

Chapter-3

ELECTRO CHEMISTRY

Oxidation-Reduction

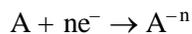
(1) **Oxidation** is a process which liberates electrons, i.e., **de-electronation**

(2) **Reduction** is a process which gains electrons, i.e., **electronation**.

Oxidation



Reduction



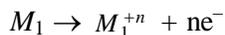
(3) Oxidants are substances which :

- (a) oxidize other substances
- (b) are reduced themselves
- (c) show electronation
- (d) show a decrease in oxidation no. during a redox change.
- (e) has higher oxidation no. in a conjugate pair redox reaction.

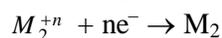
(4) Reductants are substances which

- (a) reduce other substances
- (b) are oxidized themselves
- (c) show de-electronation
- (d) show an increase in oxidation no. during a redox reaction
- (e) have lower oxidation no. in a conjugate pair of redox reaction

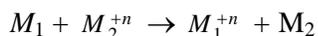
(5) A redox reaction is one in which a reductant is oxidized to liberate electrons, which are then used up by an oxidant to get itself reduced.



Oxidation



Reduction



Redox reaction

(6) In a redox reaction the oxidation and reduction is simultaneous.

Oxidation and Reduction can also be defined in many ways,

(i) Removal of hydrogen atoms is oxidation while addition of hydrogen atoms is reduction. For example,



Cl₂ is reduced to HCl



H₂S is oxidised to S

(ii) Addition of oxygen is oxidation, while removal of oxygen is reduction. For example



C is oxidised to CO₂



CuO is reduced to Cu

(iii) Increase in valency of an element is oxidation, while decrease in valency of an element is reduction.



change in valency of Fe²⁺ → Fe³⁺



change in valency of Mn⁺⁷ → Mn⁺⁴

(iv) Addition of an electronegative element is oxidation while its removal is reduction. For example,



(oxidation of Na)



(reduction of Fe)

(v) Addition of electropositive element is reduction while its removal is oxidation. For example,

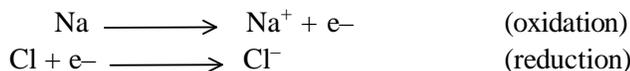


(reduction of HgCl₂)

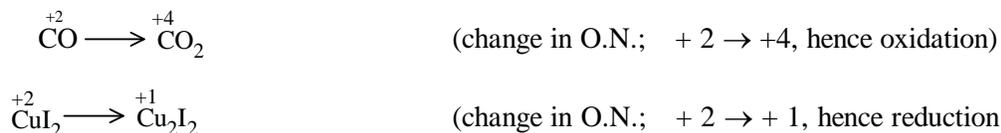


(oxidation of Fe in K₄ [Fe(CN)₆])

(vi) According to Franklin, removal or loss of electrons (de-electronation) is oxidation, while addition or gain of electrons (electronation) is reduction. For example



(vii) Increase in oxidation number is oxidation, while decrease in oxidation number is reduction. For example,



Oxidation Number

- (1) Oxidation No. of an element in a particular compound represents the no. of electrons lost or gained by an element during its change from free state into that compound or Oxidation No. of an element in a particular compound represent the extent of oxidation or reduction of an element during its change from free state into that compound.
- (2) Oxidation No. is given positive sign if electrons are lost. Oxidation No. is given negative sign if electrons are gained.
- (3) Oxidation No. represents real charge in case of ionic compounds. However, in covalent compounds it represents imaginary charge.

Rules for Deriving Oxidation Number

Following rules have been arbitrarily adopted to decide oxidation no. of elements on the basis of their periodic properties.

- (1) In uncombined state or free state, oxidation no. of an element is zero.
- (2) In combined state oxidation no. of
 - (a) F is always -1 .
 - (b) O is -2 . In peroxides it is -1 , in super oxides $-\frac{1}{2}$. However in OF_2 it is $+2$ and O_2F_2 it is $+1$.
 - (c) H is $+1$. In ionic hydrides it is -1 .
 - (d) Metals are always $+ve$.
 - (e) Alkali metals (i.e. I A group – Li, Na, K, Rb, Cs and Fr) is always $+1$.
 - (f) Alkaline earth metals (i.e. II A group – Be, Mg, Ca, Sr, Ba and Ra) are always $+2$.
- (3) The algebraic sum of all the oxidation no. of all the elements in a compound is equal to zero, e.g., K_2CrO_4 (Ox. No. of K) $\times 2$ + (Ox. No. of Cr) + (Ox. No. of O) $\times 4 = 0$
- (4) The algebraic sum of oxidation no. of all the elements in an ion is equal to the net charge on the ion, e.g., in SO_4^{2-} Ox No. of S + (OX - No. O) $\times 4 = -2$.
- (5) Oxidation number can be integer or fraction, (+)ve or (–)ve.

1. **Oxidation number of Mn in KMnO_4 .** Let the oxidation number of Mn be x. Now we know that the oxidation numbers of K is $+1$ and that of O is -2 .

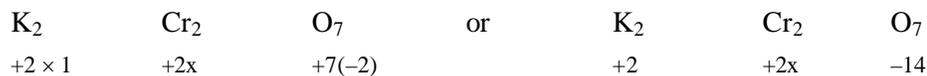


Now to the sum of oxidation numbers of all atoms in the formula of the compound must be zero, i.e.

$$+1 + x - 8 = 0$$

Hence the oxidation number of Mn in KMnO_4 is $+7$.

-
2. **Oxidation number of chromium in potassium dichromate.** Writing the known oxidation number of potassium and oxygen



Since sum of oxidation numbers = 0, i.e.

$$2 + 2x - 14 = 0$$

$$2x = 14 - 2$$

$$x = +6$$

3. Oxidation number of S in S_8 . Since in S_8 , sulphur is present in free state, its oxidation number is zero.

Formal Charge

Formal charge on an atom in a compound can be defined as the calculated charge present on the atom in a compound. Thus the formal charge present on nitrogen atom in NH_4^+ ion is +1, and that on nitrogen and boron atoms in the coordination compound $H_3N \rightarrow BF_3$ is +1 and -1 respectively. The formal charge can be calculated as below.

$$\text{Formal charge} = z - u - \frac{1}{2}s$$

Where z = Number of outer (valence shell) electrons in the atom.

u = Number of unshared electrons

s = Number of shared electrons around the atom in the compound

$$\text{Thus the formal charge on nitrogen atom in } NH_4^+ (z = 5, u = 0, s = 8) = 5 - 0 - \frac{1}{2} \times 8 = 1$$

$$\text{Similarly, formal charge on S in } SO_2 = 6 - 2 - \frac{1}{2} \times 4 = 2$$

Balancing of Redox Equations by Oxidation State Method

This method is based on the fact that the number of electrons gained during reduction must be equal to the number of electrons lost during oxidation. Following steps must be followed while balancing redox equations by this method.

- Write the skeleton equation (if not given, frame it) representing the chemical change.
- With the help of oxidation number of elements, find out which atom is undergoing oxidation/reduction, and write separate equations for the atom undergoing oxidation/reduction.
- Add the respective electrons on the right for oxidation and on the left for reduction equation. Note that the net charge on the left and right sides should be equal.
- Multiply the oxidation and reduction reactions by suitable integers so that total electrons lost in one reaction is equal to the total electrons gained by other reaction.
- Transfer the coefficients of the oxidising and reducing agents and their products as determined in the above step to the concerned molecule or ion.
- By inspection, supply the proper coefficient for the other formulae of substances not undergoing oxidation and reduction to balance the equation.

Balancing of Redox equation by Ion-Electron Method

This method involves the following steps

- Divide the complete equations into two half reactions
 - One representing oxidation
 - The other representing reduction
-

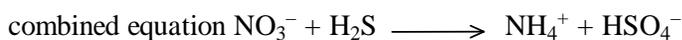
-
- II Balance the atoms in each half reaction separately according to the following steps
- Balance all atoms other than oxygen and hydrogen
 - To balance oxygen and hydrogen
 - Acidic Medium
 - Add H_2O to the side which is oxygen deficient to balance oxygen atoms
 - Add H^+ to the side which is hydrogen deficient to balance H atoms
 - Basic Medium
 - Add H_2O to the side which is oxygen deficient to balance oxygen atoms
 - Add same number of H_2O to the side following short of hydrogen eg. If 2H is excess add $2\text{H}_2\text{O}$ to the other side.
 - Add same number of OH^- to the opposite side *i.e.* 2OH^- to the other side.

Examples

1. To balance the reaction of



Here NO_3^- is undergoing reduction to NH_4^+ and H_2S undergoes oxidation



In this equation all atoms are balanced except O and H.

Adding H_2O to the side which is O deficient, we get

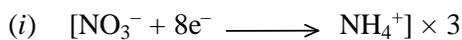


Adding now H^+ ions to balance H atoms we get



2. To balance $\text{NO}_3^- + \text{Al} \longrightarrow \text{Al}^{3+} + \text{NH}_4^+$ in basic medium

Here NO_3^- is undergoing reduction and Al^{3+} is undergoing oxidation



Adding we get after correspondingly multiplying with numbers to see that number of e^- lost and gained are same we get



Since all other atoms are balanced add OH^- to side which has less -ve charge and H_2O to the side which is oxygen deficient,



Electrical Conductors

Substances which allow the flow of current are called electrical conductors. The conductors are broadly classified into two categories.

(i) Metallic Conductors

(ii) Electrolytic Conductors

(i) **Metallic Conductors** : In these conductors conduction of electricity is due to the movement of free electrons from a higher negative potential to a lower one *without producing chemical change*.
e.g. Metals, alloys, graphite, certain solid salts like CuS , CdS etc.

(ii) **Electrolytic Conductors** : Here current flows due to the migration of ions towards oppositely charged electrodes and is accompanied by chemical changes at electrodes. *e.g.* Molten Salts, aqueous salt solutions, acids and bases etc.

Difference Between Metallic and Electrolytic Conduction

Electronic or Metallic Conduction	Electrolytic Conduction
1. Passage of current due to flow of electrons.	1. Passage of current due to movement of ions
2. Only physical change take place	2. Physical and chemical changes both take place
3. No transfer of matter takes place	3. Transfer of matter takes place
4. Metallic conduction decreases with temperature	4. Electrolytic conduction increases with temperature (Decrease in viscosity takes place)

Electrolysis

The phenomenon in which passage of current through an electrolyte brings in chemical changes involving **electronation** (reduction) as well as **de-electronation** (oxidation) of ions is known as electrolysis

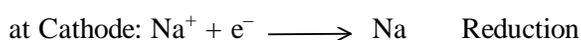
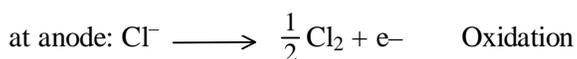
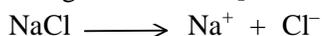
Chemical Changes During Electrolysis

The products formed during electrolysis depends upon.

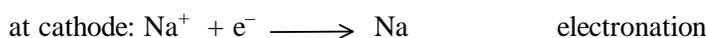
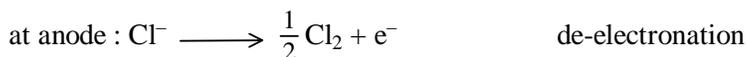
- (1) Nature of electrodes (reacting or non-reacting electrode)
- (2) Nature of electrolyte (molten or aqueous)
- (3) Concentration of solution used

Case A : Electrolysis of Molten NaCl.

