{27/3} = 1.5$; Thus 1.5 Faraday is needed.

Example : 7 A metal wire carries a current of 1 A. How many electrons move past a point in the wire in one second

- (a) 6.02×10^{23} (b) 3.12×10^{18} (c) 3.02×10^{23} (d) 6.24×10^{18}

Solution (d) Total charge passed in one second 'Q' = $I \times t = 1 \times 1 = 1C$

\therefore 96500 current carried by 6.02×10^{23} electrons

\therefore 1C current carried by $\frac{6.02 \times 10^{23}}{96500} = 6.24 \times 10^{18}$

Example : 8 How long will it take for a current of 3 Amperes to decompose 36 g of water? (Eq. wt. of hydrogen is 1 and that of oxygen 8) [BHU 1992]

- (a) 36 hours (b) 18 hours (c) 9 hours (d) 4.5 hours

Solution (a) Eq. wt. of $H_2O = 1 + 8 = 9$. Hence 9 g is decomposed by 96500 C. So 36 g of water will be decomposed by

$$Q = 96500 \times 4C$$

$$\text{Hence } t = \frac{Q}{I} = \frac{96500 \times 4}{3} S = 128666.66 \text{ sec.} = 35.7 \text{ hrs} \approx 36 \text{ hrs.}$$

Example : 9 Three Ampere current was passed through an aqueous solution of an unknown salt of metal M for 1 hour. 2.977 g of M^{n+} was deposited at cathode. The value of n is (At wt. of M = 106.4).

- (a) 1 (b) 2 (c) 3 (d) 4

Solution (d) $M^{n+} + ne^- \rightarrow M$; $\frac{W}{E} = \frac{I \times t}{96500} \Rightarrow \frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500}$ (1 hour = 60 × 60); $n = 4$.

Example : 10 Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. The total volume of the two gases (dry and S.T.P.) produced will be approximately (in litres) [AIIMS 1993]

- (a) 22.4 (b) 44.8 (c) 67.2 (d) 89.4

Solution (c) At cathode: $4H^+ + 4e^- \xrightarrow{(4F)} 2H_2$ or 2 × 22.4 litres at S.T.P.

At anode: $2O^{2-} \xrightarrow{(4F)} O_2 + 4e^-$ or 22.4 litres at S.T.P.

\therefore Total volume of the two gases produced at S.T.P. = $2 \times 22.4 + 22.4 = 67.2 \text{ litres}$

Example : 11 A current of 2 Amperes is passed through a litre of 0.100 molar solution of copper sulphate for 4825 seconds. The molarity of copper sulphate at the end of experiment is [ISM, Dhanbad 1995]

- (a) 0.075 (b) 0.050 (c) 0.025 (d) 0

Solution (b) $Cu^{2+} + 2e^- \rightarrow Cu$

$$Q = 2 \times 4825 = 9650 \text{ Coulombs}$$

\therefore 96500 Coulombs of electricity deposits 0.5 mole copper

$$\therefore 9650 C = \frac{0.5 \times 9650}{96500} = 0.05 \text{ mole of copper}$$

\therefore Molarity at the end of the experiment = $0.1 - 0.05 = 0.050$

Example : 12 2.5 Faradays of electricity is passed through a solution of $CuSO_4$. The number of gram equivalents of copper deposited on the cathode would be [DPMT 1982; CPMT 1973; MP PMT 2001]

- (a) 1 (b) 2 (c) 2.5 (d) 1.25

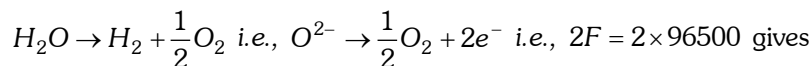
Solution (c) Number of Faraday passed = Number of equivalents deposited.

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Example : 13 How many c.c. of oxygen will be liberated by 2 Ampere current flowing for 193 seconds through acidified water [AFMC 1981]

- (a) 11.2 c.c. (b) 33.6 c.c. (c) 44.8 c.c. (d) 22.4 c.c.

Solution (d) $Q = I \times t = 2 \times 193 = 386 \text{ C}$



$$O_2 = \frac{1}{2} \text{ mole} = 11200 \text{ c.c.}$$

$$\therefore 386 \text{ c will give } O_2 = \frac{11200}{2 \times 96500} \times 386 = 22.4 \text{ c.c.}$$

Example : 14 How many Coulombs of electricity are required for reduction of 1 mole of MnO_4^- to Mn^{2+}

- (a) 96500 C (b) $1.93 \times 10^5 \text{ C}$ (c) $4.83 \times 10^5 \text{ C}$ (d) $9.65 \times 10^6 \text{ C}$

Solution (c) $(MnO_4)^- \rightarrow Mn^{2+} \text{ i.e., } Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

Thus 1 mole of MnO_4^- requires $5F = 5 \times 96500 \text{ C} = 482500 \approx 4.83 \times 10^5 \text{ C}$.

Example : 15 The quantity of electricity required to reduce 12.3 g of nitrobenzene to aniline assuming 50% current efficiency is

- (a) 115800 Coulombs (b) 57900 Coulombs (c) 231600 Coulombs (d) 28950 Coulombs

Solution (a) $C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 \text{ i.e., 1 mole (123 g) require } 6 \times 96500 \text{ C. Hence 12.3 g will require } = 6 \times 9650 \text{ C. As current efficiency is 50\%, quantity of electricity actually required} = 2 \times 6 \times 9650 = 115800 \text{ C.}$

Example : 16 A current of 3 ampere was passed for 2 hours through a solution of $CuSO_4$. 3g of Cu^{2+} ions were discharged at cathode. The current efficiency is (At. wt. of $Cu = 63.5$)

- (a) 20% (b) 42.2% (c) 60% (d) 80%

Solution (b) $W_{Cu^{2+}} = \frac{E \times I \times t}{96500}$

$$3 = \frac{63.5 \times I \times 2 \times 60 \times 60}{2 \times 96500}$$

$$I = 1.266 \text{ Ampere}$$

$$\text{Current efficiency} = \frac{\text{Current passed actually}}{\text{Total current passed experimentally}} \times 100 = \frac{1.266}{3} \times 100 = 42.2\%$$

Metallic and Electrolytic conductors.

(1) **Conductors and Non – conductors** : All substances do not conduct electrical current. The substances which allow the passage of electric current are called *conductors*. The best metal conductors are such as copper, silver, tin, etc. On the other hand, the substances which do not allow the passage of electric current through them are called **non-conductors or insulators**. Some common examples of insulators are rubber, wood, wax, etc.

(2) **Types of conductors** : The conductors are broadly classified into two types,

(i) **Metallic conductors or electronic conductors**

(a) In metallic conductors, flow of electricity takes place without the decomposition of the substances.

(b) Flow of electricity is due to the flow of electrons only i.e., there is no flow of matter.

(c) In addition to metals, **graphite** and certain minerals also conduct electricity due to presence of free electrons in them, hence they are collectively called as **electronic conductors**.

(d) Metallic conduction decreases with increase of temperature. This is because **kernel**s start vibrating which produce hinderance in the flow of electrons.

(e) The resistance offered by metals is also due to vibrating kernels.

(f) Metallic conductors obey Ohm's law.

(ii) **Electrolytic conductors or Ionic conductors**

(a) In electrolytic conductors flow of electricity takes place by the decomposition of the substance (Electrolyte).

(b) Flow of electricity is due to the movement of ions and hence there is flow of matter.

(c) Solutions of acids, bases and salts are the examples of electrolytic conductors.

(d) The electrolytic conduction will not occur unless the ions of the electrolyte are free to move. Therefore, these substances do not conduct electricity in the solid state but conduct electricity in the molten state or in their aqueous solutions.

(e) The electrical conduction increases with increase of temperature. This is generally due to increase in dissociation or decrease in the interionic attractions.

(f) The resistance shown by an electrolytic solution is due to factors like interionic attractions, viscosity of solvent etc.

(g) Electrolytic conductors also obey Ohm's law.

(h) All electrolytes do not ionise to the same extent in solution. On this basis, electrolytes are broadly divided into two types: strong electrolytes and weak electrolytes.

Strong electrolytes : The electrolytes which are almost completely dissociated into ions in solution are called strong electrolytes. For example, NaCl , KCl , HCl , NaOH , NH_4NO_3 , etc.

Weak electrolytes : The electrolytes which do not ionise completely in solution are called weak electrolytes. For example, CH_3COOH , H_2CO_3 , H_3BO_3 , HCN , HgCl_2 , ZnCl_2 , NH_4OH , etc. Thus in case of weak electrolytes, an equilibrium is established between the unionised electrolyte and the ions formed in solution. The extent of ionisation of a weak electrolyte is expressed in terms of degree of ionisation or degree of dissociation. It is defined as the fraction of total number of molecules of the electrolyte which ionise in the solution. It is generally denoted by alpha (α). For strong electrolytes, α is almost equal to 1 and for weak electrolytes, it is always less than 1.

The electrical conductivity of the solutions of electrolytes depends upon the following factors,

(a) **Interionic attractions :** These depend upon the interactions between the ions of the solute molecules, i.e., solute-solute interactions. If the solute-solute interactions are large, the extent of dissociation will be less. These interactions are also responsible for the classification of electrolytes as strong electrolytes and weak electrolytes.

(b) **Solvation of ions :** These depend upon the interactions between the ions of the solute and the molecules of the solvent and are called solute-solvent interactions. If the solute-solvent interactions are strong, the ions of the solute will be highly solvated and their electrical conductivity will be low.

(c) **Viscosity of the solvent:** The viscosity of the solvent depends upon the solvent-solvent interactions. Larger the solvent-solvent interactions, larger will be the viscosity of the solvent and lower will be the electrical conductivity of the ions.

13.4 Electrolytic conduction.

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution. The power of the electrolytes to conduct electric current is termed *conductance* or *conductivity*.

(1) **Ohm's law :** This law states that the current flowing through a conductor is directly proportional to the potential difference across it, i.e., $I \propto V$

where I is the current strength (In Amperes) and V is the potential difference applied across the conductor (In Volts)

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or $I = \frac{V}{R}$ or $V = IR$

where R is the constant of proportionality and is known as resistance of the conductor. It is expressed in Ohm's and is represented as Ω . The above equation is known as Ohm's law. Ohm's law may also be stated as,

"the strength of current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor."

(2) Resistance : It measures the obstruction to the flow of current. The resistance of any conductor is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) so that

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

where ρ (rho) is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material.

Units : The unit of resistance is ohm (Ω). In terms of SI, base unit is equal to $(kgm^2)/(s^3 A^2)$.

(3) Resistivity or specific resistance : We know that resistance R is

$$R = \rho \frac{l}{a}$$

Now, if $l = 1 \text{ cm}$, $a = 1 \text{ cm}^2$ then $R = \rho$

Thus, resistivity is defined as the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm^2 .

Units : The units of resistivity are $\rho = R \cdot \frac{a}{l} = \text{Ohm} \cdot \frac{\text{cm}^2}{\text{cm}} = \text{Ohm} \cdot \text{cm}$

Its SI units are Ohm metre (Ωm). But quite often Ohm centimetre (Ωcm) is also used.

(4) Conductance : It is a measure of the ease with which current flows through a conductor. It is an additive property. It is expressed as G . It is reciprocal of the resistance, i.e.,

$$G = \frac{1}{R}$$

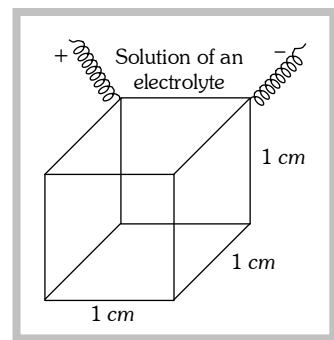
Units : The units of conductance are reciprocal Ohm (ohm^{-1}) or mho. Ohm is also abbreviated as Ω so that Ohm^{-1} may be written as Ω^{-1} .

According to SI system, the units of electrical conductance are Siemens, S (i.e., $1 \text{ S} = 1 \Omega^{-1}$).

(5) Conductivity : The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol, κ (Greek kappa). The IUPAC has recommended the use of term conductivity over specific conductance. It may be defined as, *the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section*. In other words, *conductivity is the conductance of one centimetre cube of a solution of an electrolyte*. Thus,

$$\kappa = \frac{1}{\rho}$$

Units : The units of conductivity are $\kappa = \frac{1}{\text{Ohm} \cdot \text{cm}} = \text{Ohm}^{-1} \text{ cm}^{-1}$ or $\Omega^{-1} \text{ cm}^{-1}$



In SI units, l is expressed in m area of cross-section in m^2 so that the units of conductivity are S m^{-1} .

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(6) Molar conductivity or molar conductance : Molar conductivity is defined as *the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.*

It is denoted by Λ (lambda). Molar conductance is related to specific conductance (κ) as,

$$\Lambda = \frac{\kappa}{M}$$

where, M is the molar concentration. If M is in the units of molarity i.e., moles per litre (mol L^{-1}), the Λ may be expressed as,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

For the solution containing 1 gm mole of electrolyte placed between two parallel electrodes of 1 sq. cm area of cross-section and one cm apart,

$$\text{Conductance}(G) = \text{Conductivity} = \text{Molar conductivity}(\Lambda)$$

But if solution contains 1 gm mole of the electrolyte therefore, the measured conductance will be the molar conductivity. Thus,

$$\text{Molar conductivity}(\Lambda) = 100 \times \text{Conductivity}$$

In other words, $(\Lambda) = \kappa \times V$

where V is the volume of the solution in cm^3 containing one gram mole of the electrolyte.

If M is the concentration of the solution in mole per litre, then

M mole of electrolyte is present in 1000 cm^3

1 mole of electrolyte is present in $= \frac{1000}{M} \text{ cm}^3$ of solution

Thus, $\Lambda = \kappa \times \text{Volume in } \text{cm}^3 \text{ containing 1 mole of electrolyte.}$

or
$$\Lambda = \frac{\kappa \times 1000}{M}$$

Units of Molar Conductance : The units of molar conductance can be derived from the formula ,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

The units of κ are S cm^{-1} and units of Λ are, $\square = \text{S cm}^{-1} \times \frac{\text{cm}^3}{\text{mol}} = \text{S cm}^2 \text{ mol}^{-1} = \text{S m}^2 \text{ mol}^{-1}$

According to SI system, molar conductance is expressed as $\text{S m}^2 \text{ mol}^{-1}$, if concentration is expressed as mol m^{-3} . This is because

$$\text{mol m}^{-3} = 1000 \left(\frac{\text{L}}{\text{m}^3} \right) \times \text{molarity} \left(\frac{\text{mol}}{\text{L}} \right)$$

$$\text{Now, } \Lambda = \frac{\kappa}{M} = \frac{\kappa (\text{S m}^{-1})}{(1000 \text{ L m}^{-3}) \times (\text{Molarity mol L}^{-1})} = \text{S m}^2 \text{ mol}^{-1}$$

Thus, the units of molar conductivity are $\text{S m}^2 \text{ mol}^{-1}$ (SI) and $\text{S cm}^2 \text{ mol}^{-1}$. Both types of units are used in literature and are related to each other as

$$1 \text{ S m}^2 \text{ mol}^{-1} = 10^4 \text{ S cm}^2 \text{ mol}^{-1} \text{ or } 1 \text{ S cm}^2 \text{ mol}^{-1} = 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

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(7) Equivalent conductivity : It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_e and is related to specific conductance as

$$\Lambda_e = \frac{\kappa \times 1000}{C} = \kappa \times \frac{1000}{M} \quad (M \text{ is Molarity of the solution})$$

where C is the concentration in gram equivalent per litre (or Normality). This term has earlier been quite frequently used. Now it is replaced by molar conductance. The units of equivalent conductance are $\text{Ohm}^{-1} \text{cm}^2 (\text{gmequiv})^{-1}$.

(8) Experimental measurement of conductance

(i) The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

We know that unknown resistance can be measured on a **Wheatstone bridge**. However, for measuring the resistance of an ionic solution, we face following two main difficulties,

(a) Direct current (DC) can not be passed because it may change the composition of the solution by electrolysis and polarization.

(b) A solution of unknown resistance can not be connected to the bridge like a metallic wire or other solid conductor.

First difficulty can be solved by passing an alternating current (AC) from ac source of power. The second difficulty can be solved by using a specially designed vessels called **conductivity cell**.

(ii) **Calculation of conductivity :** We have seen that conductivity (κ) is reciprocal of resistivity (ρ), i.e.,

$$\kappa = \frac{1}{\rho} \text{ and } \rho = R \frac{a}{l} \therefore \kappa = \frac{1}{R} \left(\frac{l}{a} \right) \text{ or } \kappa = G \left(\frac{l}{a} \right)$$

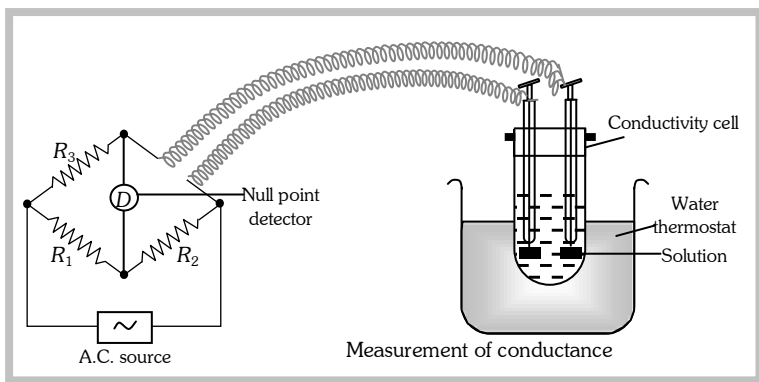
where G is the conductance of the cell, l is the distance of separation of two electrodes having cross section area $a \text{ cm}^2$. The quantity $\left(\frac{l}{a} \right)$ is called cell constant and is expressed in cm^{-1} . Knowing the value of cell constant and conductance of the solution, the specific conductance can be calculated as,

$$\kappa = G \times \text{Cell constant} \text{ i.e., } \boxed{\text{Conductivity} = \text{Conductance} \times \text{Cell constant}}$$

(iii) **Determination of cell constant :** The cell constant is generally not calculated from the values of l and a because these are difficult to measure for a given cell. However, it is usually determined accurately by measuring the conductance of a standard solution whose conductivity is known. For this purpose, a standard solution of KCl is used whose conductivity is known at different concentrations and temperatures. The conductivities of different KCl solutions at 298 K are given in table.

Conductivity and molar conductivity of KCl solutions at 298.15 K

Molarity	Concentration	Conductivity		Molar conductivity	
(mol L ⁻¹)	(mol m ⁻³)	S cm ⁻¹	S m ⁻¹	S cm ² mol ⁻¹	S m ² mol ⁻¹
1.000	1000	0.1113	11.13	111.3	111.3 × 10 ⁻⁴
0.100	100.0	0.0129	1.29	129.0	129.0 × 10 ⁻⁴
0.010	10.00	0.00141	0.141	141.0	141.0 × 10 ⁻⁴



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Example : 17 If 0.01 M solution of an electrolyte has a resistance of 40 Ohm's in a cell having a cell constant of 0.4 cm^{-1} , then its molar conductance in $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ is [CBSE 1996]

- (a) 10 (b) 10^2 (c) 10^3 (d) 10^4

Solution: (c) $\kappa = \frac{1}{R} \times \frac{l}{a}$ (where κ = specific conductance, R = Resistance, $\frac{l}{a}$ = cell constant)

$$\therefore \kappa = \frac{1}{40} \times 0.4 = 0.01\text{ ohm}^{-1}\text{cm}^{-1}$$

Strength of the solution = 0.01M

\therefore Volume of solution containing one mole of the electrolyte = 1,00,000 cc.

\therefore Molar conductance = $\kappa \times V$ in cc. = $0.01 \times 1,00,000 = 10^3 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$

Example : 18 The resistance of 1 N solution of acetic acid is 250 Ohm, when measured in a cell of cell constant 1.15 cm^{-1} . The equivalent conductance (in $\text{Ohm}^{-1}\text{cm}^2\text{equiv}^{-1}$) of 1 N acetic acid is [CBSE PMT 1994]

- (a) 4.6 (b) 9.2 (c) 18.4 (d) 0.023

Solution: (a) $\kappa = G \times \text{cell constant} = \frac{\text{Cell constant}}{R} = \frac{1.15}{250}$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}} = \frac{1.15}{250} \times \frac{1000}{1} = 4.6\Omega^{-1}\text{cm}^2\text{eq}^{-1}.$$

Example : 19 The cell constant of a given cell is 0.47 cm^{-1} . The resistance of a solution placed in this cell is measured to be 31.6 Ohm. The conductivity of the solution (in Scm^{-1} where S has usual meaning) is [Pb CET 1995]

- (a) 0.15 (b) 1.5 (c) 0.015 (d) 150

Solution: (c) $\kappa = \frac{1}{R} \times \text{cell constant} = \frac{1}{31.6} \times 0.47 = 0.015 \text{ Scm}^{-1}.$

Example : 20 A conductivity cell has two platinum electrodes of 1.2 cm^2 area, separated by a distance of 0.8 cm. The cell constant is, [Pb CET 1989]

- (a) 0.66 cm^{-1} (b) 1.5 cm^{-1} (c) 0.96 cm^{-1} (d) 0.66 cm

Solution: (a) Cell constant = $\frac{l}{a} = \frac{0.8}{1.2} = 0.66\text{ cm}^{-1}.$

Example : 21 The resistance of 0.01 N solution of an electrolyte was found to be 210 Ohm at 298 K. Its conductance is,

- (a) $4.76 \times 10^{-3} \text{ mho}$ (b) 4.76 mho (c) 210 mho (d) None of these

Solution: (a) Conductance = $\frac{1}{R} = \frac{1}{210} = 4.76 \times 10^{-3} \text{ mho}.$

Example : 22 The resistance of 0.01 N solution of an electrolyte was found to be 210 Ohm at 298 K, using a conductivity cell of cell constant 0.66 cm^{-1} . The specific conductance of solution is,

- (a) $3.14 \times 10^{-3} \text{ mho cm}^{-1}$ (b) $3.14 \times 10^{-3} \text{ mho}^{-1} \text{ cm}$
(c) 3.14 mho cm^{-1} (d) $3.14 \text{ mho}^{-1} \text{ cm}^{-1}$

Solution: (a) $\kappa = \frac{1}{R} \times \frac{l}{a} = \frac{1}{210} \times 0.66 = 3.14 \times 10^{-3} \text{ mho cm}^{-1}.$

Example : 23 Molar conductivity of a solution is $1.26 \times 10^2 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$. Its molarity is 0.01. Its specific conductivity will be [Manipal PMT 2002]

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- (a) 1.26×10^{-5} (b) 1.26×10^{-3} (c) 1.26×10^{-4} (d) 0.0063

Solution: (b) $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$ or $\kappa = \frac{\Lambda_m \times \text{Molarity}}{1000} = \frac{1.26 \times 10^{-2} \times 0.01}{1000} = 1.26 \times 10^{-3}$.

Factors affecting the electrolytic conductance.

In general, conductance of an electrolyte depends upon the following factors,

(1) Nature of electrolyte, (2) Concentration of the solution, (3) Temperature

(1) Nature of electrolyte : The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution the greater is the conductance. The number of ions produced by an electrolyte depends upon its nature. The strong electrolytes dissociate almost completely into ions in solutions and, therefore, their solutions have high conductance. On the other hand, weak electrolytes, dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

(2) Concentration of the solution : The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution. The molar conductance of a few electrolytes in water at different concentrations are given in table

C	HCl	KCl	KNO ₃	CH ₃ COOH	NH ₄ OH
0.1	391.3	129.0	120.4	5.2	3.6
0.05	399.1	133.4	126.3	—	—
0.01	412.0	141.3	132.8	16.3	11.3
0.005	415.8	143.5	131.5	—	—
0.001	421.4	146.9	141.8	49.2	34.0
0.0005	422.7	147.8	142.8	67.7	46.9
0(Infinite dilution)	426.2	149.9	146.0	390.7	271.0

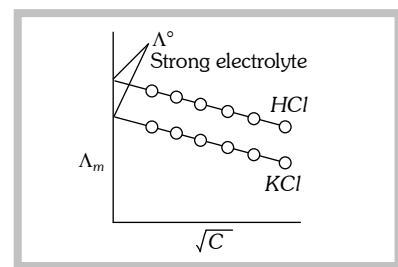
Inspection of table reveals that the molar conductance of strong electrolyte (HCl, KCl, KNO₃) as well as weak electrolytes (CH₃COOH, NH₄OH) increase with decrease in concentration or increase in dilution. The variation is however different for strong and weak electrolytes.

(i) Variation of conductivity with concentration for strong electrolytes : In case of strong electrolytes, there is a tendency for molar conductivity to approach a certain limiting value when the concentration approaches zero i.e., when the dilution is infinite. The molar conductivity when the concentration approaches zero (Infinite dilution) is called molar conductivity at infinite dilution. It is denoted by Λ^0 . Thus, $\Lambda = \Lambda^0$ when $C \rightarrow 0$ (At infinite dilution)

It has been observed that the variation of molar conductivity with concentration may be given by the expression

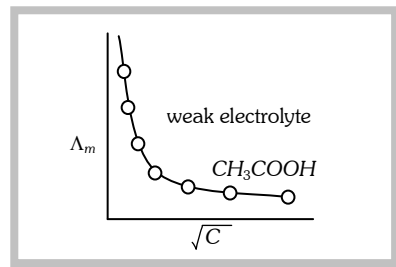
$$\Lambda = \Lambda^0 - Ac^{1/2}$$

where, A is a constant and Λ^0 is called molar conductivity at infinite dilution.



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The variation of molar conductivity with concentration can be studied by plotting the values of Λ_m against square root of concentration (\sqrt{C}). The plots of variation of molar conductivity with \sqrt{C} for KCl and HCl are given in fig. It has been noticed that the variation of Λ_m with concentration, \sqrt{C} is small (Between 4 to 10% only) so that the plots can be extrapolated to zero concentration. This gives the limiting value of molar conductance when the concentration approaches zero, called molar conductivity at infinite dilution.



(ii) **Variation of molar conductivity with concentration for weak electrolytes** : The weak electrolytes dissociate to a much lesser extent as compared to strong electrolytes. Therefore, the molar conductivity is low as compared to that of strong electrolytes.