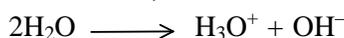
Using Pt electrode [when electrode does not react, (inert electrode)]



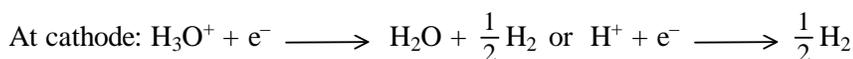
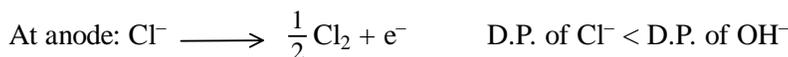
Case B : Electrolysis of Molten NaCl (using Hg electrode)



Case C : Electrolysis of aqueous NaCl. Using Pt electrode

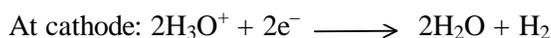


Sub Case (i) Concentrated NaCl Solution



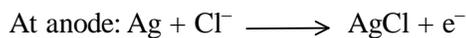
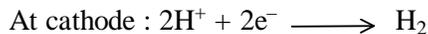
DP of H_3O^+ or H^+ < D.P. of Na^+

Sub Case (ii) Very Dilute Solution of NaCl



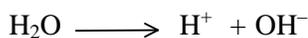
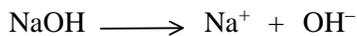
Case D : Electrolysis of aqueous NaCl using Ag electrode

Here the reactions are very similar to that using Pt electrode i.e.

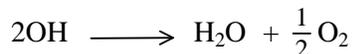
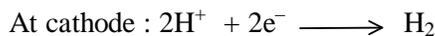


Here the D.P. of H^+ < D.P. of Na^+

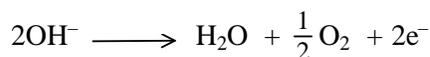
Case E : Electrolysis of aqueous solution of NaOH



Here sodium hydroxide provides the conducting medium. However the main reactions are



overall anodic reaction



Note

1. The phenomenon of electrolysis occurs only at the electrodes.
2. In case of two are more similar ions to be discharged, the higher is the discharge potential of an ion, lesser is its tendency to get itself discharged at the electrodes.
3. The discharge of ions at different electrodes takes place only for the time electricity is passed
4. If electrodes which can be attacked are used, the anode metal gets dissolved whereas deposition of metal occurs at cathode and thus no change in conc. of a solution is noticed.
5. The electrolytic solution remains electrically neutral during electrolysis since same equivalents of charge are neutralized at opposite electrodes.
6. A minimum emf is required for the electrolysis of a solution *e.g.* in the case of formation of H_2 and Cl_2 from a brine solution under standard condition, a minimum emf of 2.19 V is required

A quick reference of electrolysis is given below

Electrolyte	Electrode	Cathode Reaction	Anode Reaction
1. Molten NaCl.	Pt.	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	$\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$
2. Molten NaCl	Hg.	$2\text{Na}^+ + \text{e}^- \rightarrow 2\text{Na}$ $2\text{Na} + \text{Hg} \rightarrow 2\text{Na-Hg}$	$\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$
3. Aqueous NaCl	Pt.	$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{H}_2$ $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	$\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$
4. Aqueous NaCl	Hg	$2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}$ $2\text{Na} + \text{Hg} \rightarrow 2\text{Na-Hg}$ $2\text{Na-Hg} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH}$ $+ \text{H}_2 + \text{Hg}$	$\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$
5. Very dilute NaCl solution	Pt.	$2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{H}_2$	$2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$

Electrolyte	Electrode	Cathode Reaction	Anode Reaction
6. Aqueous HCl	Pt.	$2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{H}_2$	$\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$
7. aq. NaNO_3 or	Pt.	$2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{H}_2$	$2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$
8. aq. CuSO_4	Pt.	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$
Same is electrolysis of AgNO_3 using Pt as electrode.			
9. aq. AgNO_3	Ag.	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$
10. aq. CuCl_2	Pt.	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$
11. aq. CuCl_2	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
12. H_2SO_4 (Normal current density)	Pt.	$2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{H}_2$ or $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	$2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$
13. H_2SO_4 (High current density)	Pt.	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	$2\text{HSO}_4^- \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$

Application of Electrolysis

1. Extraction of Metals : e.g. alkali metals, alkaline earth metals and Al.
2. Preparation of Chemicals : e.g. NaOH , Cl_2 , H_2O_2 , F_2 , KMnO_4
3. Corrosion and its prevention
4. Electroplating
5. Purification of Metals

Faraday's Law

First Law : The amount (w) of an ion oxidised or reduced at either electrode during the passage of current (*i.e.* during electrolysis) is directly proportional to the quantity of electricity passed through electrolyte solution

$$W \propto Q. \quad \therefore Q = I \times t$$

$$W \propto I \times t \quad \Rightarrow \quad W = zIt$$

I = current strength in amperes

t = time in seconds

Where Q is total charge (electricity) passed through solution in coulombs and Z is electrochemical equivalent of the substance

$$\text{Unit of } Z = \text{g C}^{-1}$$

Points to Remember

- (a) One equivalent of substance (weighing equal to g eq. wt.) is deposited when 96500 C of electricity is passed through an electrolyte
- (b) 96500 C = 1 Faraday = charge on 1 mole of electrons *i.e.* charge on electron = 1.602×10^{-19} C
- (c) 96500 C deposits E g (E = Eq. wt)

$$\Rightarrow 1 \text{ coulomb deposits } \frac{E}{96500} = Z \text{ (electrochemical equivalent)}$$

- (d) Number of equivalent deposited = number of Faradays electricity passed

$$\frac{W}{E} = \frac{Q \text{ (coulombs)}}{96500} = \frac{Q}{F}$$

Second Law of Electrolysis : It states that the ratio of the weights of the substances deposited at any electrode is in the ratio of their chemical equivalents, provided same amount of electricity is passed through the electrolytes.

$$\frac{E_1}{E_2} = \frac{W_1}{W_2} \quad \text{or} \quad \frac{W_1}{E_1} = \frac{W_2}{E_2}$$

Thus the number of equivalents of substances deposited at various electrodes are equal provided same quantity of electricity is passed through different electrolytes

$$\text{Also, } \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$$

$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2}$$

This implies that the ratio of the weights of substances deposited will be in the ratio of their electrochemical equivalents.

Conductance of Solution

Electrolytic solutions behave just like metallic conductors and obey ohm's law, which relates EMF, applied to a conductor and the strength of the current flowing through it.

According to ohm's law $I = V/R$

The resistance of any uniform conductor varies directly as its length (l meter) and inversely to its area of cross section (A meter²)

$$\text{i.e. } R \propto \frac{l}{A} \Rightarrow R = \rho \times \frac{l}{A}$$

ρ (rho) = Sp. resistance or resistivity units = ohm meter⁻¹

Specific conduction or conductivity of any conductor is defined as the reciprocal of specific resistance

$$\frac{1}{R} = \frac{1}{\rho} \times \frac{A}{l}$$

where $\frac{1}{R}$ = conductance and $\frac{1}{\rho}$ = specific conductance

$$\Rightarrow \text{Conductance} = \text{Specific conductance} \times \frac{A}{l} \quad \text{or} \quad \text{conductance} \times \frac{l}{A} = \text{specific conductance}$$

$$\text{Conductance} \times \text{cell constant} = \text{specific conductance or conductivity}$$

Specific conductance is defined as conductance of a material of a unit length and unit area of cross section.

Alternatively specific conductance is conductance of one cubic metre of material or solution.

$$\text{Hence specific conductance} = \frac{\text{Conductance}}{\text{Volume of solution}}$$

$$\text{or} \quad \text{Conductance} = \text{Specific conductance} \times \text{Volume}$$

Equivalent Conductance :

The conductance observed when a given volume(V) of an electrolyte solution contains one equivalent of the substance.

$$i.e. \quad \wedge_{eq} = K \times V$$

$$\text{However if } (C_{eq} \text{ are present in } V \text{ ml of solutions then } \wedge_{eq} = \frac{K \times V}{C_{eq}}$$

However if C_{eq} equivalents are present in 1 litre of solutions then

$$\wedge_{eq} = K \times \frac{1000}{C_{eq}} = \frac{K \times 1000}{N}$$

(Because number of equivalent in 1L of solution = normality)

Molar Conductance :

It is the conducting power of all the ions present in a solution having one mole of electrolyte, in a given volume (V) of electrolyte solution.

If one mole of electrolyte is present in V ml of solution then

$$\wedge_m = KV$$

If C_{moles} of electrolytes are present in V ml of solutions then

$$\wedge_m = \frac{K \times V}{C_{moles}}$$

If C_{moles} of electrolyte are present in one litre of solution then

$$\wedge_m = \frac{K \times 1000}{C_{mole}} = \frac{K \times 1000}{M}$$

Factors Which Effect the Electrolytic Conductance

1. The inter ionic attraction (depends upon solute-solute interaction).
 2. The solvation of ions (depends upon solute - solvent interaction).
 3. The viscosity of the solvent (depends upon solvent - solvent interaction).
 4. Concentration of the solutions.
 5. Temperature.
 6. Effect of high voltage and high frequency.
-

(1) *Interionic Attraction :*

If the interionic forces of attraction are stronger then electrolytic conductance is less. because ionic mobility is reduced

(2) *Effect of Solvent :*

In solvents with low dielectric constant having small ionization effect on electrolytes the electrostatic forces of attraction between oppositely charged ions would be appreciable and there by decrease the electrolytic conductions. However solvents with high dielectric constants increase conducting capacity of the solution. Also if solvations of ions is high then electrolytic conductance decreases or becomes low.

(3) *Viscosity of Medium :*

The dependence of conductance on viscosity of medium is given by Walden's rule, which says. Electrolytic conductance (equivalent conductance) is inversely proportional to the viscosity of the medium

(4) *Concentration of Solutions :*

If the concentration of the solution increases then

- (i) Conductance increases
- (ii) Molar and equivalent conductance decreases
- (iii) Specific conductance increases

(5) *Effect of Temperature :*

The conductance of all electrolytes increase with increasing temperature. The rise in conductance with increases in temperature is due to

- (a) decrease in viscosity of solutions
- (b) increase in the speed of the ion
- (c) increase in degree of dissociation in case of weak electrolyte.

Variation of Conductance with Dilution

1. The conductance of solution increases with increase in dilution due to increase in number of ions as well as increase in ionic mobility. The term ionic mobility refers to the speed of ion under unit potential gradient.

$$\text{Speed of ion} = \frac{\text{distance travelled by ions}}{\text{time taken}} \quad (\text{units} = \text{cm sec}^{-1})$$

$$\text{Ionic mobility} = \frac{\text{Speed of ion}}{\text{Potential gradient}} \quad (\text{units} = \text{cm}^3 \text{ volt}^{-1} \text{ sec}^{-1})$$

2. The specific conductivity decreases with dilution because number of ions per ml. decreases.
 3. The molar conductance and the equivalent conductance increases with dilution because the volume of the electrolyte solution containing one mole of electrolyte or one equivalent of electrolyte increases.
-

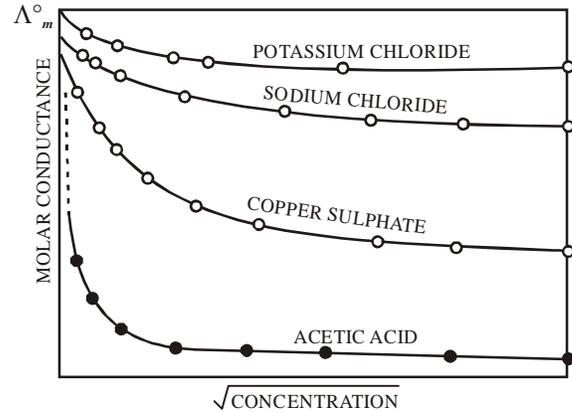
- The increase in molar/equivalent conductance for strong electrolytes is very small even at infinite dilution because degree of dissociation for strong electrolytes do not increase appreciably. It is only that the interionic forces are broken.
- The increase in the molar/equivalent conductance for weak electrolyte is very large and at infinite dilution the value shoots up. This could be attributed to the fact that upon dilution the degree of dissociation of weak electrolyte increases largely and the interionic forces of attractions also decreases.

Kohlrausch suggested that

$$\Lambda_m = \Lambda_m^0 - b\sqrt{C}$$

where Λ_m^0 = molar conductance at infinite dilution.

From this it is possible to determine the molar conductance at infinite dilutions for strong electrolytes by extrapolating the graph. For most electrolytes it is not possible to determine the molar conductance at infinite dilution. There are indirect methods for determining the molar conductance at infinite dilution for most electrolytes



Kohlrausch Law of Independent migration of Ions

The law states that at infinite dilution where ionization of all electrolytes is complete and where all interionic effects are absent, each ion migrates independently of its counter ion, and contributes a definite share to the total conductance of the electrolyte

$$\text{i.e., } \Lambda^0 = \Lambda_+^0 + \Lambda_-^0$$

$$\text{e.g. } \Lambda_{\text{KCl}}^0 = \Lambda_{\text{K}^+}^0 + \Lambda_{\text{Cl}^-}^0$$

Calculation of Λ^0 of weak electrolyte e.g. CH_3COOH

$$\Lambda_{\text{CH}_3\text{COOH}}^0 = \Lambda_{\text{CH}_3\text{COO}^-}^0 + \Lambda_{\text{H}^+}^0$$

Hence we can get the $\Lambda_{\text{CH}_3\text{COOH}}^0$ from the Λ_m^0 of strong electrolytes such as HCl, NaCl and CH_3COONa

$$\begin{aligned} \Lambda_{\text{CH}_3\text{COOH}}^0 &= \Lambda_{\text{CH}_3\text{COONa}}^0 + \Lambda_{\text{HCl}}^0 - \Lambda_{\text{NaCl}}^0 \\ &= \Lambda_{\text{H}^+}^0 + \Lambda_{\text{CH}_3\text{COO}^-}^0 \end{aligned}$$

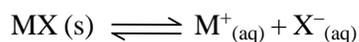
Applications of Conductance Measurements

- Degree of Ionization or dissociation :** We know that at infinite dilution electrolytes are completely dissociated and at any other concentration it is partially ionized. Thus

$$\alpha = \text{degree of dissociation} = \frac{\Lambda_m}{\Lambda_m^0} = \frac{\Lambda_{eq}}{\Lambda_{eq}^0}$$

(2) **Determination of solubility of sparingly soluble salt.**

Consider a salt



Here $K_{\text{sp}} = [\text{M}^+][\text{X}^-]$

Let K_{B} = Specific conductance of saturated solution of salt

$K_{\text{H}_2\text{O}}$ = Specific conductance of pure water

$\Rightarrow K_{\text{salt}} = \text{Specific conductance of salt only}$

$$K_{\text{salt}} = K_{\text{B}} - K_{\text{H}_2\text{O}}$$

The equivalent conductance or molar conductance is given by

$$\Lambda_{\text{eq}} = \frac{K_{\text{salt}} \times 1000}{C_{\text{eq}}} \quad \text{or} \quad \Lambda_{\text{m}} = \frac{K_{\text{salt}} \times 1000}{C_{\text{moles}}} \quad \text{or} \quad \Lambda_{\text{eq}} = \frac{K_{\text{salt}} \times 1000}{N} \quad \text{or} \quad \Lambda_{\text{m}} = \frac{K \times 1000}{M}$$

This solution can be regarded as infinitely dilute

$$\Lambda_{\text{m}}^0 = \frac{K_{\text{salt}} \times 1000}{C_{\text{moles}}} = \frac{K_{\text{salt}} \times 1000}{\text{Solubility}}$$

$$\Lambda_{\text{m}}^0 = \lambda_{+}^0 + \lambda_{-}^0$$

$$\frac{K_{\text{salt}} \times 1000}{(\lambda_{+}^0 + \lambda_{-}^0)} = \text{Concentration in moles /L} = \text{solubility}$$

By knowing the solubility in moles/L we can calculate K_{sp} of salt

The above principle can also be used for determining the

- (a) ionic product of water
- (b) degree of hydrolysis of salts

Ionic Mobilities and Conductance

The ionic conductance depends upon the charge and velocity of ions

$$\lambda_{+}^0 \propto \mu^{+} \quad \Rightarrow \quad \lambda_{+}^0 = \mu^{+} \times F$$

$$\lambda_{-}^0 \propto \mu^{-} \quad \Rightarrow \quad \lambda_{-}^0 = \mu^{-} \times F$$

$$\Rightarrow \Lambda^0 = \lambda_{+}^0 + \lambda_{-}^0$$

$$= F(\mu^{+} + \mu^{-})$$

$$\frac{\text{Fall around anode}}{\text{Fall around cathode}} = \frac{\mu_{+}}{\mu_{-}}$$

Transport Number : The fraction of total current carried by each ion is called transport number

$$t_{+} = \frac{\text{current carried by cation}}{\text{Total current}}$$

Also quantity of current carried is proportional to ionic mobilities

$$\Rightarrow t_+ = \frac{\mu_+}{\mu_+ + \mu_-} = \frac{\lambda_+^0}{\lambda_+^0 + \lambda_-^0}$$
$$t_- = \frac{\mu_-}{\mu_+ + \mu_-} = \frac{\lambda_-^0}{\lambda_+^0 + \lambda_-^0}$$

Redox Reactions in Aqueous Solutions

Redox reactions in aqueous solutions are of two types :

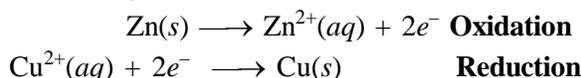
(1) Direct Redox Reaction

A Redox reaction in which both oxidation and reduction takes place in the same beaker (or container) is called a direct redox reaction.

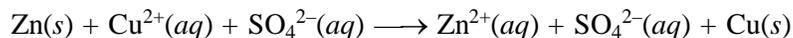
For example, when a zinc rod is dipped in an aq. solution of CuSO_4 in a beaker a spontaneous reaction takes place and the following observations are made.

- (i) Zinc rod starts dissolving and loses its weight gradually.
- (ii) The blue colour of the solution slowly fades away.
- (iii) The reddish brown ppt. of copper settles down at the bottom of the beaker.
- (iv) The reaction is exothermic i.e., takes place with the evolution of heat.
- (v) The solution remains electrically neutral.
- (vi) The reaction stops after some time.

The above reaction may be written as two half reactions which takes place simultaneously.



The overall reaction may be represented as

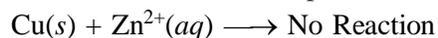


and cancelling the common sulphate ions from both sides, we get



It is also observed that during the reaction Chemical energy is converted into heat energy.

Now, if we place copper rod in a ZnSO_4 solution no chemical reaction takes place. This means that reverse reaction does not take place.



It is thus evident that Zn has more tendency to lose electrons than Cu.

(2) Indirect Redox Reactions

The redox reactions in which oxidation and reduction takes place in two separate containers, are called indirect redox reactions.

Electro-chemical Cell

Redox reactions, which occur in the same beaker, chemical energy in form of heat is produced. By suitable means, it is possible to convert this chemical energy into electrical energy. A device used to convert chemical energy produced in a redox reaction into electrical energy is called an Electro-chemical Cell or simply a Chemical Cell.

Construction of an Electro-chemical Cell

The main requirements of such cells are :

- (i) The redox reaction should be separable into two partial reactions so that electrons are lost by one reactant and are simultaneously gained by another.
-

-
- (ii) The substance that loses electrons and the one that accepts the electrons should not be in direct contact with each other, so that electron transfer occurs through an external circuit.

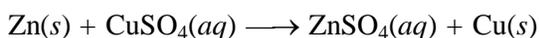
The following is the observations made when the two compartment are joined :

- (i) The galvanometer shows deflection indicating that the electricity is produced in this experiment. The deflection of the needle indicates that electrons are flowing from zinc towards copper.
- (ii) With passage of time Zn rod goes on dissolving in one beaker. In second beaker copper metal is precipitated, and get attached to copper rod. Thus Zn rod loses weight and copper rod gains weight.
- (iii) The weight of zinc dissolved and the weight of copper precipitated are in the ratio of their equivalent weights,

$$\frac{\text{Weight of Zn-dissolved}}{\text{Weight of Cu precipitated}} = \frac{\text{Eq. wt. of Zn}}{\text{Eq. wt. of Cu}} = \frac{65.4}{63.5}$$

- (iv) The concentration of ZnSO_4 solution increases in the zinc half cell and concentration of copper sulphate decreases in copper half cell (i.e., blue colour of solution fades away).
- (v) The solutions in both the beakers remain electrically neutral.
- (vi) The temperature of solutions remain constant. Thus no evolution of heat is observed during the reaction.
- (vii) The cell stops working after some time.**

The above observations can be explained on the basis of the following reaction.

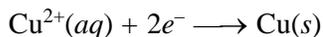


Each Zn atom in the zinc rod loses two electrons to form Zn^{2+} ions



The Zn^{2+} ions migrate from the rod into the solution while the electrons move from the rod into the copper wire, and through copper wire, ultimately reaches the copper rod.

On reaching the copper rod, they come at the surface of the copper rod and combines with $\text{Cu}^{2+}(aq)$ ions present in the solution to form neutral copper atoms, which in turn get deposited on the copper rod.



- (viii) As the Zn^{2+} ion concentration increases the solution becomes +vely charged at anode and as Cu^{2+} ion concentration decreases the solution at cathode becomes -vely charged . Hence cell stops functions.
- (ix) To have a continuous supply of electricity a salt bridge is used. A salt bridge contains a semi-solid paste obtained by adding gelatin or agar-agar to the solution of a strong electrolyte (such as K_2SO_4 , NaNO_3 , NH_4NO_3 , KNO_3 etc.) which does not react during the process.