However, the variation of Λ_m with \sqrt{C} is very large and so much so that we cannot obtain molar conductance at infinite dilution (Λ^0) by extrapolation of the Λ_m versus \sqrt{C} plots. The behavior of weak electrolytes such as CH_3COOH is shown in figure.

Note : * The Λ^0 value for weak electrolytes can be obtained by an indirect method based upon Kohlrausch law.

Explanation for the variation : The variation of molar conductance with concentration can be explained on the basis of conducting ability of ions for weak and strong electrolytes.

For weak electrolytes the variation of Λ with dilution can be explained on the bases of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance (Λ^0) corresponds to degree of dissociation equal to 1 i.e., the whole of the electrolyte dissociates.

Thus, the degree of dissociation can be calculated at any concentration as,

$$\alpha = \frac{\Lambda^c}{\Lambda^0}$$

where α is the degree of dissociation, Λ^c is the molar conductance at concentration C and Λ^0 is the molar conductance at infinite dilution.

For strong electrolytes, there is no increase in the number of ions with dilution because strong electrolytes are completely ionised in solution at all concentrations (By definition). However, in concentrated solutions of strong electrolytes there are strong forces of attraction between the ions of opposite charges called inter-ionic forces. Due to these inter-ionic forces the conducting ability of the ions is less in concentrated solutions. With dilution, the ions become far apart from one another and inter-ionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very-very low, the inter-ionic attractions become negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is characteristic of each electrolyte.

(3) Temperature : The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

Migration of ions.

Electricity is carried out through the solution of an electrolyte by **migration of ions**. Therefore,

- (1) Ions move toward oppositely charged electrodes at different speeds.
- (2) During electrolysis, ions are discharged or liberated in equivalent amounts at the two electrodes, *no matter what their relative speed is*.
- (3) Concentration of the electrolyte changes around the electrode due to difference in the speed of the ions.

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(4) Loss of concentration around any electrode is proportional to the speed of the ion that moves away from the electrode, so

$$\frac{\text{Loss around anode}}{\text{Loss around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

The relation is valid only when the discharged ions do not react with atoms of the electrodes. But when the ions combine with the material of the electrode, the concentration around the electrode shows an increase. For example, during electrolysis of AgNO_3 solution using Ag electrodes, the concentration of AgNO_3 around the anode increases, because every nitrate ion that reaches at the anode dissolve from it one Ag^+ ion to form AgNO_3 .

Transport number or Transference number.

(1) **Definition** : “The fraction of the total current carried by an ion is known as transport number, transference number or Hittorf number may be denoted by sets symbols like t_+ and t_- or t_c and t_a or n_c and n_a .”

From this definition,

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}}; \quad t_c = \frac{\text{Current carried by a cation}}{\text{Total current passed through the solution}}$$

evidently, $t_a + t_c = 1$.

(2) **Determination of transport number** : Transport number can be determined by **Hittorf's method, moving boundary method, emf method and from ionic mobility**.

(3) **Factors affecting transport number**

(i) **Temperature** : A rise in temperature tends to bring the transport number of cation and anion more closer to 0.5. It means that the transport number of an ion, if less than 0.5 at the room temperature increases and if greater than 0.5 at room temperature decreases with rise in temperature.

(ii) **Concentration of the electrolyte** : Transport number generally varies with the concentration of the electrolyte. In case of partially dissociated CdI_2 , the value decreases from 0.49 at low concentration to almost zero at higher concentration and becomes negative at still higher concentration. The transport numbers of Cd^{2+} ions in 0.01 N, 0.05 N, 0.02 N and 0.50 N CdI_2 at 25°C are 0.449, 0.402, 0.131 and 0.005 respectively. This abnormal behavior may be explained by assuming,

(a) *That in very dilute solution* : CdI_2 ionises to Cd^{2+} ions and I^- ions. Thus Cd^{2+} shows the usual transport number.

(b) *That with increase in concentration* : CdI_2 takes on I^- ions and form complex, $\text{CdI}_2 + 2\text{I}^- \rightleftharpoons [\text{CdI}_4]^{2-}$. This explains the negative value for transport number of Cd^{2+} ions at higher concentration.

(iii) **Nature of the other ions present in solution** : The transport number of anion depends upon the speed of the anion and the cation and vice versa. For example, the transport number of Cl^- ion in NaCl is 0.0004 but in HCl it is 0.16. This is because H^+ moves faster than Na^+ .

(iv) **Hydration of ion** : In general, a decrease in the degree of hydration of anion will increase its transport number. For example, the transport number of $\text{Li}^+, \text{Na}^+, \text{K}^+$ ions in $\text{LiCl}, \text{NaCl}, \text{KCl}$ solutions are 0.328, 0.396, 0.496 respectively. Thus the ionic mobility of the cations is in the order $\text{Li}^+ \leq \text{Na}^+ \leq \text{K}^+$ which is in the reverse

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order than that expected from the size of the ions. This anomaly can be explained by saying that Li^+ is hydrated to greater extent than Na^+ which in turn is more than K^+ . Thus the effective size of Li^+ is more than that of Na^+ which in turn is more than that of K^+ .

(4) **Transport number and Ionic mobility : Ionic mobility or Ionic conductance** is the conductivity of a solution containing 1 g ion, at infinite dilution, when two sufficiently large electrodes are placed 1 cm apart.

$$\text{Ionic mobilities } (\lambda_a \text{ or } \lambda_c) \propto \text{speeds of ions } (u_a \text{ or } u_c)$$

Unit of ionic mobility is $\text{Ohm}^{-1} \text{cm}^2$ or $\text{V}^{-1} \text{S}^{-1} \text{cm}^2$: Ionic mobility and transport number are related as,

$$\lambda_a \text{ or } \lambda_c = t_a \text{ or } t_c \times \lambda_{\infty}$$

Absolute ionic mobility is the mobility with which the ion moves under unit potential gradient. Its unit is cm sec^{-1} .

$$\text{Absolute ionic mobility} = \frac{\text{Ionic mobility}}{96,500}$$

Kohlrausch's law.

(1) Kohlrausch law states that, "At time infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions" i.e., $\Lambda_m^{\infty} = \nu_+ \lambda_+^{\infty} + \nu_- \lambda_-^{\infty}$, where, ν_+ and ν_- are the number of cations and anions per formula unit of electrolyte respectively and, λ_+^{∞} and λ_-^{∞} are the molar conductivities of the cation and anion at infinite dilution respectively. The use of above equation in expressing the molar conductivity of an electrolyte is illustrated below,

(i) **Molar conductivity of HCl** : The molar conductivity of HCl at infinite dilution can be expressed as,

$$\Lambda_{HCl}^{\infty} = \nu_{H^+} \lambda_{H^+}^{\infty} + \nu_{Cl^-} \lambda_{Cl^-}^{\infty}; \text{ For } HCl, \nu_{H^+} = 1 \text{ and } \nu_{Cl^-} = 1. \text{ So,}$$

$$\Lambda_{HCl}^{\infty} = (1 \times \lambda_{H^+}^{\infty}) + (1 \times \lambda_{Cl^-}^{\infty}); \text{ Hence, } \Lambda_{HCl}^{\infty} = \lambda_{H^+}^{\infty} + \lambda_{Cl^-}^{\infty}$$

(ii) **Molar conductivity of $MgCl_2$** : For $MgCl_2$, the molar conductivity at infinite dilution can be expressed as,

$$\Lambda_{MgCl_2}^{\infty} = \nu_{Mg^{2+}} \lambda_{Mg^{2+}}^{\infty} + \nu_{Cl^-} \lambda_{Cl^-}^{\infty}; \text{ For } MgCl_2, \nu_{Mg^{2+}} = 1 \text{ and } \nu_{Cl^-} = 2$$

$$\text{So, } \Lambda_{MgCl_2}^{\infty} = 1 \times \lambda_{Mg^{2+}}^{\infty} + 2 \times \lambda_{Cl^-}^{\infty}; \text{ Hence, } \Lambda_{MgCl_2}^{\infty} = \lambda_{Mg^{2+}}^{\infty} + 2\lambda_{Cl^-}^{\infty}$$

(iii) **Molar conductivity of CH_3COOH** : CH_3COOH in solution ionises as,

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$; So, the molar conductivity of CH_3COOH (acetic acid) at infinite dilution can be expressed as, $\Lambda_{CH_3COOH}^{\infty} = \nu_{H^+} \lambda_{H^+}^{\infty} + \nu_{CH_3COO^-} \lambda_{CH_3COO^-}^{\infty}$; For, CH_3COOH , $\nu_{H^+} = 1$ and $\nu_{CH_3COO^-} = 1$

$$\text{So, } \Lambda_{CH_3COOH}^{\infty} = 1 \times \lambda_{H^+}^{\infty} + 1 \times \lambda_{CH_3COO^-}^{\infty} \text{ or } \Lambda_{CH_3COOH}^{\infty} = \lambda_{H^+}^{\infty} + \lambda_{CH_3COO^-}^{\infty}$$

The molar conductivities of some ions at infinite dilution and 298 K

Cation	$\square_+^{\infty} \text{S cm}^2 \text{mol}^{-1}$	Cation	$\square_+^{\infty} \text{S cm}^2 \text{mol}^{-1}$	Anion	$\square_-^{\infty} \text{S cm}^2 \text{mol}^{-1}$	Anion	$\square_-^{\infty} \text{S cm}^2 \text{mol}^{-1}$
H^+	349.8	Ba^{2+}	127.2	OH^-	198.0	ClO_4^-	68.0
Tl^+	74.7	Ca^{2+}	119.0	Br^-	78.4	SO_4^{2-}	159.2
K^+	73.5	Sr^{2+}	119.0	I^-	76.8	CH_3COO^-	40.9

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Na^+	50.1	Mg^{2+}	106.2	Cl^-	76.3
Li^+	38.7			NO_3^-	71.4

(2) Applications of Kohlrausch's law : Some typical applications of the Kohlrausch's law are described below,

(i) **Determination of Λ_m^∞ for weak electrolytes :** The molar conductivity of a weak electrolyte at infinite dilution (Λ_m^∞) cannot be determined by extrapolation method. However, Λ_m^∞ values for weak electrolytes can be determined by using the Kohlrausch's equation. For acetic acid this is illustrated below. According to the Kohlrausch's law, the molar conductivity of acetic acid (CH_3COOH) is given by,

$\Lambda_{\text{CH}_3\text{COOH}}^\infty = \nu_{\text{H}^+} \lambda_{\text{H}^+}^\infty + \nu_{\text{CH}_3\text{COO}^-} \lambda_{\text{CH}_3\text{COO}^-}^\infty = 1 \times \lambda_{\text{H}^+}^\infty + 1 \times \lambda_{\text{CH}_3\text{COO}^-}^\infty$; Taking the values of $\lambda_{\text{H}^+}^\infty$ and $\lambda_{\text{CH}_3\text{COO}^-}^\infty$ (from table), we can write, $\lambda_{\text{CH}_3\text{COOH}}^\infty = (349.8 + 40.9) \text{ S cm}^2 \text{ mol}^{-1} = 390.7 \text{ S cm}^2 \text{ mol}^{-1}$.

Sometimes, the molar conductivity values for the ions may not be available. In such cases, the following procedure may be followed,

(a) Select a series of strong electrolytes, so that their sum or difference gives the weak electrolyte. Generally, three strong electrolytes are selected.

(b) Measure Λ_m values of these salts at various concentrations (C_m) and plot Λ_m against $\sqrt{C_m}$ for each salt separately. Determine Λ_m^∞ for each salt (Strong electrolyte) by extrapolation method.

(c) Add or subtract the equations to get the Λ_m^∞ of the weak electrolyte.

Suppose we have to determine the molar conductivity of a weak electrolyte MA at infinite dilution. For this purpose, we take three salts, viz., MCl , NaA and NaCl , and determine their Λ_m^∞ values by extrapolation method. Then, according to the Kohlrausch's law, $\Lambda_{\text{MCl}}^\infty = \lambda_{\text{M}^+}^\infty + \lambda_{\text{Cl}^-}^\infty$; $\Lambda_{\text{NaA}}^\infty = \lambda_{\text{Na}^+}^\infty + \lambda_{\text{A}^-}^\infty$; $\Lambda_{\text{NaCl}}^\infty = \lambda_{\text{Na}^+}^\infty + \lambda_{\text{Cl}^-}^\infty$

From these equations, we can write,

$$\Lambda_{\text{MCl}}^\infty + \Lambda_{\text{NaA}}^\infty - \Lambda_{\text{NaCl}}^\infty = (\lambda_{\text{M}^+}^\infty + \lambda_{\text{Cl}^-}^\infty) + (\lambda_{\text{Na}^+}^\infty + \lambda_{\text{A}^-}^\infty) - (\lambda_{\text{Na}^+}^\infty + \lambda_{\text{Cl}^-}^\infty) = \lambda_{\text{M}^+}^\infty + \lambda_{\text{A}^-}^\infty = \Lambda_{\text{MA}}^\infty$$

$$\text{So, } \Lambda_{\text{MA}}^\infty = \Lambda_{\text{MCl}}^\infty + \Lambda_{\text{NaA}}^\infty - \Lambda_{\text{NaCl}}^\infty$$

Thus, we can obtain the molar conductivity of a weak electrolyte at infinite dilution from the Λ_m^∞ values of three suitable strong electrolytes.

(ii) **Determination of the degree of ionisation of a weak electrolyte :** The Kohlrausch's law can be used for determining the degree of ionisation of a weak electrolyte at any concentration. If λ_m^c is the molar conductivity of a weak electrolyte at any concentration C and, λ_m^∞ is the molar conductivity of a electrolyte at infinite dilution.

Then, the degree of ionisation is given by,
$$\alpha_c = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{\Lambda_m^c}{(\nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty)}$$

Thus, knowing the value of Λ_m^c , and Λ_m^∞ (From the Kohlrausch's equation), the degree of ionisation at any concentration (α_c) can be determined.

(iii) **Determination of the ionisation constant of a weak electrolyte :** Weak electrolytes in aqueous solutions ionise to a very small extent. The extent of ionisation is described in terms of the degree of ionisation (α). In solution, the ions are in dynamic equilibrium with the unionised molecules. Such an equilibrium can be described by a constant called **ionisation constant**. For example, for a weak electrolyte AB, the ionisation

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equilibrium is, $AB \rightleftharpoons A^+ + B^-$; If C is the initial concentration of the electrolyte AB in solution, then the equilibrium concentrations of various species in the solution are, $[AB] = C(1 - \alpha)$, $[A^+] = C\alpha$ and $[B^-] = C\alpha$

Then, the ionisation constant of AB is given by,
$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

We know, that at any concentration C , the degree of ionisation (α) is given by, $\alpha = \Lambda_m^c / \Lambda_m^\infty$

Then,
$$K = \frac{C(\Lambda_m^c / \Lambda_m^\infty)^2}{[1 - (\Lambda_m^c / \Lambda_m^\infty)]} = \frac{C(\Lambda_m^c)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^c)}$$
; Thus, knowing Λ_m^∞ and Λ_m^c at any concentration, the ionisation

constant (K) of the electrolyte can be determined.

(iv) **Determination of the solubility of a sparingly soluble salt** : The solubility of a sparingly soluble salt in a solvent is quite low. Even a saturated solution of such a salt is so dilute that it can be assumed to be at infinite dilution. Then, the molar conductivity of a sparingly soluble salt at infinite dilution (Λ_m^∞) can be obtained from the relationship,
$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty \quad \dots\dots(i)$$

The conductivity of the saturated solution of the sparingly soluble salt is measured. From this, the conductivity of the salt (κ_{salt}) can be obtained by using the relationship, $\kappa_{\text{salt}} = \kappa_{\text{sol}} - \kappa_{\text{water}}$, where, κ_{water} is the conductivity of the water used in the preparation of the saturated solution of the salt.

$$\Lambda_{\text{salt}}^\infty = \frac{1000 \kappa_{\text{salt}}}{C_m} \quad \dots\dots(ii)$$

From equation (i) and (ii);

$$C_m = \frac{1000 \kappa_{\text{salt}}}{(\nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty)}, \quad C_m \text{ is the molar concentration of the sparingly soluble salt in its saturated solution.}$$

Thus, C_m is equal to the solubility of the sparingly soluble salt in the *mole per litre* units. The solubility of the salt in *gram per litre* units can be obtained by multiplying C_m with the molar mass of the salt.

Example : 24 The equivalent conductivity of 0.1 M weak acid is 100 times less than that at infinite dilution. The degree of dissociation is [Tamil Nadu CET 2001,02]

- (a) 100 (b) 10 (c) 0.01 (d) 0.001

Solution: (c)
$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{x/100}{x} = \frac{1}{100} = 0.01.$$

Example : 25 Equivalent conductances of NaCl , HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and $90 \text{ Ohm}^{-1}\text{cm}^2$ respectively. The equivalent conductance of CH_3COOH at infinite dilution would be [CBSE PMT 1997]

- (a) $101.38 \text{ Ohm}^{-1}\text{cm}^2$ (b) $253.62 \text{ Ohm}^{-1}\text{cm}^2$ (c) $390.71 \text{ ohm}^{-1}\text{cm}^2$ (d) $678.90 \text{ ohm}^{-1}\text{cm}^2$

Solution: (c)
$$\Lambda^0(\text{CH}_3\text{COOH}) = \Lambda^0(\text{CH}_3\text{COONa}) + \Lambda^0(\text{HCl}) - \Lambda^0(\text{NaCl}) = 91 + 426.16 - 126.45 = 390.71 \text{ Ohm}^{-1}\text{cm}^2.$$

Example : 26 Molar ionic conductivities of a bivalent electrolyte are 57 and 73. The molar conductivity of the solution will be [DPMT 2002]

- (a) $130 \text{ S cm}^2 \text{ mol}^{-1}$ (b) $65 \text{ S cm}^2 \text{ mol}^{-1}$ (c) $260 \text{ S cm}^2 \text{ mol}^{-1}$ (d) $187 \text{ S cm}^2 \text{ mol}^{-1}$

Solution: (a)
$$\Lambda_m^0 = 57 + 73 = 130 \text{ S cm}^2 \text{ mol}^{-1}.$$

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Example : 27 The ionic mobilities of the cation and the anion of a salt are 140 and 80 mho respectively. The equivalent conductivity of the salt at infinite dilution will be [Haryana CET 1991]

- (a) 160 mho (b) 280 mho (c) 60 mho (d) 220 mho

Solution: (d) $\Lambda_{eq}^0 = \lambda_c^0 + \lambda_a^0 = 140 + 80 = 220 \text{ mho}$.

Example : 28 The ionization constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is $19.6 \text{ S cm}^2 \text{ eq}^{-1}$. The equivalent conductance of the electrolyte at infinite dilution (in $\text{S cm}^2 \text{ eq}^{-1}$) will be

- (a) 250 (b) 196 (c) 392 (d) 384

Solution: (c) $\frac{HA}{C(1-\alpha)} = \frac{H^+}{C\alpha} + \frac{A^-}{C\alpha}$; $K = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2$
 $25 \times 10^{-6} = 10^{-2} \times \alpha^2$ or $\alpha = 5 \times 10^{-2}$
 $\alpha = \frac{\Lambda^c}{\Lambda^0}$ or $\Lambda^0 = \frac{\Lambda^c}{\alpha} = \frac{19.6}{5 \times 10^{-2}} = 392 \Omega^{-1} \text{ cm}^2$.

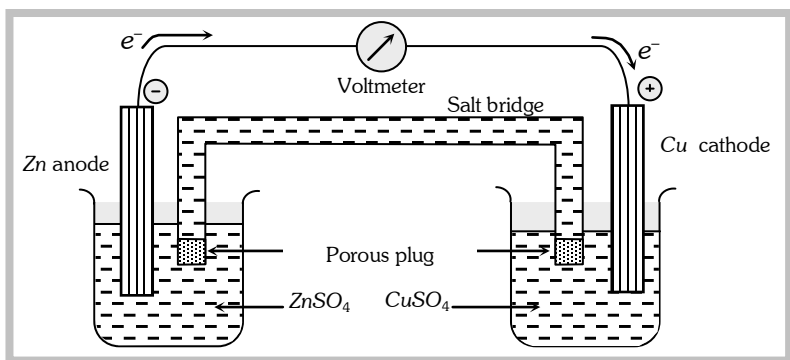
Electrochemical or Galvanic cell.

“Electrochemical cell or Galvanic cell is a device in which a spontaneous redox reaction is used to convert chemical energy into electrical energy i.e. electricity can be obtained with the help of oxidation and reduction reaction”.

(1) **Characteristics of electrochemical cell :** Following are the important characteristics of electrochemical cell,

- (i) Electrochemical cell consists of two vessels, two electrodes, two electrolytic solutions and a salt bridge.
- (ii) The two electrodes taken are made of different materials and usually set up in two separate vessels.
- (iii) The electrolytes are taken in the two different vessels called as half - cells.
- (iv) The two vessels are connected by a salt bridge/porous pot.
- (v) The electrode on which oxidation takes place is called the **anode** (or – ve pole) and the electrode on which reduction takes place is called the **cathode** (or + ve pole).
- (vi) In electrochemical cell, ions are discharged only on the cathode.
- (vii) Like electrolytic cell, in electrochemical cell, from outside the electrolytes electrons flow from anode to cathode and current flow from cathode to anode.
- (viii) For electrochemical cell,

$$E_{cell} = +ve, \Delta G = -ve.$$
- (ix) In a electrochemical cell, cell reaction is exothermic.



(2) Salt bridge and its significance

(i) Salt bridge is U – shaped glass tube filled with a jelly like substance, agar – agar (plant gel) mixed with an electrolyte like KCl, KNO₃, NH₄NO₃ etc.

(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.

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(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, viz. KCl, KNO_3, NH_4NO_3 etc.

(iv) The following are the functions of the salt bridge,

(a) It connects the solutions of two half - cells and completes the cell circuit.

(b) It prevent transference or diffusion of the solutions from one half cell to the other.

(c) It keeps the solution of two half - cells electrically neutral.

(d) It prevents liquid – liquid junction potential i.e. the potential difference which arises between two solutions when they contact with each other.

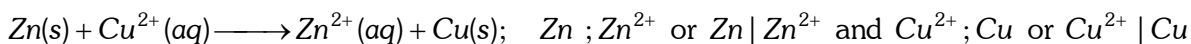
Note : * Salt bridge can be replaced by a porous partition which allows the migration of ions without intermixing of solution.

* $KCl(aq)$ cannot be used as a salt bridge for the cell, $Cu(s)|CuSO_4(aq)||AgNO_3(aq)|Ag(s)$.

Because $AgCl$ is precipitated as follows, $AgNO_3 + KCl \longrightarrow AgCl \downarrow + KNO_3$
(ppt.)

(3) Representation of an electrochemical cell

(i) The interfaces across which a potential difference exists are shown by a semicolon (;) or a single vertical line (|). For example, the two half- cells of the following electrochemical cell can be represented as follows,



These indicate that potential difference exists at the Zn and Zn^{2+} ions interface, and similarly at the Cu^{2+} and Cu interface. Sometimes coma or plus signs is observed in the formulation of half-cells. For example,

$Ag, AgCl | Cl^-$ or $Ag + AgCl | Cl^-$. These indicate that Ag and $AgCl$ together constitute the electrode.

(ii) The contact between two solutions by means of a salt bridge is indicated by double vertical line (||) between them e.g.; $Cu^{2+} || Zn^{2+}$

(iii) The anode half-cell (or the oxidation half cell) is always written on the left hand side and the cathode half cell (or the reduction half-cell) on the right hand side, with the respective metal electrode on the outside extremes, e.g., $Zn ; Zn^{2+} || Cu^{2+}; Cu$ or $Zn | Zn^{2+} || Cu^{2+} | Cu$. Sometimes negative and positive signs are put on the electrodes to show that they are negative (anode) and positive (cathode) electrodes.

e.g. $(-) Zn ; Zn^{2+} || Cu^{2+} ; Cu (+)$

(iv) An arrow when drawn below the cell formulation gives the direction of the current inside the cell while an arrow drawn above the formulation gives the direction of the electrons flown in the outer circuit.

e.g., $Zn ; Zn^{2+} \xrightarrow{\quad} || \xrightarrow{\quad} Cu^{2+} ; Cu$

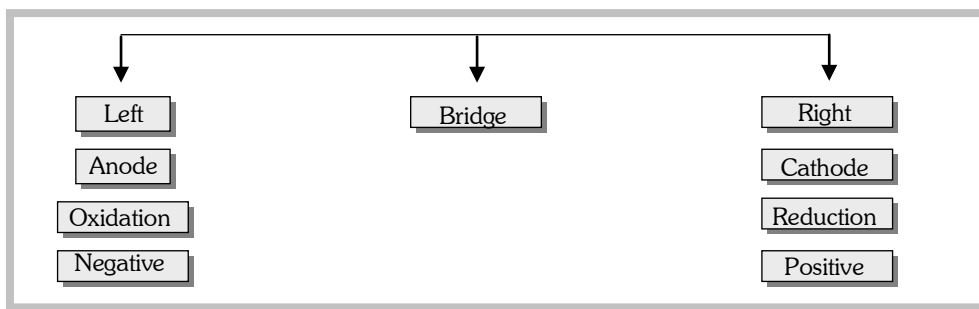
(v) The potential difference between the electrodes (i.e., the cell potential or EMF or emf) is stated in volts along with the temperature at which it is applicable. For example, $E_{25^\circ C} = 1.130$ volt or $E_{298K} = 1.130$ volt

With the usual above conventions, the emf of the cell will have a positive value. However, when the cell is formulated in the reverse order, the emf will have a negative value. In other words, the negative value of emf indicates that the oxidation process expected on the left hand electrode will not occur spontaneously and in case oxidation must be made to occur on the left hand electrode, an emf of a value of somewhat larger than that of the specified cell potential will be required from an external source.