Functions of Salt Bridge

The main functions of the salt bridge are :

- (i) **To Complete the Electrical Circuit :** The electrons flow in the outer circuit through the wire, while the inner circuit is complete by flow of ions from one solution to the other. Hence current flows.
- (ii) **To Maintain the Solutions Electrically Neutral :** The main function of the salt bridge is to provide a path for the migration of positive and negative ions so as to keep the solutions in both the beakers electrically neutral and thus maintain the flow of electric current through the circuit.
-

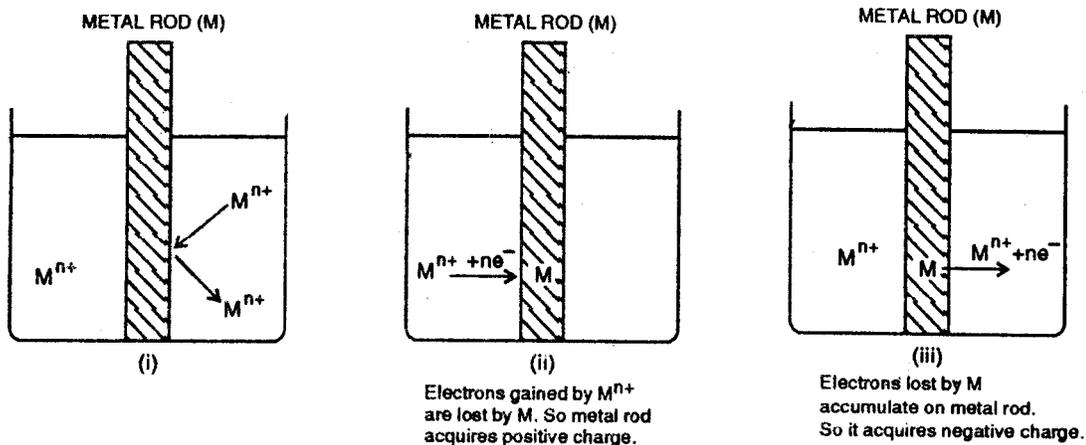
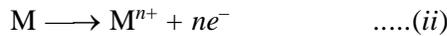
Electrode Potential

To understand the concept of electrode potential, consider a metal rod (M) placed in contact with its own ions (M^{n+}). Then there is one of the following three possibilities.

- (i) M^{n+} ions may collide with the metal rod and deflected back without undergoing any change.
- (ii) M^{n+} ions, on collision with the metal rod may gain electrons and change into metal atoms i.e. M^{n+} ions are reduced.



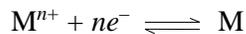
- (iii) Metal atoms of the metal rod may lose electrons and change into M^{n+} ions i.e. metal atoms get oxidised.



If metal has relatively higher tendency to get oxidized, reaction (ii) will occur, the electrons will accumulate on the metal rod which will, therefore, develop a negative charge. This in turn may attract some metal ions from the solution which may change into metal atoms. Ultimately, an equilibrium is reached as follows :



If metal ions have relatively higher tendency to get reduced, reaction (i) will occur. Metal ions (M^{n+}) will gain electrons from the metal rod. As a result metal rod will develop a positive charge with respect to the solution and ultimately the following equilibrium will be attained.



Hence, the electrical potential difference set up between the metal and its ions in the solution is called **electrode potential** or the electrode potential may be simply defined as the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.

Electrode Potential

(i) Electrode Potential :

The potential difference arising when the metal is put inside its metallic salt solution is called Electrode Potential.

(ii) **Standard Electrode Potential :**

The potential difference arising when a pure metal strip is put inside its metallic salt solution of 1M concentration at 25°C is called standard electrode potential E° .

(iii) **Oxidation Potential :**

Potential generated due to the process of oxidation.

(iv) **Reduction Potential :**

Potential generated due to the process of reduction.

Electro-Chemical Series

The arrangement of elements in the order of increasing reduction potential values is called an electrochemical series or activity series.

Standard Reduction Electrode Potentials (at 298 K)

Electrode	Electrode Reaction (Reduction)	$E^\circ_{Mn^+/M}$ (volts)
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
Cd	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40
Co	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
Sn	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.14
Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13
H	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	-0.00
Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
Hg	$Hg_2^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+0.79
Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Au	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.42
F	$F_2 + 2e^- \longrightarrow 2F^-$	+2.87

Reference Electrodes

The electrode which has an accurately known potential at 298K and is used to find single electrode potential of other electrodes; are called reference electrodes.

(a) Primary Reference Electrode

(b) Secondary Reference Electrode

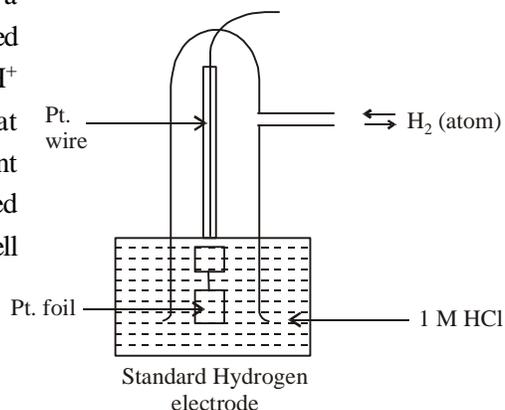
- (a) **Primary Reference Electrode:** Standard hydrogen electrode is employed as primary reference electrode.

Standard Hydrogen Electrode: It has been observed that

- (i) A half cell reaction can not take place independently.
- (ii) For purpose of measurement, as soon as another metal conductor is put into the solution, it will set up its own potential.

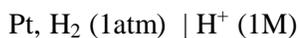
In view of these difficulties, the electrode potential has to be measured against some reference electrode. It is called Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE).

It consists of a platinum wire sealed in a glass tube and has a platinum foil attached to it. The foil is coated with finely divided platinum black. It is dipped in an acid solution containing H^+ ions in 1M concentration (1M HCl). Pure Hydrogen gas at 1atm pressure is constantly bubbled into solution at constant temperature at 298K. The surface of the foil gets surrounded by hydrogen gas. The following reactions occur in this half cell depending upon whether it act as an anode or cathode.



- (i) If SHE acts as anode $H_2(g) \longrightarrow 2H^+ + 2e^-$

This electrode is usually represented as



- (ii) If SHE acts as cathode



This electrode is usually represented as $H^+ (1M) | Pt, H_2 (1atm)$

The standard hydrogen electrode is regarded as reversible electrode.



The electrode potential of the standard hydrogen electrode is taken as zero.

In using SHE, many difficulties arise, such as

- (i) It is very difficult to maintain a pressure at 1 atm of H_2 gas. Purity of H_2 gas is another problem.
- (ii) It is difficult to use liquid junctions.
- (iii) It can not be used in presence of reducible ions.

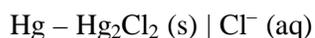
- (b) **Secondary Reference Electrodes:** Some other secondary reference electrodes are used. Such as

(1) Calomel electrode (2) Quinhydrone electrode (3) Glass electrode (4) Ag - AgCl electrode.

We will discuss here only Calomel electrode

Calomel Electrode: Calomel electrode consists of Hg in contact with a paste of insoluble or sparingly soluble mercurous chloride (Hg_2Cl_2). The solution of KCl of definite concentration is taken above the paste and is added from the side tube on RHS. The electrode potential depends upon the concentration of Cl^- ions.

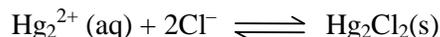
The electrode may be represented as



When the electrode reaction involves **oxidation**, electrons are liberated and Hg_2^{2+} ions enter the solution

where these combine with Cl^- ions to form sparingly soluble Hg_2Cl_2 . As a result there is a decrease in the concentration of Cl^- ions.

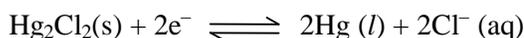
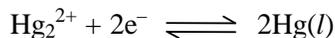
Oxidation



This reaction may be represented as,



Reduction



\therefore electrode is reversible w.r. t. Cl^- ions.

Cell Potential or EMF of A cell

The force which causes flow of electrons from an electrode at higher potential to the electrode at lower potential, due to their potential difference is called electromotive force (EMF) of a cell or Cell Potential or Cell Voltage or simply, the difference between the electrode potentials of the two half cell is known as EMF of a cell.

It depends upon.

- (i) nature of reaction
- (ii) concentration of solutions in the two half cells
- (iii) temperature

It is expressed in Volts.

Differentiate EMF and Potential Difference

	EMF	Potential Difference
1.	EMF is the potential difference between the two electrodes of the cell when no current is flowing in the circuit (i.e., in open circuit)	Potential difference is the difference between the electrode potential of the two electrodes under any conditions i.e., closed circuit.
2.	It is determined by means of a potentiometer.	It is determined by means of simple voltmeter.
3.	It is the maximum obtainable voltage from the cell.	It is less than the maximum obtainable voltage from the cell.
4.	It is maximum obtainable work from the cell.	It is less than maximum obtainable work from the cell.
5.	EMF is responsible for the flow of steady current in the circuit.	Potential difference is not responsible for the flow of steady current in the circuit.

Applications of Electrode potential

1. To compare the relative oxidising and reducing powers.

Elements with high reduction potentials are strong oxidising agents while those with high oxidation potentials are strong reducing agents.

2. To compare the relative activities of metals.

Greater the negative value of reduction potential of an element, greater is its power to reduce the

other element.

3. In predicting anode and cathode. Electrons always move from lower reduction potential (LRP) to higher reduction potential (HRP) and oxidation occurs at LRP, i.e. Anode, whereas reduction occurs at HRP i.e., cathode. Thus electrode having lower reduction potential act as anode and the electrode having higher reduction potential acts as cathode.
4. To calculate the standard EMF of any electrochemical cell

$$E^{\circ}_{\text{Cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Ex: Calculate the standard EMF of a cell which involves the following cell reaction



Given that $E^{\circ} \text{Zn}^{2+} | \text{Zn} = -0.76$ volt and $E^{\circ} \text{Ag}^+ | \text{Ag} = +0.80$ volt

Sol.:(a) The cell reaction be split into two half reactions as:

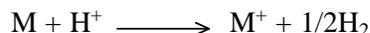


Alternatively, as oxidation takes place at the zinc electrode and reduction at the silver electrode by convention the cell may be represented as



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.80 - (-0.76) = 1.56 \text{ volts.}$$

5. To predict whether a metal reacts with acid to evolve hydrogen gas : In order that a metal M (assuming it to be monovalent) may react with an acid to give H_2 gas, following reactions should take place :



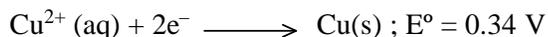
which can be split into half reactions as



If the E.M.F. of a cell having above reaction is +ve metal will react with acid to evolve H_2

6. To Predict spontaneity of a reaction

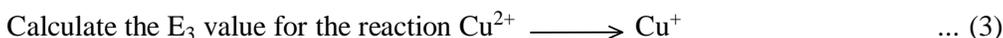
Ex: Knowing that



Again if the E.M.F. of the cell having above reaction as cell reaction is +ve metal will react with acid to evolve hydrogen.

Find out whether 1 M silver nitrate solution can be stored in copper vessel or 1 M copper sulphate solution can be stored in silver vessel.

7. To know the E° of other reactions



The electrode potentials are path functions so they are non-additive. But $\Delta G = -nFE$. Hence we calculate ΔG for eq. 3 and then get the value for E_3

Eq-3 can be obtained by subtracting Eq-1 from Eq-2

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

$$\Rightarrow -n_3 FE_3^\circ = -n_2 FE_2^\circ - (-n_1 FE_1^\circ)$$

$$\Rightarrow n_3 E_3^\circ = n_2 E_2^\circ - n_1 E_1^\circ$$

$$E_3^\circ = \frac{n_2 E_2^\circ - n_1 E_1^\circ}{n_3}$$

$$\Rightarrow E_3^\circ = -0.34 - 0.15 = -0.49 \text{ v.}$$

Concentration Cells

In the electrochemical cells discussed so far, the cell consisted of two different electrodes and the emf produced was due to the chemical reaction taking place in the cell. For example *Daniel cell*.

However, it is possible to prepare a cell in which the two electrodes are of the same type and they differ only in the concentration of the electrolytes with which they are in contact. EMF produced in such cells is only due to the difference in concentration and there is no net Chemical Reaction.

Such cells in which the EMF is produced only due to the difference in the concentration of the solution of the electrolytes with which they are in contact are called concentration cells.

Concentration cells are of following types:

The two electrodes are immersed in the same solution of the electrolyte and thus there is no transference of electrolyte involved. Hence these cells are called concentration cells without transfer.

Examples : Pt ; H₂(P₁) | H⁺, HCl | H₂ (P₂) Pt.

(i) In which the two electrodes are same, having different concentration of electrolytes and connected by a salt bridge.

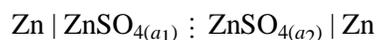
e.g. H₂ (1 atm) | H⁺ (a₁) || H⁺ (a₂) | H₂ (1 atm)



$$E = E^\circ - \frac{0.0591}{2} \log \frac{\text{Zn}(a_+)_1}{\text{Zn}(a_+)_2}$$

(ii) In which the two electrodes are same having different concentration of electrolytes but the two solutions are in direct contact with each other.

e.g. H₂ (1 atm) | HCl_(a₁) : HCl_(a₂) | H₂ (1 atm)



The junction at which the two solutions meet is called as liquid junction.

(iii) Cells obtained by combination of chemical cells:

In electrolyte concentration cells of type (i) and (iii) there is no direct transfer of electrolyte, therefore, they also constitute concentration cells without transfer, while type (ii) constitutes

concentration cells with transfer.

Liquid Junction Potential

In a chemical cell or in a concentration cell, when the two solutions are in direct contact (*i.e.*, in a cell with transfer) there is a diffusion of ions across the boundary between the two solutions. If the ions move with equal speed to the two sides through the boundary there would be no separation of charge. However, usually as the ions move across the boundary with different speed, a separation of charge results. This produces a potential at the boundary *i.e.* at the junction. Thus, the potential set up at the junction of the two solutions because of the difference in the speeds of the ions moving across the boundary is called as **Liquid Junction Potential (LJP)**.

However, the type of junction employed most commonly is the salt bridge containing an electrolyte such as KCl. It is believed that K^+ and Cl^- ions move with almost equal speed and the junction potential is almost reduced to zero.

Thus, LJP in normal electrochemical cells, can be eliminated by choosing a suitable electrolyte.

Applications of EMF Measurement

(1) In the determination of Valency of Ions

This determination is based upon the fact that the EMF of concentration cell without transference is given by

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1} \approx \frac{RT}{nF} \ln \frac{c_2}{c_1}$$

In this expression n is the valency of ion involved. Thus knowing all other quantities, n can be calculated

(2) In the determination of the Solubility and Solubility Product

Principle: The EMF of a concentration cell is given by

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1}$$

Thus knowing EMF of the cell and concentration of the ions in one of the solutions, that in the other can be calculated. If the second solution is that of the sparingly soluble salt, its ionic concentration is equal to its solubility assuming that the substance is completely dissociated.

(3) Determination of H^+ ion concentration or pH of a solution.

One of the most important application of EMF measurement is in the determination of H^+ ion concentration and hence pH of solution ($pH = -\log [H^+]$).

$$E_{H^+, H_2} = 0 - 0.0591 \log \frac{1}{[H^+]}$$

$$E_{\text{H}^+/\text{H}_2} = -0.0591 \text{ pH}$$

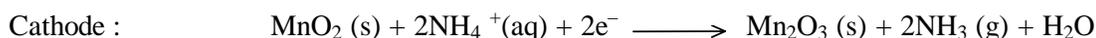
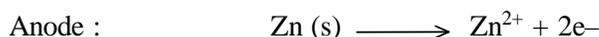
Cells

There are three main types of commercial cells

- (1) **Primary Cells** : are those in which redox reactions occurs only once and cell becomes dead after some time and can not be used again. e.g., Dry Cell, Mercury Cell.
- (2) **Secondary Cells** : are those which can be recharged again by passing an electric current, and can be used over and again e.g., Lead storage battery and Nickel-Cadmium storage Cell.
- (3) **Fuel Cells** : are those in which the energy produced from the combustion of fuels (such as H_2 , CO , CH_4 etc.) is directly converted to electrical energy - Such a conversion is possible because combustion reactions are also redox reactions.

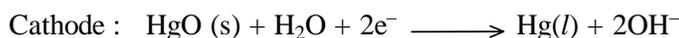
(1) **Primary Cells** :

- (a) **Structure of a dry cell** : A dry cell consists of zinc container as anode and cathode is graphite rod surrounded by a powdered MnO_2 and carbon. The space between the two electrodes is filled with a moist paste of NH_4Cl and ZnCl_2 which act as electrolyte. The electrode reactions are quite complex, but they can be approximately written as



- (b) **Mercury Cell** : Another dry cell which is commonly used in hearing aids, watches and camera is Zinc-Mercury cell. In this cell, Zn-Hg (Zinc amalgam) act as anode and a paste of Mercury (II) oxide HgO and carbon act as cathode.

The electrolyte is the paste of KOH and ZnO .

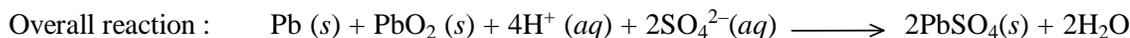
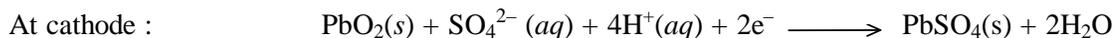


(2) **Secondary Cells** :

- (a) **Lead storage battery** : This is one of the most commonly used batteries in the automobiles. A 12 V lead storage battery is generally used which consists of 6 cells each producing 2 V. Each cell consists of a lead anode (or a grid of lead filled with finely divided spongy lead as the anode) and a grid of lead packed with lead dioxide as the cathode. These electrodes are arranged alternately, separated by thin wooden or fibre glass sheets and suspended in dilute sulphuric acid (38% by mass or having a density of 1.30 g cm^{-3}) which acts as the electrolyte.

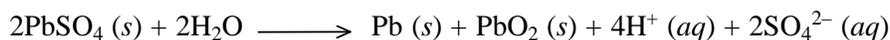
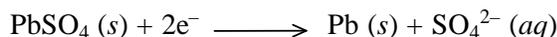
The electrode reactions that occur during discharge (i.e., when the external circuit is closed) are as follows :





From the above equations, it is obvious that H_2SO_4 is used up during the discharge. As a result, the density of H_2SO_4 falls. When it falls below 1.20 g cm^{-3} , the battery needs recharging.

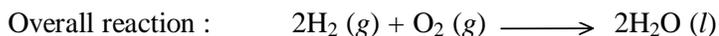
During recharging, the cell is operated like an electrolytic cell *i.e.*, now electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge.



(3) Fuel Cells :

It is an electrochemical device for continuous conversion of the portion of free energy change into electrical energy. Such cell converts 74% of chemical energy into electrical energy. The fuel used is in the gaseous state, $\text{H}_2 - \text{O}_2$ fuel cell is a common example.

It consists of porous carbon electrodes containing catalyst (Pt, Ag) incorporated in them; conc. NaOH or KOH solution is placed between electrodes and act as electrolyte. Following electrode reactions take place.



These fuel cells are more efficient than conventionally used methods of generating electricity on a large scale by burning hydrogen, carbon fuels.

Advantages of fuel cells over ordinary batteries

1. The fuel cells convert the energy of the fuel directly into electricity, while the conventional methods of generating electricity by burning hydrogen, carbon fuels first convert fuels into thermal energy and then into electrical energy. Although theoretically, fuel cells are expected to have an efficiency of 100%, practically only 60–70% efficiency has been attained. Efficiency of the conventional method is only about 40%.
2. Use of the fuel cells do not cause any pollution problem.

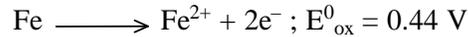
Corrosion

Any process of deterioration (destruction) and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment starting at its surface is called corrosion.

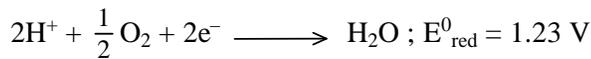
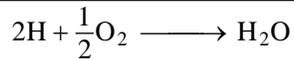
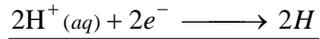
Corrosion always occurs at anodic areas. More active metals are corroded more easily. Corrosion is enhanced by the presence of (a) impurities, (b) air and moisture, (c) electrolytes and (d) strains in metal like dents, scratches, welding parts, etc. Corrosion of iron is called rusting.

Electrode reactions in rusting of iron

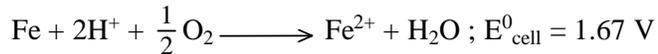
Oxidation at anode



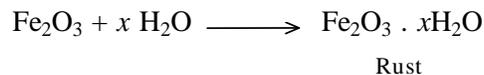
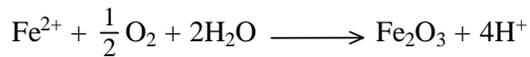
Reduction at cathode



Net reaction of corrosion cell



The Fe^{2+} ions so formed move through water and reach at the surface of iron where they are oxidised to Fe^{3+} ions by atmospheric oxygen and constitute the rust which is hydrated ferric oxide.



Prevention of corrosion

1. By coating with a suitable material (barrier protection)
 2. By alloying with suitable metals e.g. Fe, Cr, V, Ni, W, etc.
 3. By cathodic protection
 4. By using artificial anode (Sacrificial protection)
-

SOLVED EXAMPLES

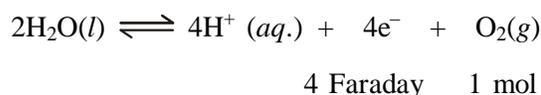
Example 1 : Calculate the volume of a gas liberated at anode at N.T.P. from the electrolysis of CuSO_4 solution by a current of 2 ampere passed for 10 minutes. When Pt electrodes are used.

Solution : As we know, $Q = Ct$

$$= 2 \times 10 \times 60$$

$$= 1200 \text{ Coulomb.}$$

For electrolysis of CuSO_4 solution the gas liberated is oxygen according to the following electrochemical reaction :

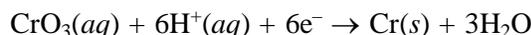


i.e., 4×96500 coulomb liberate = 22.4 litre O_2 at N.T.P.

$$1200 \text{ coulomb will liberate} = \frac{22.4 \times 1200}{4 \times 96500} \text{ litre at N.T.P.}$$

$$= 0.0696 \text{ litre}$$

Example 2 : Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation.



Calculate

(a) the mass of chromium plated out by 24,000 C

(b) how long will it take to plate out 1.5 g of chromium by using 12.5 A current.

Solution : (a) $w = ZQ$

$$= \frac{52 \times 24000}{6 \times 96500} \text{ g}$$

$$= 2.155 \text{ g}$$

(b) $Q = It$

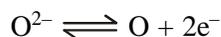
$$\text{So } 1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500 \times 60}$$

$$\text{or } t = 22.27 \text{ min}$$

Example 3 : Electric current is passed through two cells A and B. Cell A contains an aqueous solution of Ag_2SO_4 with platinum electrodes. Cell B contains aqueous solution of CuSO_4 and copper electrodes. The current is passed till 1.6 g of oxygen is liberated at the anode in cell A. Calculate the quantities of copper and silver deposited at the cathodes of two cells.