(vi) The concentration of solutions, pressure of gases and physical state of solids and liquids involved, are indicated in the cell formation. For example, $Pt, H_2(0.9 \text{ atm}); H^+(a = 0.1) || Cu^{2+}(a = 0.1); Cu$

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Note : Sometimes we get confused in the nomenclature of electrodes. As a memory aid keep in mind the alphabetical order of the first e.g. A (anode) comes before C (cathode). The cell may be written by arranging each of the pair left – right, anode – cathode, oxidation – reduction, negative and positive in the alphabetical order as,



(4) Reversible and irreversible cells : A cell is said to be reversible if the following two conditions are fulfilled

(i) The chemical reaction of the cell stops when an exactly equal external *emf* is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external *emf* is slightly higher than that of the cell. Any other cell, which does not obey the above two conditions, is termed as irreversible. Daniell cell is reversible but $Zn|H_2SO_4|Ag$ cell is irreversible in nature

(5) Types of electrochemical cells : Two main types of electrochemical cells have been reported, these are,

(i) **Chemical cells :** The cells in which electrical energy is produced from the energy change accompanying a chemical reaction or a physical process are known as chemical cells. Chemical cells are of two types,

(a) *Chemical cells without transference :* In this type of chemical cells, the liquid junction potential is neglected or the transference number is not taken into consideration. In these cells, one electrode is reversible to cations while the other is reversible to the anions of the electrolyte.

(b) *Chemical cells with transference :* In this type of chemical cells, the liquid-liquid junction potential or diffusion potential is developed across the boundary between the two solutions. This potential develops due to the difference in mobilities of +ve and -ve ions of the electrolytes.

(6) Concentration cells : “A cell in which electrical energy is produced by the transference of a substance from a system of high concentration to one at low concentration is known as **concentration cells**”. Concentration cells are of two types.

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

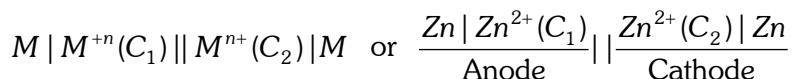
$$\frac{Pt, H_2(\text{pressure } p_1)}{\text{Anode}} \mid H^+ \mid \frac{H_2(\text{pressure } p_2)Pt}{\text{Cathode}}; E_{\text{cell}} = \frac{0.0591}{2} \log \frac{(p_1)}{(p_2)} \text{ at } 25^\circ C$$
 If $p_1 > p_2$, oxidation occurs at L. H. S. electrode and reduction occurs at R. H. S. electrode.

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution. $M(HgC_1) \mid M^{n+} \mid Zn(HgC_2)$

The *emf* of the cell is given by the expression,
$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_1}{C_2} \text{ at } 25^\circ C$$

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



The *emf* of the cell is given by the following expression, $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2(R.H.S)}}{C_{1(L.H.S.)}} e$ at 25° C

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

Note : ✱ In concentration cell net redox change is zero and the decrease in free energy during transfer of substance from one concentration to other is responsible for production of electrical energy.

(7) **Heat of reaction in an electrochemical cell** : Let n Faraday charge flows out of a cell of *emf* E , then

$$-\Delta G = nFE \quad \dots\dots(i)$$

Gibbs – Helmholtz equation from thermodynamics may be given as

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p \quad \dots\dots(ii)$$

From equation (i) and (ii) we get, $-nFE = \Delta H + T \left[\frac{\partial(-nFE)}{\partial T} \right]_p = \Delta H - nFT \left(\frac{\partial E}{\partial T} \right)_p$; $\Delta H = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_p$

where $\left(\frac{\partial E}{\partial T} \right)_p$ = Temperature coefficient of cell

Case I: When $\left(\frac{\partial E}{\partial T} \right)_p = 0$, then $\Delta H = -nFE$

Case II: When $\left(\frac{\partial E}{\partial T} \right)_p > 0$, then $nFE > \Delta H$, i.e. process inside the cell is endothermic.

Case III: When $\left(\frac{\partial E}{\partial T} \right)_p < 0$, then $nFE < \Delta H$, i.e., process inside the cell is exothermic.

Some Commercial cells (Batteries).

One of the main use of galvanic cells is the generation of portable electrical energy. These cells are also popularly known as **batteries**. The term battery is generally used for two or more Galvanic cells connected in series. Thus, a **battery** is an arrangement of electrochemical cells used as an energy source. The basis of an electrochemical cell is an oxidation – reduction reaction. However, for practical purposes there are some limitations to the use of redox reactions. A useful battery should also fulfil the following requirements;

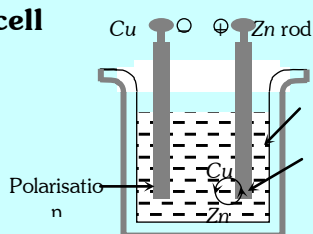
- It should be light and compact so that it can be easily transported.
- It should have reasonably long life both when it is being used and when it is not used.
- The voltage of the battery should not vary appreciably during its use.

Types of commercial cells : There are mainly two types of commercial cells,

Electrochemistry

(1) **Primary cells** : In these cells, the electrode reactions cannot be reversed by an external electric energy source. In these cells, reactions occur only once and after use they become dead. Therefore, they are **not chargeable**. Some common example are, dry cell, mercury cell, Daniell cell and alkaline dry cell.

(i) Voltaic cell



Cathode : Cu rod

Anode : Zn rod

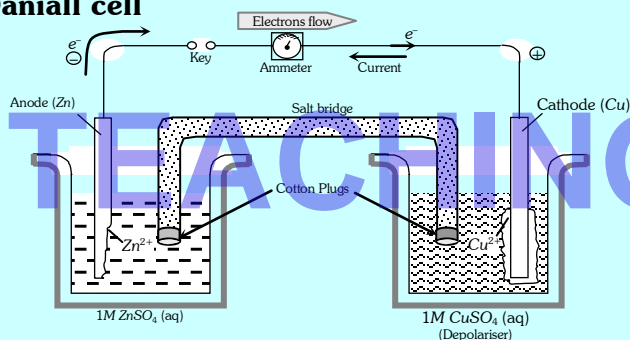
Electrolyte : dil. H_2SO_4

$$E_{mf} : 1.08 \text{ V}$$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$ **At Anode :** $Zn \rightarrow Zn^{2+} + 2e^-$ **Over all**

reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(ii) **Daniell cell**



Cathode : Cu rod

Anode : Zn rod

Electrolyte : dil. H_2SO_4

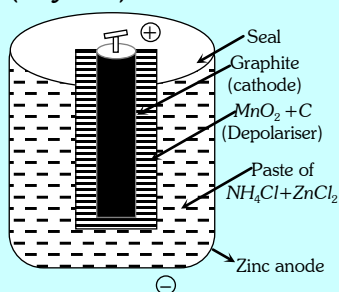
***Emf* : 1.1 V**

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(iii) **Lechlanche cell (Dry cell)**



Cathode : Graphite rod

Anode : Zn pot

Electrolyte : Paste of $NH_4Cl + ZnCl_2$ in starch

Emf : 1.2 V to 1.5 V

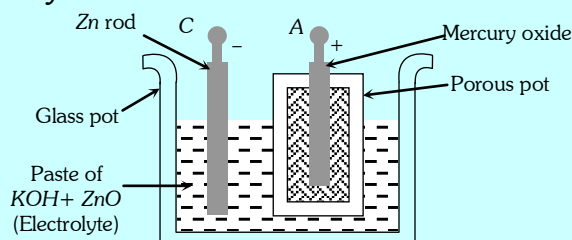
At cathode : $NH_4^+ + MnO_2 + 2e^- \rightarrow MnO(OH)^- + NH_3$

At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Over all reaction :

$$\text{Zn} + \text{NH}_4^+ + \text{MnO}_2 \rightarrow \text{Zn}^{2+} + \text{MnO}(\text{OH})^- + \text{NH}_3$$

(iv) **Mercury cell**



Cathode : Mercury (II) oxide

Anode : Zn rod

Electrolyte : Paste of $KOH + ZnO$

$$E_{mf} : 1.35 \text{ V}$$

At cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$

At Anode : $Zn_{(s)} + 20H_{(aq)}^- \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
(amalgam)

Over all reaction : $Zn_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$

Electrochemistry

Note : * In a dry cell ZnCl_2 combines with NH_3 produced to form the complex $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$, otherwise the pressure developed due to NH_3 would crack the seal of the cell.

* Mercury cell give a constant voltage throughout its life because the electrolyte KOH is not consumed in the reaction.

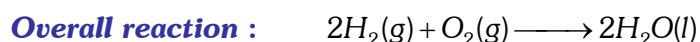
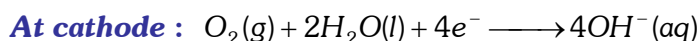
(2) Secondary cells: In the secondary cells, the reactions can be reversed by an external electrical energy source. Therefore, these cells can be **recharged** by passing electric current and used again and again. These are also called **storage cells**. Examples of secondary cells are, lead storage battery and nickel – cadmium storage cell.

In charged	Lead storage cell	Alkali cell
	<p style="margin-left: 400px;">Glass vessel PbO_2 Pb dil. H_2SO_4</p>	<p style="margin-left: 400px;">$\text{Ni}(\text{OH})_2$ $\text{Fe}(\text{OH})_2$ Perforated steel grid $\text{KOH } 20\%$ + $\text{Li}(\text{OH}), 1\%$</p>
Positive electrode	Perforated lead plates coated with PbO_2	Perforated steel plate coated with $\text{Ni}(\text{OH})_4$
Negative electrode	Perforated lead plates coated with pure lead	Perforated steel plate coated with Fe
Electrolyte	dil. H_2SO_4	20% solution of KOH + 1% LiOH
During charging	<p>Chemical reaction</p> <p>At cathode : $\text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb} + \text{H}_2\text{SO}_4$</p> <p>At anode : $\text{PbSO}_4 + \text{SO}_4^{--} + 2\text{H}_2\text{O} - 2\text{e}^- \rightarrow \text{PbO}_2 + 2\text{H}_2\text{SO}_4$</p> <p>Specific gravity of H_2SO_4 increases and when specific gravity becomes 1.25 the cell is fully charged.</p> <p>Emf of cell: When cell is fully charged then $E = 2.2$ volt</p>	<p>Chemical reaction</p> <p>At cathode : $\text{Ni}(\text{OH})_2 + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{Ni}(\text{OH})_4$</p> <p>At anode : $\text{Fe}(\text{OH})_2 + 2\text{K}^+ + 2\text{e}^- \rightarrow \text{Fe} + 2\text{KOH}$</p> <p>Emf of cell : When cell is fully charged then $E = 1.36$ volt</p>
During discharging	<p>Chemical reaction</p> <p>At cathode : $\text{Pb} + \text{SO}_4^{--} - 2\text{e}^- \rightarrow \text{PbSO}_4$</p> <p>At anode : $\text{PbO}_2 + 2\text{H}^+ - 2\text{e}^- + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$</p> <p>Specific gravity of H_2SO_4 decreases and when specific gravity falls below 1.18 the cell requires recharging.</p> <p>Emf of cell : When emf of cell falls below 1.9 volt the cell requires recharging.</p>	<p>Chemical reaction</p> <p>At cathode : $\text{Fe} + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{Fe}(\text{OH})_2$</p> <p>At anode : $\text{Ni}(\text{OH})_4 + 2\text{K}^+ + 2\text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + 2\text{KOH}$</p> <p>Emf of cell : When emf of cell falls below 1.1 V it requires charging.</p>
Efficiency	80%	60%

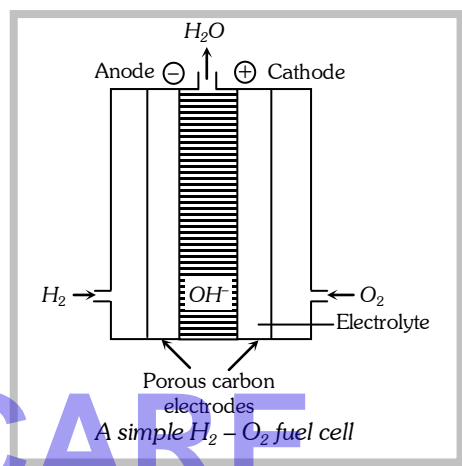
Fuel cells.

These are Voltaic cells in which the reactants are continuously supplied to the electrodes. These are designed to convert the energy from the combustion of fuels such as H_2 , CO , CH_4 , etc. directly into electrical energy. The common example is **hydrogen-oxygen fuel cell** as described below,

In this cell, hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide or potassium hydroxide. Hydrogen (the fuel) is fed into the anode compartment where it is oxidised. The oxygen is fed into cathode compartment where it is reduced. The diffusion rates of the gases into the cell are carefully regulated to get maximum efficiency. The net reaction is the same as burning of hydrogen and oxygen to form water. The reactions are



Each electrode is made of porous compressed carbon containing a small amount of catalyst (Pt , Ag or CoO). This cell runs continuously as long as the reactants are fed. These fuel cells are more efficient than conventionally used methods of generating electricity on a large scale by burning hydrogen, carbon, fuels because these fuel cells convert the energy of the fuel directly into electricity. This cell has been used for electric power in the **Apollo space programme**. Fuel cells offer great promises for energy conversion in future. The important advantages of fuel cells over ordinary batteries are



(1) **High efficiency** : The fuel cells convert the energy of a fuel directly into electricity and therefore, they are more efficient than the conventional methods of generating electricity on a large scale by burning hydrogen, carbon fuels. Though we expect 100 % efficiency in fuel cells, so far **60 – 70% efficiency** has been attained. The conventional methods of production of electrical energy involve combustion of a fuel to liberate heat which is then used to produce electricity. The efficiency of these methods is only about 40%.