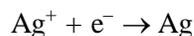
(At Wt. of O = 16, Cu = 63.5, Ag = 108)

Solution : According to electrochemical equation



$$1.6 \text{ g oxygen} = \frac{1.6}{8} = 0.2 \text{ g eq. of oxygen}$$

Electrochemical equations for silver and copper are



$$\text{Hence equivalent weight of silver} = \frac{108}{1} = 108$$

$$\text{and equivalent weight of copper} = \frac{63.5}{2} = 31.75$$

For the same current; 0.2 g eq. of Ag and Cu each will be liberated at their respective cathodes
Hence

$$\begin{aligned} 0.2 \text{ g eq. of Ag} &= 0.2 \times 108 \\ &= 21.6 \text{ g} \end{aligned}$$

$$\begin{aligned} 0.2 \text{ g eq. of Cu} &= 0.2 \times 31.75 \\ &= 6.35 \text{ g} \end{aligned}$$

Example 4 : After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time, 600 ml of 1.0 N solution was left which was found to be sodium hydroxide. During the same time 31.75 of copper was deposited in a copper voltameter in series with the electrolytic cell. Calculate the percentage of the theoretical yield of sodium hydroxide obtained.

Solution : As we know, eq.wt. of NaOH = 40

$$1000 \text{ ml of N NaOH} = 40 \text{ g NaOH}$$

$$\begin{aligned} \text{So } 600 \text{ ml of N NaOH} &= \frac{40}{1000} \times 600 \text{ g NaOH} \\ &= 24 \text{ g NaOH} \end{aligned}$$

According to Faraday's law of electrolysis,

$$\frac{\text{Weight of Cu}}{\text{Weight of NaOH}} = \frac{\text{Eq. weight of Cu}}{\text{Eq. weight of NaOH}}$$

Suppose the weight of NaOH produced is x g.

$$\frac{31.75}{x} = \frac{31.75}{40} \quad (\text{since Eq. wt. of Cu} = 31.75)$$

$$x = 40 \text{ g} \quad (\text{which should theoretically be produced})$$

$$\begin{aligned} \text{Hence percentage of theoretical yield} &= \frac{24}{40} \times 100 \\ &= 60\% \end{aligned}$$

Example 5 : Consider the cell



The standard reduction potentials are :

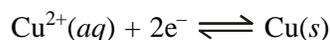


- Write down the cell reaction
- Calculate the e.m.f. of the cell
- Is the cell reaction spontaneous or not ?

Solution : (a) Reaction at anode



Reaction at cathode



The cell reaction :



(b) $E_{\text{cell}} = E^{\circ}_{\text{R.H.S.}} - E^{\circ}_{\text{L.H.S.}}$

$$= 0.35 - (-0.763)$$

$$= 1.113 \text{ Volt}$$

(c) Since e.m.f. of cell is positive the reaction is spontaneous.

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

Solution : We know

$$E = 0.059 \log \frac{C_2}{C_1}$$

where $C_2 > C_1$ and $C_2 = \text{conc. } [\text{H}^{+}] \text{ at +ve electrode.}$

$$\text{or, } 0.118 = 0.059 \log \frac{C_2}{10^{-6}}$$

$$\text{or } \log \frac{C_2}{10^{-6}} = \frac{0.118}{0.059}$$

$$\text{or } \log \frac{C_2}{10^{-6}} = 2$$

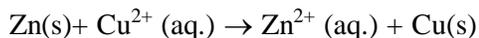
$$= 100$$

$$C_2 = 100 \times 10^{-6}$$

$$\text{or } = 10^{-4} \text{ M}$$

Example 7 : Find the potential of a daniel cell, initially containing 100 L each of 1.00 M Cu^{2+} ion and 1.00 M Zn^{2+} ion, after passage of 10^5 coulombs of charge. (Given: $E^\circ_{\text{cell}} = 1.10 \text{ V}$)

Solution : The cell reaction is



Due to same valency, equal amounts of Zn^{2+} will be formed and Cu^{2+} will be reduced.

$$\therefore \text{Amount of substance, oxidised/reduced} = \frac{10^5}{2 \times 96500} = 0.51 \text{ moles}$$

$$\text{So, } [\text{Zn}^{2+}] = 1.51$$

$$[\text{Cu}^{2+}] = 0.49$$

$$\therefore E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.10 - \frac{0.059}{2} \log \frac{(1.51)}{0.49}$$

Example 8 : From the following standard electrode potentials at 25°C



Calculate equilibrium constant of the reaction $\text{Cu} + \text{Cu}^{2+} \rightarrow 2\text{Cu}^+$.

Solution : $\text{Cu} = \text{Cu}^{2+} + 2e; E^\circ = -0.34; \Delta G^\circ = -2(-0.34) \text{ F} = 0.68 \text{ F}$



On adding,



$$-\Delta G^\circ = 2.303 \text{ RT} \log K$$

$$-0.38 \text{ F} = 2.303 \text{ RT} \log K$$

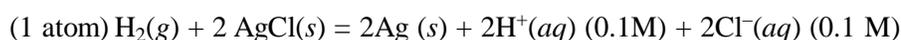
$$\text{or} \quad -0.38 = \frac{2.303 \text{ RT}}{\text{F}} \log K$$

$$-0.38 = 0.0591 \log K$$

$$\text{or} \quad \log K = -\frac{0.38}{0.0591} = -6.429$$

$$\therefore K = 3.72 \times 10^{-7}.$$

Example 9 : For the reaction,



$$\Delta G^\circ = -42927 \text{ joules at } 25^\circ\text{C}.$$

Calculate the e.m.f. of the cell in which the given reaction takes place.

Solution : We know,

$$\Delta G^\circ = -nF E^\circ$$

$$\therefore E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{42927}{2 \times 96500} = 0.2224 \text{ volt}$$

Now, for the above cell reaction

$$\begin{aligned} E_{\text{cell}} &= E^\circ - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{[\text{H}_2]} \\ &= 0.2224 - \frac{0.0591}{2} \log \frac{(0.1)^2 (0.1)^2}{(1)} \\ &= 0.3406 \text{ volt.} \end{aligned}$$

Example 10: The resistance of a N/10 KCl solution is 245 ohms. Calculate the specific conductance and the equivalent conductance of the solution if the electrodes in the cell are 4 cm apart and each having an area of 7.0 sq. cm.

Solution : Cell constant = $\frac{1}{a} = \frac{4}{7} \text{ cm}^{-1}$

Specific conductance = Conductance \times Cell constant

$$\begin{aligned} &= \frac{1}{\text{Resistance}} \times \frac{1}{a} \\ &= \frac{1}{245} \times \frac{4}{7} = 2.332 \times 10^{-3} \text{ mho cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Equivalent conductance} &= \text{Sp. cond.} \times \text{Volume (cc) (containing 1 eq. of the substance)} \\ &= 2.332 \times 10^{-3} \times 10,000 \text{ (for N/10 solution, } V = 10,000 \text{ cc)} \\ &= 23.32 \text{ mho cm}^2. \end{aligned}$$

Example 11: A 0.01 M solution of KCl has a specific conductance value of 0.00141 mho cm^{-1} . A cell filled with this solution has a resistance of 4.2156 ohm.

- (a) What is the cell constant ?
(b) The same cell filled with a solution of HCl has a resistance of 1.0326 ohm. What is specific conductivity of the HCl solution ?

Solution: (a) Cell constant = $\frac{\text{Specific conductance}}{\text{Conductance}}$

$$\begin{aligned} &= \frac{\text{Specific conductance}}{1/\text{Resistance}} \\ &= \frac{0.00141}{1/4.2156} = 0.00594 \text{ cm}^{-1}. \end{aligned}$$

(b) Conductance of HCl solution = $\frac{1}{1.0326} \text{ mho.}$

Since the same cell is used, we shall take the same value of cell constant in this case.

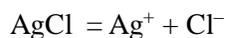
$$\text{Sp. conductance} = \text{Cell constant} \times \text{Conductance}$$

$$= 0.00594 \times \frac{1}{1.0326}$$

$$= 0.00575 \text{ mho cm}^{-1}.$$

Example12: The specific conductance of a saturated solution of AgCl at 25°C after subtracting the specific conductance of conductivity of water is $2.28 \times 10^{-6} \text{ mho cm}^{-1}$. Find the solubility product of AgCl at 25°C. ($A^\circ_{\text{AgCl}} = 138.3 \text{ mho cm}^2$)

Solution: For equilibrium,



$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

If the solubility of AgCl in water is, say, $x \text{ mol/litre}$ of $x \text{ eq./l}$,

$$K_{sp} = x \cdot x = x^2.$$

$$\therefore \text{Volume containing 1 eq. of AgCl} = \frac{1000}{x}$$

$$\text{AgCl} = \text{Specific conductance} \times V$$

$$= 2.28 \times 10^{-6} \times \frac{1000}{x}.$$

Since AgCl is sparingly soluble in water, $A_{\text{AgCl}} = A^\circ_{\text{AgCl}} = 138.3$.

$$\therefore 2.28 \times 10^{-6} \times \frac{1000}{x} = 138.3$$

or

$$x = 1.644 \times 10^{-5} \text{ eq./litre or mole/litre.}$$

$$K_{sp} = x^2 = (1.644 \times 10^{-5})^2$$

$$= 2.70 \times 10^{-10} \text{ (mole/litre)}^2.$$

OBJECTIVE QUESTIONS

1. For $I_2 + 2e^- \rightarrow 2I^-$, standard reduction potential = +0.54 volt. For $2Br^- \rightarrow Br_2 + 2e^-$, standard oxidation potential = -1.09 volt. For $Fe \rightarrow Fe^{2+} + 2e^-$, standard oxidation potential = +0.44 volt. Which of the following reactions is non-spontaneous ?



2. A hydrogen electrode placed in a buffer solution of CH_3COONa and acetic acid in the ratio's x:y and y:x has electrode potential values E_1 volts and E_2 volts respectively at 25°C. The pK_a value of acetic acid is (E_1 & E_2 are oxidation potential).

(a) $\frac{E_1+E_2}{0.118}$ (b) $\frac{E_2-E_1}{0.118}$ (c) $-\frac{E_1+E_2}{0.118}$ (d) $\frac{E_1-E_2}{0.118}$

3. The standard reduction potentials of $Cu^{2+}|Cu$ and $Cu^{2+}|Cu^+$ are 0.337 and 0.153 V respectively. The standard electrode potential of $Cu^+|Cu$ half cell is

(a) 0.184 V (b) 0.827 V (c) 0.521 V (d) 0.490 V

4. Hydrogen peroxide H_2O_2 can be an oxidizing agent and reducing agent as well. The oxidation and reduction processes can be presented by the following equations :



H_2O_2 acts as a reducing agent in

(a) 1, 2 (b) 1, 3 (c) 3, 4 (d) 2, 4.

5. To calculate the solubility product of AgI , the following cell was constructed



If E° is the standard electrode potential, then K_{sp} is given as

(a) $\log K_{sp} = \frac{nFE^\circ}{2.303 RT}$ (b) $K_{sp} = \frac{nFE^\circ}{2.303 RT} \log E^\circ$
(c) $\ln K_{sp} = \frac{nF}{E^\circ}$ (d) None of these

6. A galvanic cell is set up using a zinc bar weighing 100 g and 1.0 litre of 1.0M $CuSO_4$ solution. How long would the cell run if it is assumed to deliver a steady current of 1.0 amp. (Atomic mass of Zn = 65)

(a) 1.1 hr (b) 46 hr (c) 53.6 hr (d) None of these

7. If ionic conductivities at infinite dilution of potassium ions, sodium ions and oxalate ions are a , b & c , respectively, then the molar conductance and equivalent conductance of $\begin{matrix} \text{COONa} \\ | \\ \text{COOK} \end{matrix}$ are, respectively

- (a) $(a + b + c)$ & $(a + b + c)$ (b) $(a + b + c)$ & $\left(\frac{a+b+c}{3}\right)$
 (c) $\left(\frac{a+b+c}{3}\right)$ & $(a + b + c)$ (d) $(a + b + c)$ & $\left(\frac{a+b+c}{2}\right)$

8. The e.m.f. of the following three galvanic cells



are represented by E_1 , E_2 and E_3 . Which of the following statement is true ?

- (a) $E_1 > E_2 > E_3$ (b) $E_3 > E_2 > E_1$ (c) $E_3 > E_1 > E_2$ (d) None of these

9. A solution containing one mole per litre each of $\text{A}'\text{X}$, $\text{B}'\text{X}_2$, $\text{C}'\text{X}_2$ and $\text{D}'\text{X}_2$ is electrolyzed using inert electrodes. The values of standard potential for reduction reaction of A'^+/A , B'^{2+}/B , C'^{2+}/C and D'^{2+}/D are $+0.80$, $+0.34$, -0.76 and -1.66 volts respectively. The correct sequence in which these metals will be deposited on cathode is

- (a) A' , B' , C' , D' (b) D' , C' , B' , A'
 (c) A' , C' , B' , D' (d) D' , B' , C' , A' .

10. The molar conductance of acetic acid at infinite dilution is ∞ . If the specific conductivity of 0.1 M acetic acid is S , the apparent degree of ionisation is

- (a) $\frac{10,000 S}{\lambda_\infty}$ (b) $\frac{10 S}{\lambda_\infty}$ (c) $\frac{\lambda_\infty}{100 S}$ (d) None of these

11. A mixture of fuel gases is fed to the anode. The gases are absorbed by a catalyst, activated and caused to react in an electrolyte. This reaction releases a stream of electrons, making direct current. Meanwhile at the cathode, oxygen is adsorbed and reacts with incoming current to complete the chemical and electrical circuit. The over-all process yields water and CO_2 , plus electricity. The above is a description of

- (a) Regeneration (b) Reduction
 (c) A battery (d) A fuel cell

12. Zinc is used to protect corrosion of iron because

- (a) E_{oxi} of $\text{Zn} < E_{\text{oxi}}$ of iron (b) E_{red} of $\text{Zn} < E_{\text{red}}$ of iron
 (c) Zn is cheaper than iron (d) Zn is abundantly available.

13. The standard reduction potential of Pb and Zn electrodes are -0.126 and -0.763 volts respectively. The e.m.f. of the cell



- (a) 0.637 V (b) < 0.637 V (c) > 0.637 V (d) 0.889

14. An element forms two different sulphates in which its weight % is 28 and 37. What is the ratio of oxidation numbers of the element in these sulphates?

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

15. The reduction electrode potential for the electrode $\text{Pt} \mid \text{Tl}^{3+}, \text{Tl}^{+}$ may be written as

(a) $E = E^{\circ} \frac{RT}{F} \ln \frac{a_{(\text{Tl}^{3+})}}{a_{(\text{Tl}^{+})}}$ (b) $E = E^{\circ} \frac{RT}{2F} \ln \frac{a_{(\text{Tl}^{+})}}{a_{(\text{Tl}^{3+})}}$

(c) $E = E^{\circ} - \frac{RT}{F} \log \frac{a_{(\text{Tl}^{+})}}{a_{(\text{Tl}^{3+})}}$ (d) None of these

16. The nearest equation for the e.m.f. of the cell for the $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$ is

(a) $E = E^{\circ} + \frac{RT}{nF} \ln \frac{(a_{\text{C}})^c (a_{\text{D}})^d}{(a_{\text{A}})^a (a_{\text{B}})^b}$ (b) $E + E^{\circ} = \frac{RT}{nF} \ln \frac{(a_{\text{C}})^c (a_{\text{D}})^d}{(a_{\text{A}})^a (a_{\text{B}})^b}$

(c) $E = E^{\circ} - \frac{RT}{nF} \ln \frac{(a_{\text{C}})^c (a_{\text{D}})^d}{(a_{\text{A}})^a (a_{\text{B}})^b}$ (d) $E = E^{\circ} + \frac{RT}{nF} \ln \frac{(a_{\text{C}})^c (a_{\text{D}})^d}{(a_{\text{A}})^a (a_{\text{B}})^b}$

17. Calculate the weight of copper that will be deposited at the cathode in the electrolysis of a 0.2 M solution of copper sulphate when quantity of electricity equal to that required to liberate 2.24 L of hydrogen at STP from a 0.1 M aqueous sulphuric acid, is passed (Atomic mass of Cu = 63.5)

- (a) 1.59 g (b) 6.35 g (c) 3.18 g (d) None of these

18. The O.S. of oxygen in O_2PtF_6 is

- (a) Zero (b) $+1/2$ (c) $+1$ (d) $-1/2$.

19. For the redox reaction : $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$, the correct coefficients of the reactants for the balanced reaction are

	MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

-
20. How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7.
- (a) Increases by 0.059 V (b) Decreases by 0.059 V
(c) Increases by 0.41 V (d) Decreases by 0.41 V
21. When the specific conductivity of a weak electrolyte is plotted on the y-axis of a graph and the concentration along the x-axis, the graph shows
- (a) A steady increase in conductivity with increase in concentration
(b) The conductivity rising to a maximum then remaining constant with increase in concentration
(c) A steady decrease in conductivity with increase in concentration
(d) The conductivity rising to a maximum, then beginning to fall again with increase in concentration.
22. If the pressure of hydrogen gas is increased from 1 atm to 100 atm, keeping the hydrogen ion concentration constant at 1 M, the voltage of the hydrogen half-cell at 25°C will be
- (a) 0.059 V (b) 0.59 V (c) 0.295 V (d) None of these
23. When a lead storage battery is charged, it acts as
- (a) A fuel cell (b) An electrolytic cell
(c) A galvanic cell (d) A concentration cell.
24. Zn rod dipped in a solution of 1 M ZnSO₄ is connected to Cu rod dipped in a solution of 10⁻⁴⁰ M CuSO₄. The reaction that will take place in this electrochemical cell is
[E° Zn²⁺/Zn = -0.76, E° Cu²⁺/Cu = 0.34]
- (a) Zn + Cu²⁺ → Zn²⁺ + Cu (b) Zn²⁺ + Cu → Zn + Cu²⁺
(c) Both (a) & (b) (d) None of these
25. The time required to plate a spoon 14.0 cm² in an area to a depth of 0.01 cm with Ag using Potassium argentocyanide as an electrolyte with a current of 0.01 amp. (density of Ag = 10.5 g cm³) is
- (a) 40.30 hours (b) 30.40 hours (c) 30.90 hours (d) None of these
26. The equilibrium constant (K) for a cell reaction can be calculated from the e.m.f. of the cell (E°) by the relation
- (a) $K = \frac{2.303 RT}{nF} \log E^\circ$ (b) $\log K = \frac{nFE^\circ}{2.303 RT}$ (c) $K = \frac{2.303 RT}{nFE}$ (d) $K = \frac{2.303}{RT} \log E^\circ$
27. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10⁻⁶ M hydrogen ions. The e.m.f. of the cell is 0.118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode.
- (a) 10⁻¹ M (b) 10⁻² M (c) 10⁻³ M (d) None of these
-

28. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (At. wt. Ni = 59, Cr = 52)

- (a) 0.1 g (b) 0.176 g (c) 0.3 g (d) 0.6 g.

29. Which of the following statements is/are incorrect?

1. Specific conductance increases with dilution
2. Equivalent conductance decreases with dilution
3. The conductance of all electrolytes increase with temperature.

Select the correct answer using the codes give below :

Codes :

- (a) 2 and 3 (b) 1 alone (c) 1 and 2 (d) 1 and 3.

30. The resistance of solution A is 50 ohm that of B is 100 ohm. Both are taken in same cell. If equal volume of A and B are mixed and the mixture is taken in same cell then the resistance is

- (a) 150 ohm (b) 75 ohm (c) 66.67 ohm (d) 33.3 ohm

MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

31. Which one is/are correct among the following given, $E_{\text{Cu}^{+1}/\text{Cu}}^{\circ} = 0.521$, $E_{\text{Cu}^{2+}/\text{Cu}^{+}}^{\circ} = 0.153$

- (a) Cu^{+} disproportionate (b) Cu^{+2} disproportionate
(c) $E_{\text{Cu}^{+}/\text{Cu}^{+2}}^{\circ} + E_{\text{Cu}^{+1}/\text{Cu}}^{\circ}$ is positive (d) all of these

32. During the purification of Copper by electrolysis:

- (a) The anode used is made of Copper ore.
(b) Pure Copper is deposited on the cathode.
(c) The impurities such as Ag, Au are present in solutions as ions.
(d) Concentration of CuSO_4 solution remains constant during dissolution of Cu.

33. For the cell at 298 K; $\text{Ag(s)}|\text{AgCl(s)}|\text{KCl(aq)}||\text{AgNO}_3|\text{Ag(s)}$. Which of the following are wrong?

- (a) The EMF of the cell is zero when $[\text{Ag}^{+}]_{\text{anodic}} = [\text{Ag}^{+}]_{\text{cathodic}}$
(b) The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell
(c) The concentration of $[\text{Ag}^{+}]$ is constant in anodic compartment with the working of cell

(d) $E_{\text{cell}} = E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - E_{\text{Cl}^{-}/\text{AgCl}/\text{Ag}}^{\circ} - \frac{0.059}{1} \log \frac{1}{[\text{Cl}^{-}]}$ anodic

34. The standard redox potentials E° of the following systems are:

System	E° (Volts)
(i) $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
(ii) $\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + 2e^-$	-0.15
(iii) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
(iv) $\text{Ce}^{3+} \longrightarrow \text{Ce}^{4+} + e^-$	-1.61

The oxidizing power of the various species are related as



35. Consider the cell: $\text{Ag(s)} | \text{AgCl (standard solution)} || \text{AgNO}_3(\text{aq}) (1.0 \text{ M}) | \text{Ag(s)}$.

EMF of the above cell is given by (K_{sp} of $\text{AgCl} = 1.0 \times 10^{-10} \text{M}^2$)

(a) $E_{\text{cell}} = E_{\text{Ag}^+/\text{Ag}}^\circ + 0.0592 \log [\text{K}_{\text{sp}}(\text{AgCl})]^{1/2}$ (b) $E_{\text{cell}} = 0.0592 \log \frac{1}{[\text{K}_{\text{sp}}(\text{AgCl})]^{1/2}}$

(c) $E_{\text{cell}} = 0.0592 \times 5V$ (d) $E_{\text{cell}} = 296 \text{ mV}$

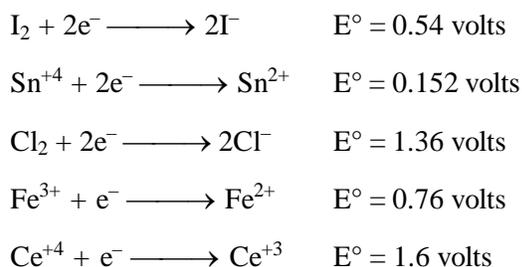
36. Which of the following cells give the cell potentials to be their standard values?