(2) **Continuous source of energy** : There is no electrode material to be replaced as in ordinary battery. The fuel can be fed continuously to produce power. For this reason, $H_2 - O_2$ fuel cells have been used in space crafts.

(3) **Pollution free working** : There are no objectionable byproducts and, therefore, they do not cause pollution problems. Since fuel cells are efficient and free from pollution, attempts are being made to get better commercially practical fuel cells.

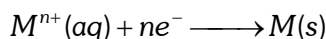
Thermodynamic characteristics of some Fuel cells

Fuel cells	Cell reaction	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	E (volt)
$H_2 - O_2$	$2H_2 + O_2 \rightarrow 2H_2O$	- 237.2	- 258.9	1.23
$C - O_2$	$C + O_2 \rightarrow CO_2$	- 137.3	- 110.5	0.71
$CH_4 - O_2$	$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$	- 818.0	- 890.4	1.060
$CH_3OH - O_2$	$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$	- 706.9	- 764.0	1.22

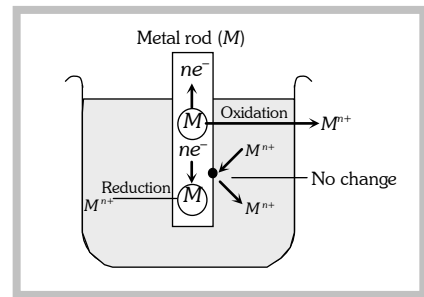
Electrode Potential.

(1) When a metal (M) is placed in a solution of its ions (M^{n+}), either of the following three possibilities can occur, according to the **electrode potential solution pressure theory of Nernst**.

- (i) A metal ion M^{n+} collides with the electrode, and undergoes no change.
- (ii) A metal ion M^{n+} collides with the electrode, gains n electrons and gets converted into a metal atom M , (i.e. the metal ion is reduced).



- (iii) A metal atom on the electrode M may lose n electrons to the solution, and enter to the solution as M^{n+} , (i.e. the metal atom is oxidised).



Thus, “the electrode potential is the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.”

(2) The magnitude of electrode potential depends on the following factors,

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

(3) **Types of electrode potential** : 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. $M \longrightarrow M^{n+} + ne^-$

(ii) **Reduction potential** : When electrode is positively charged with respect to solution, i.e. it acts as cathode. Reduction occurs. $M^{n+} + ne^- \longrightarrow M$

(4) **Standard electrode potential** : “If in the half cell, the metal rod (M) is suspended in a solution of one molar concentration, and the temperature is kept at 298 K, the electrode potential is called **standard electrode potential**, represented usually by E° ”. ‘or’

The standard electrode potential of a metal may be defined as “the potential difference in volts developed in a cell consisting of two electrodes, the pure metal in contact with a molar solution of one of its ions and the normal hydrogen electrode (NHE)”.

Standard oxidation potential for any half - cell = – (Standard reduction potential)
 Standard reduction potential for any half - cell = – (Standard oxidation potential)

(5) Reference electrode or reference half - cells

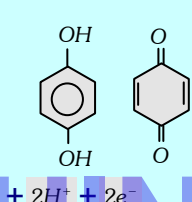
It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode or reference half - cells**. Various types of half – cells have been used to make complete cell with spontaneous reaction in forward direction. These half – cells have been summarised in following table,

Various Types of Half – cells

Type	Example	Half - cell reaction	$Q =$	Reversible to	Electrode Potential (oxdn), $E =$
Gas ion half - cell	$Pt(H_2) H^+(aq)$	$\frac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-$	$[H^+]$	H^+	$E^\circ - 0.0591 \log[H^+]$
	$Pt(Cl_2) Cl^-(aq)$	$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$	$\frac{1}{[Cl^-]}$	Cl^-	$E^\circ + 0.0591 \log[Cl^-]$

Electrochemistry

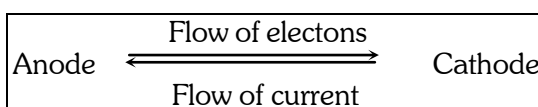
Metal – metal ion half – cell	$Ag Ag^+(aq)$	$Ag(s) \rightarrow Ag^+(aq) + e^-$	$[Ag^+]$	Ag^+	$E^0 - 0.0591 \log [Ag^+]$
Metal insoluble salt anion half – cell	$Ag, AgCl Cl^-(aq)$	$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$	$\frac{1}{[Cl^-]}$	Cl^-	$E^0 + 0.0591 \log [Cl^-]$
Calomel electrode	$Hg, Hg_2Cl_2 Cl^-(aq)$	$2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$	$\frac{1}{[Cl^-]^2}$	Cl^-	$E^0 + 0.0591 \log [Cl^-]$
Metal – metal oxide hydroxide half - cell	$Hg, HgO OH^-(aq)$	$Hg(l) + 2OH^-(aq) \rightarrow HgO(s) + H_2O(l) + 2e^-$	$\frac{1}{[OH^-]^2}$	OH^-	$E^0 + 0.0591 \log [OH^-]$
Oxidation – reduction half – cell	$Pt Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)}$	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	$\frac{[Fe^{3+}]}{[Fe^{2+}]}$	Fe^{2+}, Fe^{3+}	$E^0 - 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$
Mercury –mercury sulphate half – cell	$Hg, HgSO_4 SO_4^{2-}(aq)$	$SO_4^{2-}(aq) + Hg(l) \rightarrow HgSO_4(s) + 2e^-$	$\frac{1}{[SO_4^{2-}]}$	SO_4^{2-}	$E^0 + \frac{0.0591}{2} \log [SO_4^{2-}]$
Quinhydrone half – cell	$Pt Quinhydrone H^+(aq)$		$[H^+]^2$	H^+	$E^0 - 0.0591 \log [H^+]$

\rightleftharpoons


Cell potential or EMF of the cell .

(1) “The difference in potentials of the two half – cells of a cell known as **electromotive force** (*emf*) of the cell or cell potential.”

The difference in potentials of the two half – cells of a cell arises due to the flow of electrons from anode to cathode and flow of current from cathode to anode.



(2) The *emf* of the cell or cell potential can be calculated from the values of electrode potentials of two the half – cells constituting the cell. The following three methods are in use :

(i) When oxidation potential of anode and reduction potential of cathode are taken into account

$$E_{\text{cell}}^0 = \text{Oxidation potential of anode} + \text{Reduction potential of cathode} = E_{\text{ox}}^0 (\text{anode}) + E_{\text{red}}^0 (\text{cathode})$$

(ii) When reduction potentials of both electrodes are taken into account

$$E_{\text{cell}}^0 = \text{Reduction potential of cathode} - \text{Reduction potential of anode} = E_{\text{Cathode}}^0 - E_{\text{Anode}}^0 = E_{\text{right}}^0 - E_{\text{left}}^0$$

(iii) When oxidation potentials of both electrodes are taken into account

$$E_{\text{cell}}^0 = \text{Oxidation potential of anode} - \text{Oxidation potential of cathode} = E_{\text{ox}}^0 (\text{anode}) - E_{\text{ox}}^0 (\text{cathode})$$

(3) Difference between *emf* and potential difference : The potential difference is the difference between the electrode potentials of the two electrodes of the cell under any condition while *emf* is the potential generated by a cell when there is zero electron flow, i.e., it draws no current. The points of difference are given below

Electrochemistry

Emf	Potential difference
It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation.
It is the maximum voltage that the cell can deliver.	It is always less than the maximum value of voltage which the cell can deliver.
It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

(4) **Cell EMF and the spontaneity of the reaction :** We know, $\Delta G = -nFE_{\text{cell}}$

(i) For a spontaneous process, ΔG is negative. Then, according to the equation for a spontaneous process, E_{cell} should be positive. Thus, the cell reaction will be spontaneous when the cell *emf* is positive.

(ii) For a non-spontaneous process, ΔG is positive. Then, according to equation for a non-spontaneous process, E_{cell} should be negative. Thus, the cell reaction will be non-spontaneous when the cell *emf* is negative.

(iii) For the process to be at equilibrium, $\Delta G = 0$. Then, according to the equation E_{cell} should be zero. Thus, the cell reaction will be at equilibrium when the cell *emf* is zero. These results are summarized below

Nature of reaction	$\Delta G(\text{or } \Delta G^\circ)$	$E_{\text{cell}}(\text{or } E_{\text{cell}}^\circ)$
Spontaneous	-	+
Equilibrium	0	0
Non-spontaneous	+	-

Example : 29 Calculate the *emf* of the following cell at 25°C . $\text{Ag(s)} | \text{AgNO}_3(0.01\text{mol kg}^{-1}) || \text{AgNO}_3(0.05\text{mol kg}^{-1}) | \text{Ag(s)}$
 (a) -0.414 V (b) -0.828 V (c) -0.414 V (d) -0.0414 V

Solution: (d) It is a concentration cell. The *emf* of a concentration cell is

$$E_{\text{cell}} = + \frac{0.0592}{n} \log \frac{C_1}{C_2} \text{ at } 25^\circ\text{C and } n = 1$$

$$= +0.0592 \log \frac{0.01}{0.05} = 0.0591 \log 0.2 = 0.0591 \times (-0.699) = -0.0414\text{ V}$$

Example : 30 The standard electrode potentials of the two half cells are given below

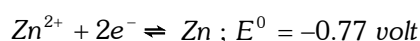


The voltage of cell formed by combining the two half-cells would be

[BHU 1987]

(a) -1.02 V (b) $+0.52\text{ V}$ (c) $+1.02\text{ V}$ (d) -0.52 V

Solution: (b) $\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}; E^\circ = -0.25\text{ volt}$



$$E_{\text{cell}} = \text{Reduction potential of cathode} - \text{Reduction potential of anode} = -0.25 - (-0.77)$$

$$= -0.25 + 0.77 = 0.52\text{ V}$$

Example : 31 The EMF of the cell, $\text{Ni} | \text{Ni}^{2+} || \text{Cu}^{2+} | \text{Cu}$ is 0.59 volt . The standard electrode potential (reduction potential) of copper electrode is 0.34 volt . The standard electrode potential of nickel electrode will be

(a) 0.25 volt (b) -0.25 volt (c) 0.93 volt (d) -0.93 volt

Solution: (b) $E_{\text{cell}}^\circ = E_{\text{Red}}^\circ(\text{RHS}) - E_{\text{Red}}^\circ(\text{LHS}) = E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{Ni}^{2+}/\text{Ni}}^\circ$

Electrochemistry

$$\text{i.e. } 0.59 = 0.34 - E_{\text{Ni}^{2+}/\text{Ni}}^0 \quad \text{or} \quad E_{\text{Ni}^{2+}/\text{Ni}}^0 = 0.34 - 0.59 = -0.25 \text{ Volt}$$

Nernst's equation.

(1) Nernst's equation for electrode potential

The potential of the electrode at which the reaction, $M^{n+}(aq) + ne^- \rightarrow M(s)$

takes place is described by the equation, $E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$

$$\text{or} \quad E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{2.303 RT}{nF} \log \frac{[M(s)]}{[M^{n+}(aq)]}$$

above eq. is called the **Nernst equation**.

Where, $E_{M^{n+}/M}$ = the potential of the electrode at a given concentration,

$E_{M^{n+}/M}^0$ = the standard electrode potential

R = the universal gas constant, $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$,

T = the temperature on the absolute scale,

n = the number of electrons involved in the electrode reaction,

F = the Faraday constant : (96500 C),

$[M(s)]$ = the concentration of the deposited metal,

$[M^{n+}(aq)]$ = the molar concentration of the metal ion in the solution,

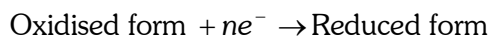
The concentration of pure metal $M(s)$ is taken as unity. So, the Nernst equation for the M^{n+}/M electrode is written as,

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}(aq)]}$$

At 298 K, the Nernst equation for the M^{n+}/M electrode can be written as,

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

For an electrode (half - cell) corresponding to the electrode reaction,



The Nernst equation for the electrode is written as,

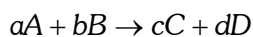
$$E_{\text{half-cell}} = E_{\text{half-cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

At 298 K, the Nernst equation can be written as,

$$E_{\text{half-cell}} = E_{\text{half-cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

(2) Nernst's equation for cell EMF

For a cell in which the net cell reaction involving n electrons is,



The Nernst equation is written as,

Electrochemistry

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where, $E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$. The E_{cell}^0 is called the standard cell potential.

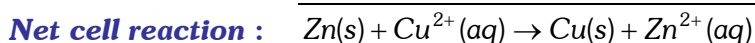
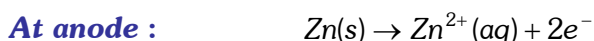
$$\text{or } E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At 298 K, above eq. can be written as,

$$\text{or } E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

It may be noted here, that the concentrations of A, B, C and D referred in the eqs. are the concentrations at the time the cell *emf* is measured.

(3) Nernst's equation for Daniell's cell : Daniell's cell consists of zinc and copper electrodes. The electrode reactions in Daniell's cell are,



Therefore, the Nernst equation for the Daniell's cell is,

$$E_{\text{cdll}} = E_{\text{cell}}^0 - \frac{2.303 RT}{2F} \log \frac{[\text{Cu(s)}][\text{Zn}^{2+}(\text{aq})]}{[\text{Zn(s)}][\text{Cu}^{2+}(\text{aq})]}$$

Since, the activities of pure copper and zinc metals are taken as unity, hence the Nernst equation for the Daniell's cell is,

$$E_{\text{cdll}} = E_{\text{cell}}^0 - \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

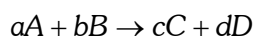
The above eq. at 298 K is,

$$E_{\text{cdll}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \text{ V}$$

For Daniell's cell, $E_{\text{cell}}^0 = 1.1 \text{ V}$

(4) Nernst's equation and equilibrium constant

For a cell, in which the net cell reaction involving n electrons is,



The Nernst equation is

$$E_{\text{Cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots\dots(i)$$

At equilibrium, the cell cannot perform any useful work. So at equilibrium, E_{Cell} is zero. Also at equilibrium, the ratio

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$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \left[\frac{[C]^c [D]^d}{[A]^a [B]^b} \right]_{\text{equil}} = K_c$$

Where, K_c is the equilibrium constant for the cell reaction. Then, at equilibrium eq.(i) becomes,

$$0 = E_{\text{cell}}^0 - \frac{RT}{nF} \ln K_c \quad \text{.....(ii)}$$

or $\ln K_c = \frac{nFE_{\text{cell}}^0}{RT}$

or $K_c = \exp(nFE_{\text{cell}}^0 / RT)$ (iii)

At 298 K, eq. (ii) can be written as,

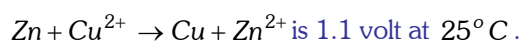
$$0 = E_{\text{cell}}^0 - \frac{0.0592}{n} \log K_c$$

This gives, $\log K_c = (nE_{\text{cell}}^0 / 0.0592)$

$$K_c = 10^{(nE_{\text{cell}}^0 / 0.0592)} \quad \text{..... (iv)}$$

eq. (iii) and (iv) may be used for obtaining the value of the equilibrium constant from the E_{cell}^0 value.

Example : 32 The standard *emf* for the cell reaction



The *emf* for the cell reaction, when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solution are used, at 25°C is

[MNR 1994, Manipal PMT 2001]

- (a) 1.10 V (b) 0.10 V (c) -1.10V (d) -0.110 V

Solution : (a) $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right]$

$$E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log \left[\frac{0.1}{0.1} \right]$$

$$E_{\text{cell}} = 1.10 \text{V} \quad (\because \log 1 = 0)$$

Example : 33 The hydrogen electrode is dipped in a solution of pH 3 at 25°C . The potential of the cell would be (the value of $2.303RT/F$ is 0.059V)

[KCET 1993]

- (a) 0.177 V (b) -0.177 V (c) 0.087 V (d) 0.059 V

Solution : (b) $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$

$$E = E^0 - \frac{0.0591}{n} \log \frac{P_{\text{H}_2}^{1/2}}{[\text{H}^+]} \left\{ \begin{array}{l} \because \text{Because pressure is not given} \\ \text{So } [\text{H}_2] = 1 \text{ then} \end{array} \right\}$$

Electrochemistry

$$= E^0 - 0.0591 \log \frac{1}{[H^+]} = E^0 - 0.0591 pH \left(\because pH = \log \frac{1}{[H^+]} \right) = 0 - 0.0591 \times 3 = -0.177V$$

Example : 34 E^0 for the cell $Zn / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu$ is 1.10V at 25°C. The equilibrium constant for the reaction $Zn + Cu^{2+}_{(aq)} \rightleftharpoons Cu + Zn^{2+}_{(aq)}$ is of the order of [CBSE PMT 1997]

- (a) 10^{-28} (b) 10^{-37} (c) 10^{+18} (d) 10^{37}

Solution : (d) $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu; E^0 = 1.10V$

$$E = E^0 - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium $E = 0$ and $\frac{[Zn^{2+}]_{eqm}}{[Cu^{2+}]_{eqm}} = K$

$$\therefore 0 = 1.10 - \frac{0.0591}{2} \log K \text{ or } 1.10 = \frac{0.0591}{2} \log K \text{ or } K = 1.94 \times 10^{37}$$

Example : 35 For the half cell reaction, $H^+(aq) + e \rightarrow \frac{1}{2} H_2(g)_{1atm}$

- (a) $E(H^+ / H_2) = -59.2mV \times pH$ (b) $E^0(H^+ / H_2) = -59.2mV \times pH$
 (c) $E^0(H^+ / H_2) = pH \log [H^+]$ (d) $E(H^+ / H_2) = -pH \log [H^+]$

Solution : (a) $E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0592}{1} \log \frac{P_{H_2}^{1/2}}{[H^+]}$

Because SHE = 0; then, $= 0 + 0.0592 \log [H^+] = -0.0592 pH = -59.2 mV \times pH$ ($mV = \text{milli Volt}$)

Example : 36 A Galvanic cell is constructed as follows. A half- cell consists of a platinum wire immersed in a solution containing 1.0 M of Sn^{2+} and 1.0M of Sn^{4+} and another half- cell has a thallium rod immersed in a 1.0 M solution of Tl^+

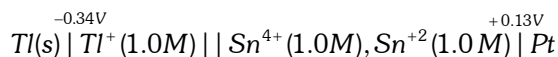
Given $Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq); E^0 = +0.13V$

and $Tl^+(aq) + e \rightarrow Tl(s); E^0 = -0.34V,$

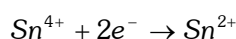
What is the cell voltage if the Tl^+ concentration is increased tenfold

- (a) 0.411V (b) 4.101 V (c) 0.492 V (d) 0.222 V

Solution : (a) The cell is represented as



The cell reaction is $[Tl(s) \rightarrow Tl^+ + e \times 2]$



Overall reaction : $2Tl(s) + Sn^{4+} \rightarrow 2Tl^+ + Sn^{2+}$ [Concentration (Tl^+) = (10M), (Sn^{2+}) = 1M, (Sn^{4+}) = 1M]

$$E = (E^0_R - E^0_L) - \frac{0.0592}{2} \log \frac{[Tl^+]^2 [Sn^{2+}]}{[Sn^{4+}]}$$

$$= 0.47V - 0.0296 \log (10)^2 \quad [Tl^+ \text{ concentration increases tenfold}]$$

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$$= 0.47 - 0.0592 = 0.411V$$

Relationship between cell potential, Gibbs Energy and Equilibrium constant .

The electrical work (electrical energy) is equal to the product of the *EMF* of the cell and electrical charge that flows through the external circuit *i.e.*,

$$\boxed{W_{\max} = nFE_{\text{cell}}}$$
(i)

According to thermodynamics the free energy change (ΔG) is equal to the maximum work. In the cell work is done on the surroundings by which electrical energy flows through the external circuit, So

$$-W_{\max} = \Delta G$$
(ii)

from eq. (i) and (ii) $\boxed{\Delta G = -nFE_{\text{cell}}}$

In standard conditions $\boxed{\Delta G^0 = -nFE_{\text{cell}}^0}$

Where ΔG^0 = standard free energy change

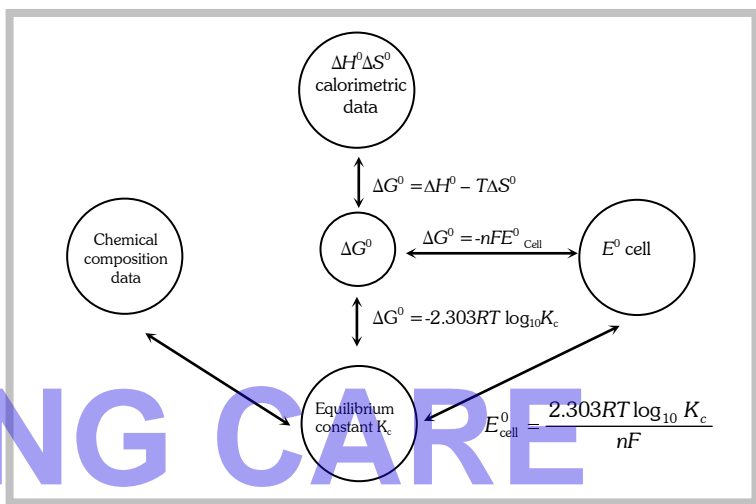
But $E_{\text{cell}}^0 = \frac{2.303}{nF} RT \log K_c$

$$\therefore \Delta G^0 = -nF \times \frac{2.303}{nF} RT \log K_c$$

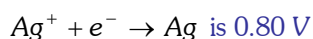
$$\boxed{\Delta G^0 = -2.303 RT \log K_c}$$

$$\Delta G^0 = -2.303 RT \log K_c$$

$$\Delta G^0 = -RT \ln K_c \quad (2.303 \log X = \ln X)$$



Example : 37 Calculate the standard free energy change for the reaction, $2Ag + 2H^+ \rightarrow H_2 + 2Ag^+$ E^0 for



[ISM Dhanbad 1994]

- (a) +154.4kJ (b) +308.8kJ (c) -154.4kJ (d) - 308.8kJ

Solution : (a) For the given reaction $E_{\text{cell}}^0 = -0.80V$

$$\Delta G = -nFE_{\text{cell}}^0 = -2 \times 96500 \times (-0.80)J = 154400J = 154.4kJ$$

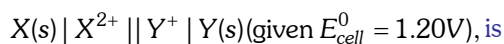
Example : 38 The standard *EMF* of Daniell cell is 1.10 volt. The maximum electrical work obtained from the Daniell cell is

[MP PET 2002]

- (a) 212.3kJ (b) 175.4 kJ (c) 106.15 kJ (d) 53.07kJ

Solution : (a) Electrical work obtained $= -W_{\max} = \Delta G = -nE_{\text{cell}}^0 F = 2 \times 96500 \times (1.1)J = 212300J = 212.3kJ$

Example: 39 The logarithm of the equilibrium constant, $\log K_{\text{eq}}$, of the net cell reaction of the cell,



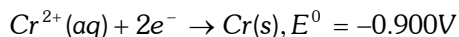
- (a) 47.2 (b) 40.5 (c) 21.4 (d) 12.5

Solution : (b) $\Delta G^0 = -nE^0 F = -RT \ln K_{\text{eq}} \Rightarrow \ln K_{\text{eq}} = \frac{nE^0 F}{RT} = \frac{nE^0}{RT/F}$

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$$\log K_{eq} = \frac{nE^0}{2.303 \frac{RT}{F}} = \frac{nE^0}{0.0592} \text{ (at } 25^\circ \text{C)}; \log K_{eq} = \frac{2 \times 1.20}{0.0592} = 40.5$$

Example : 40 Give that at 25°C , for $\text{Cr}^{3+}(\text{aq}) + e^- \rightarrow \text{Cr}^{2+}(\text{aq})$, $E^0 = -0.424\text{V}$



find E^0 at 25°C for $\text{Cr}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Cr}(\text{s})$

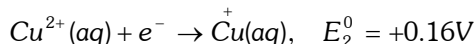
(a) -0.741V (b) $+0.741\text{V}$ (c) -1.324V (d) -0.476V

Solution : (a) Adding the first two reactions, we get the third equation and using the free energy concept, we have

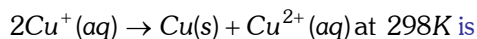
$$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0; -n_1 E_1^0 F - n_2 E_2^0 F = -n_3 E_3^0 F \quad (n = \text{number of electron involved})$$

$$E_3^0 = \frac{n_1 E_1^0 + n_2 E_2^0}{n_3} = \frac{1 \times (-0.424) + 2 \times (-0.900)}{3} = -0.741\text{V}$$

Example : 41 Given the half - cell reactions, $\text{Cu}^+(\text{aq}) + e^- \rightarrow \text{Cu}(\text{s}), E_1^0 = +0.52\text{V};$

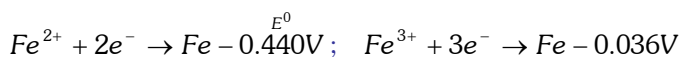


the equilibrium constant for the disproportionation reaction



Solution : (a) 6×10^4 (b) 6×10^6 (c) 1.2×10^6 (d) 1.2×10^{-6}
 (c) $E^0 = E_1^0 - E_2^0 = 0.52 - 0.16 = 0.36\text{V}$
 $\log K_{eq} = \frac{nE^0}{0.0592} = \frac{1 \times 0.36}{0.0592} = 6.081, \therefore K_{eq} = 1.20 \times 10^6$

Example : 42 Given standard electrode potentials

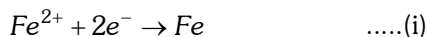


The standard electrode potential (E^0) for $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ is

[AIIMS 1982]

(a) -0.476V (b) -0.404V (c) $+0.404\text{V}$ (d) $+0.772\text{V}$

Solution : (d) $\Delta G^0 = -nFE^0$



$$\Delta G^0 = -2 \times F \times (-0.440\text{V}) = 0.880F;$$



$\Delta G^0 = -3 \times F \times (-0.036) = 0.108F$, On subtracting equation (i) from equation (ii) we get

$$\Delta G^0 = 0.108F - 0.880F = -0.772F$$

$$E^0 \text{ for the reaction} = \frac{\Delta G^0}{nF} = -\frac{(-0.772F)}{1 \times F} = +0.772\text{V}$$

Electrochemical series .

(1) The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing or decreasing order of their reduction potentials. The arrangement of elements in order of increasing reduction potential values is called **electrochemical series**.

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The electrochemical series, also called **activity series**, of some typical electrodes is being given in Table.

Standard reduction electrode potentials at 298K

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E^0 , volt
Li	$\text{Li}^+ + e^- = \text{Li}$	-3.05
K	$\text{K}^+ + e^- = \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e^- = \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^- = \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^- = \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3e^- = \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2e^- = \text{Zn}$	-0.7628
Cr	$\text{Cr}^{3+} + 3e^- = \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2e^- = \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2e^- = \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2e^- = \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2e^- = \text{Sn}$	-0.14
H_2	$2\text{H}^+ + 2e^- = \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2e^- = \text{Cu}$	+0.337
I_2	$\text{I}_2 + 2e^- = 2\text{I}^-$	+0.535
Ag	$\text{Ag}^+ + e^- = \text{Ag}$	+0.799
Hg	$\text{Hg}^{2+} + 2e^- = \text{Hg}$	+0.885
Br_2	$\text{Br}_2 + 2e^- = 2\text{Br}^-$	+1.08
Cl_2	$\text{Cl}_2 + 2e^- = 2\text{Cl}^-$	+1.36
Au	$\text{Au}^{3+} + 3e^- = \text{Au}$	+1.50
F_2	$\text{F}_2 + 2e^- = 2\text{F}^-$	+2.87

(2) Characteristics of Electrochemical series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with *SHE* acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is -0.76 volt, When zinc electrode is joined with *SHE*, it acts as anode ($-ve$ electrode) i.e., oxidation occurs on this electrode. Similarly, the $+ve$ sign of standard reduction potential indicates that the electrode when joined with *SHE* acts as cathode and reduction occurs on this electrode.

(ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances, which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative value of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

(3) Application of Electrochemical series

(i) **Reactivity of metals:** The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active. The *chemical*

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reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like *Fe, Pb, Sn, Ni, Co*, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like *Cu, Ag* and *Au* which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) **Electropositive character of metals** : The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups

(a) *Strongly electropositive metals* : Metals having standard reduction potential near about -2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

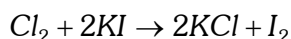
(b) *Moderately electropositive metals* : Metals having values of reduction potentials between 0.0 and about -2.0 volt are moderately electropositive *Al, Zn, Fe, Ni, Co*, etc., belong to this group.

(c) *Weakly electropositive* : The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. *Cu, Hg, Ag*, etc., belong to this group.

(iii) Displacement reactions

(a) *To predict whether a given metal will displace another, from its salt solution*: A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) *Displacement of one nonmetal from its salt solution by another nonmetal*: A non-metal higher in the series (towards bottom side), i.e., having high value of reduction potential will displace another non-metal with lower reduction potential, i.e., occupying position above in the series. The non-metal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential,. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.



[The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.]

(c) *Displacement of hydrogen from dilute acids by metals* : The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.



The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

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The metals which are below hydrogen in electrochemical series like *Cu, Hg, Au, Pt*, etc., do not evolve hydrogen from dilute acids.

(d) **Displacement of hydrogen from water** : Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series. Alkali and alkaline earth metals liberate hydrogen from cold water but *Mg, Zn* and *Fe* liberate hydrogen from hot water or steam.

(iv) **Reducing power of metals**: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases, as the standard reduction potential becomes more and more negative. Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron. (decreasing order of reducing nature)

Element:	<i>Na</i>	>	<i>Zn</i>	>	<i>Fe</i>
Reduction potential:	- 2.71		- 0.76		- 0.44

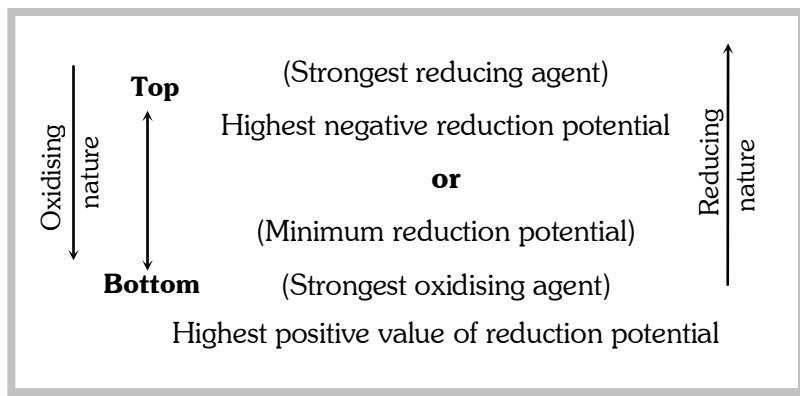
Alkali and alkaline earth metals are strong reducing agents.

(v) **Oxidising nature of non-metals** : Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. Thus, oxidising nature increases from top to bottom in the electrochemical series. The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

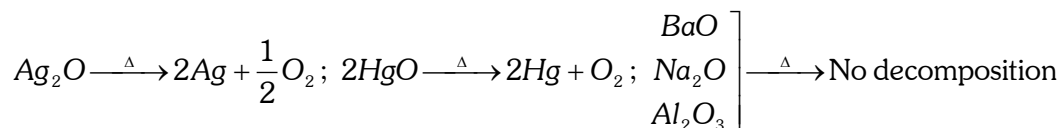
*F*₂ (Fluorine) is a stronger oxidant than *Cl*₂, *Br*₂ and *I*₂. *Cl*₂ (Chlorine) is a stronger oxidant than *Br*₂ and *I*₂

Element :	<i>I</i> ₂	<i>Br</i> ₂	<i>Cl</i> ₂	<i>F</i> ₂
Reduction potential :	+ 0.53	+ 1.06	+ 1.36	+ 2.85
	→ Oxidising nature increases →			

Thus, in **electrochemical series**



(vi) **Thermal stability of metallic oxides** : The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.



(vii) **Extraction of metals** : A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of *Ag* and *Au* by cyanide process. silver from the solution

containing sodium argento cyanide, $\text{NaAg}(\text{CN})_2$, can be obtained by the addition of zinc as it is more electro-positive than Ag. $2\text{NaAg}(\text{CN})_2 + \text{Zn} \rightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$

Corrosion.

(1) When metals are exposed to atmospheric conditions, they react with air or water in the environment to form undesirable compounds (usually oxides). This process is called **corrosion**. Almost all metals except the least active metals such as gold, platinum and palladium are attacked by environment i.e., undergo corrosion. For example, silver tarnishes, copper develops a green coating, lead or stainless steel lose their lustre due to corrosion. Corrosion causes enormous damage to building, bridges, ships and many other articles made of iron.

Thus **corrosion** is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.

In case of iron, corrosion is called rusting. Chemically, rust is hydrated form of ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Rusting of iron is generally caused by moisture, carbon dioxide and oxygen present in air. It has been observed that rusting takes place only when iron is in contact with moist air. Iron does not rust in dry air and in vacuum.

(2) **Factors which affect corrosion** : The main factors which affect corrosion are

(i) **Position of metals in emf series** : The reactivity of metal depends upon its position in the electrochemical series. More the reactivity of metal, the more will be the possibility of the metal getting corroded.

(ii) **Presence of impurities in metals** : The impurities help in setting up voltaic cells, which increase the speed of corrosion

(iii) **Presence of electrolytes** : Presence of electrolytes in water also increases the rate of corrosion. For example, corrosion of iron in sea water takes place to larger extent than in distilled water.

(iv) **Presence of CO_2 in water** : Presence of CO_2 in natural water increase rusting of iron. Water containing CO_2 acts as an electrolyte and increases the flow of electrons from one place to another

(v) **Presence of protective coatings** : When the iron surface is coated with layers of metals more active than iron, then the rate of corrosion is retarded. For example, coating of zinc on iron prevents rusting.

(vi) **Temperature** : A rise in temperature (within a reasonable limit) increases the rate of corrosion.

(3) **Classification of corrosion process** : Depending upon the nature of corrosion, and the factors affecting it, the corrosion may be classified as follows.

(i) **Chemical corrosion** : Such corrosion, generally takes place when

(a) Reactive gases come in contact with metals at high temperatures e.g., corrosion in chemical industry.

(b) Slow dissolution of metal takes place when kept in contact with non conducting media containing organic acids.

(ii) **Bio-chemical corrosion or Bio-corrosion**: This is caused by the action of microorganisms. Soils of definite composition, stagnant water and certain organic products greatly favour the bio-corrosion.

(iii) **Electrochemical corrosion** : It occurs in a gaseous atmosphere in the presence of moisture, in soils and in solutions. For example, the following corruptions are electrochemical in nature

(a) Corrosion of insoluble anodes

(b) Corrosion of pipelines with current carrying liquids flowing through them.

(c) Corrosion of underground metal structure

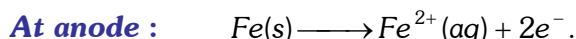
(4) **Mechanism of rusting of iron : Electrochemical theory of rusting**. The phenomenon of corrosion can be explained with the help of electrochemical theory which involves oxidation and reduction reactions. According to electrochemical theory of corrosion, it is believed that non-uniform surface of metal or impurities

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present in iron behave like small electric cells (**called corrosion couples**) in the presence of water containing dissolved oxygen or carbon dioxide. A film of moisture with dissolved CO_2 constitutes electrolytic solution covering the metal surface at various places. The schematic representation of mechanism of rusting of iron is shown in Fig.

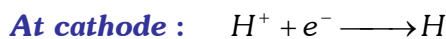
In the small electrolytic cells, pure iron acts as anode while cathodes are impure portions. The overall rusting involves the following steps,

(i) Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidised to ferrous ions.



Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.

(ii) At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^+ ions are obtained either from water or from acidic substances (e.g. CO_2) in water

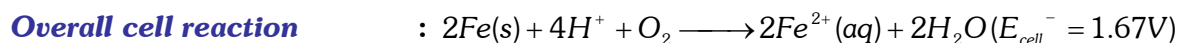
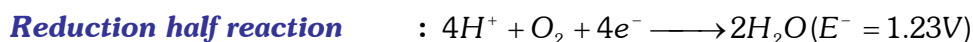
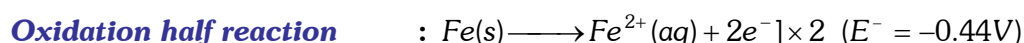


The hydrogen atoms on the iron surface reduce dissolved oxygen. $4\text{H} + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$

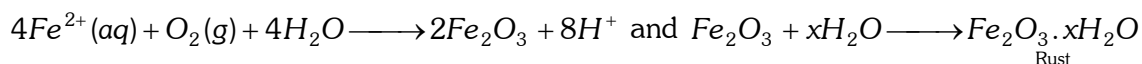
Therefore, the overall reaction at cathode of different electrochemical cells may be written as,



(iii) The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalise number of electrons lost and gained i.e.



The ferrous ions are oxidised further by atmospheric oxygen to form rust.

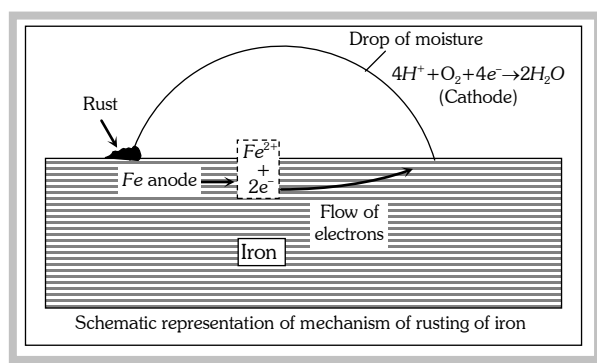


It may be noted that salt water accelerates corrosion. This is mainly due to the fact that salt water increases the electrical conduction of electrolyte solution formed on the metal surface. Therefore, rusting becomes more serious problem where salt water is present.

(5) Corrosion protection : Corrosion of metals can be prevented in many ways. Some commonly used methods are described below.

(i) By surface coating : Corrosion of metals can be prevented by coating their surfaces with any of the following

(a) By applying, oil, grease, paint or varnish on the surface.



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(b) By coating/depositing a thin layer of any other metal which does not corrode. For example, iron surface can be protected from corrosion by depositing a thin layer of zinc, nickel or chromium on it. Copper/brass can be protected by coating it with a thin layer of tin. Tinning of brass utensils is a very common practice in our country.

(c) *By Galvanization* : Prevention of corrosion of iron by Zn coating.

(ii) **By connecting metal to a more electropositive metal** : A metal can be protected from corrosion by connecting it to a more electropositive metal. As long as the more electropositive metal is there, the given metal does not get corroded. For example, iron can be protected from corrosion by connecting it to a block/plate of zinc or magnesium. This method of corrosion protection is called **cathodic protection**.

(iii) **By forming insoluble phosphate or chromate coating** : Metal surfaces are treated with phosphoric acid to form an insoluble phosphate **By connecting metal to a more** coating on the surface. This phosphate coating protects the metal from corrosion. Formation of a thin chromate layer also prevents the corrosion of metals.

(iv) **Using anti – rust solutions** : To retard the corrosion of iron certain anti – rust solutions are used. For example, solutions of alkaline phosphates and alkaline chromates are generally used as anti – rust solutions. Due to the alkaline nature of these solutions, the H^+ ions are removed from the solutions, and rusting is prevented. For example, iron articles are dipped in boiling alkaline sodium phosphate solutions, when a protective insoluble sticking film of iron phosphate is formed.

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