- (a) $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) (0.21 \text{ M}) || \text{H}_3\text{O}^+(\text{aq}) (0.1 \text{ M}) | \text{H}_2(\text{g}) (1 \text{ atm}), \text{Pt}$
- (b) $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}) (0.25 \text{ M}) || \text{Ag}^+(\text{aq}) (0.5 \text{ M}) | \text{Ag}$
- (c) $\text{Cd(s)} | \text{Cd}^{2+}(\text{aq}) (0.01 \text{ M}) || \text{pH} = 1 | \text{H}_2(\text{g}) (1 \text{ atm}), \text{Pt}$
- (d) $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) (0.1 \text{ M}) || \text{pH} = 1 | \text{H}_2(\text{g}) (1 \text{ atm}), \text{Pt}$

37. Which of the following statement(s) is/are correct?

- (a) F_2 is the strongest oxidizing agent. (b) Li is the strongest reducing agent.
- (c) Li^+ is the weakest oxidizing agent. (d) F_2 has the highest reduction potential.

38. The values of E° of some reactions are given:



Hence

- (a) Fe^{3+} oxidizes Ce^{3+} (b) Ce^{4+} can oxidize Fe^{2+}
- (c) Sn^{2+} will reduce Fe^{3+} to Fe^{2+} (d) Cl_2 will be liberated from KCl by passing I_2
-

39. Identify the correct statements:

- (a) Λ_m increases with increase in temperature
- (b) Λ_m decreases with increase in concentration
- (c) Specific conductance increases with increase in concentration
- (d) Specific conductance decreases with increasing temperature

40. The function of salt bridge in a galvanic cell is:

- (a) To keep the electrolytic solution neutral.
 - (b) To allow the ions into solution
 - (c) To complete the circuit by allowing electrons to flow through it
 - (d) To increase a potential difference.
-

MISCELLANEOUS ASSIGNMENT

Comprehension-1

The conductivity of an electrolytic solution always decreases while its molar conductivity always increases with the decrease in concentration both, for weak and strong electrolytes. This is because the conductivity of a solution at any given concentration is the conductance of one unit volume of solution while the molar conductivity is the conductance of the volume V of solution. The molar conductivity of a solution at infinite dilution for a strong electrolyte can be calculated graphically.

- The molar conductivity at infinite dilution for a weak electrolyte can be calculated.
 - graphically using extrapolation method
 - by Kohlrausch's law
 - both (a) and (b)
 - none of these
- The expression $\alpha = \frac{\wedge^m}{\wedge^{\circ}_m}$ does not hold good for the electrolyte
 - CH_3COOH
 - NH_4OH
 - NaCl
 - H_2CO_3
- The highest electrical conductivity of the following aqueous solutions is of
 - 0.1 M CH_3COOH
 - 0.1 M $\text{C}_6\text{H}_5\text{COOH}$
 - 0.1 M HCOOH
 - same in all the above cases
- The ionic conductance of the following cations in a given concentration is in the order
 - $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$
 - $\text{Li}^+ < \text{Na}^+ > \text{K}^+ > \text{Rb}^+$
 - $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$
 - $\text{Li}^+ = \text{Na}^+ < \text{K}^+ < \text{Rb}^+$

Comprehension-2

The arrangement of metals and ions in increasing order of their electrode potential value from top to bottom is known as electrochemical series. Down the electrochemical series, oxidising power of the species increases while reducing power decreases. In electrochemical series, a metal with lower electrode potential displaces another metal with higher electrode potential from its salt solution. Potentials are additive for the process in which half reactions are added to yield an overall reaction but they are not additive when added to yield a third half reaction.

- Which of the following is weakest oxidising agent?
 - Li^+
 - Ba^{++}
 - Ca^{++}
 - Mg^{++}
 - If $E^{\circ}_{\text{MnO}_4^-/\text{Mn}^{++}} = + 1.51 \text{ V}$ and $E^{\circ}_{\text{MnO}_2/\text{Mn}^{2+}} = + 1.23 \text{ V}$ then which of the following will be the strongest oxidising agent in solution
 - $\text{MnO}_4^- \longrightarrow \text{Mn}^{++}$
 - $\text{MnO}_2 \longrightarrow \text{Mn}^{++}$
 - $\text{MnO}_4^- \longrightarrow \text{MnO}_2$
 - all are equally efficient for oxidation
-

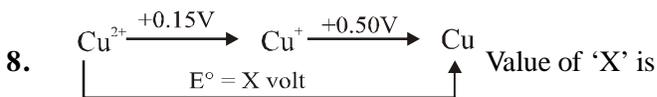
7. For the exact quantitative estimation of ferrous nitrate, with the help of data given below

$$E^{\circ}_{\text{MnO}_4^-/\text{Mn}^{2+}} = + 1.51 \text{ V} ; E^{\circ}_{\text{Cr}_2\text{O}_7/\text{Cr}^{3+}} = + 1.38 \text{ V}$$

$$E^{\circ}_{\text{Cl}_2/\text{Cl}^-} = + 1.40 \text{ V} ; E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = + .77 \text{ V}$$

choose the only incorrect statement

- (a) KMnO_4 in presence of H_2SO_4 may be used (b) $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of HCl may be used
 (c) KMnO_4 in presence of HCl may be used (d) $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of H_2SO_4 may be used

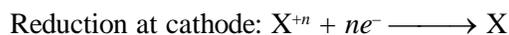
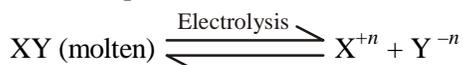


- (a) + 0.325 V (b) +0.35 V (c) + 0.65 V (d) + 0.30 V

Comprehension-3

Electrolysis is a phenomenon in a reaction is carried out by passing electricity through the molten electrolyte or the electrolytic solution. In electrolysis electrolyte first decomposes into anions and cation and thereafter anions undergo oxidation at anode and cations undergo reduction at cathode.

For Example,



When aqueous solution of 100 mL of 1M NaCl is electrolysed using Pt-electrodes, then answer the following questions.

9. What will be the electrolytic product(s) of the 100 mL 1 M aq. NaCl solution?
 (a) H_2 (b) Cl_2 (c) Na and Cl_2 (d) H_2 , Cl_2 and NaOH
10. The weight of the liberated gas at anode upon passage of 0.2 F charge into the solution will be
 (a) 7.1 g (b) 3.55 g (c) 0.2 g (d) 0.4 g
11. What will be the volume of total gases obtained at STP, which 0.1 F charge is passed?
 (a) 3.24 litre (b) 11.2 litre (c) 1.12 litre (d) 2.24 litre

MATRIX MATCH TYPE QUESTIONS

12. A. $\text{Zn}|\text{Zn}^{2+}(\text{C})||\text{Zn}^{2+}(2\text{C})|\text{Zn}$ (p) Spontaneous cell reaction.
 B. $\text{H}_2(\text{P} = 1 \text{ atm})|\text{HCl}(1 \text{ N})||\text{H}_2\text{SO}_4(1 \text{ N})|\text{H}_2(\text{P} = 1 \text{ atm})$ (q) Working cell representation
 C. $\text{Cu}|\text{Cu}^{2+}(0.01 \text{ M})||\text{Ag}^+(0.1 \text{ M})|\text{Ag}$ (r) By increasing concentration of cation in cathodic compartment then cell works.
 D. $\text{Ag}|\text{AgCl}(\text{KCl}, 0.1 \text{ M})||\text{Ag}^+(0.01 \text{ M})|\text{Ag}$ (s) Concentration cell

13. Match column I with column II

Column I (Quantities)

- A. Molar conductance
- B. emf of a cell in operation
- C. Electrode potential
- D. Standard reduction potential

Column II (Factors on which dependency exist)

- (p) Temperature
- (q) Concentration of species involved
- (r) Nature of substance involved
- (s) No. of electrons lost or gained in the reaction

INTEGER TYPE QUESTIONS

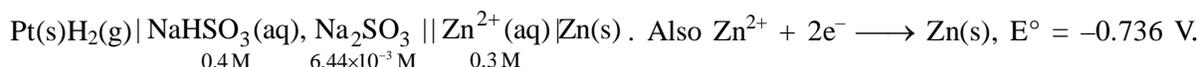
14. The chlorate ion can disproportionate in basic solution according to reaction: $2\text{ClO}_3^- \rightleftharpoons \text{ClO}_2^- + \text{ClO}_4^-$. What is the equilibrium concentration of perchlorate ions from a solution initially at 0.1 M in chlorite ions at 298 K?. The equilibrium constant is 10^{-x} . Then x is:
Given: $E_{\text{ClO}_4^-/\text{ClO}_3^-}^{\circ} = 0.33 \text{ V}$ at 298 K.

15. 3 ampere current was passed through an aqueous solution of an unknown salt of Pd for 1 hour. 2.977 gm of Pd^{n+} was deposited at cathode. The value of n is (At. Wt. of Pd is 106):

16. The $k = 4.95 \times 10^{-5} \text{ s cm}^{-1}$ for a 0.00099 M solution. Calculate the reciprocal of the degree of dissociation of acetic acid, if $\lambda_{\text{M}}^{\infty}$ for acetic acid is $400 \text{ s cm}^2 \text{ mol}^{-1}$.

17. How many moles of electrons are gained by one mol of Nitrobenzene to convert into Aniline under acidic condition?

18. The voltage of the cell given is -0.46V



$$K = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 6.44 \times 10^{-x}$$
. What will be 'x'?

19. The potential of the cell containing two hydrogen electrodes as represented below :
 $\text{Pt}, \text{H}_2(\text{g})/\text{H}^+(10^{-6}\text{M})//\text{H}^+(10^{-4}\text{M})/\text{H}_2(\text{g}), \text{Pt}$ at 298 K is $a \times 0.059 \text{ V}$, then (a) is:

20. Number of moles of electrons needed to pass through 2 litres of AlCl_3 solution containing 267 g of salt to discharge $2/3^{\text{rd}}$ of the Chloride ions present in the solution:

21. Reduction potential of Hydrogen electrode is -0.355 V . The pH of the HCl solution used in the Hydrogen electrode is:

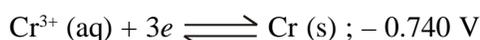
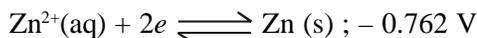
22. How many grams of water will be electrolysed by 96500 coulomb charge?

23. The specific conductance of saturated solution of AgCl is found to be $1.86 \times 10^{-6} \text{ ohm cm}^{-1}$ and that of water is $6 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. The solubility of AgCl in mol/L is 1.31×10^{-x} , x is equal to (given $\Lambda_0 \text{AgCl} = 137.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$).

PREVIOUS YEAR QUESTIONS

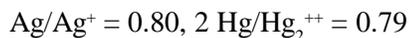
IIT-JEE/JEE-ADVANCE QUESTIONS

1. The standard reduction potentials at 298 K for the following half reactions are given against each



Which is the strongest reducing agent?

- (a) Zn(s) (b) Cs(s) (c) H₂(g) (d) Fe³⁺(aq)
2. Faraday's laws of electrolysis are related to
- (c) equivalent weight of the electrolyte (d) speed of the cation
3. A solution containing one mole per litre of each Cu(NO₃)₂, AgNO₃, Hg₂(NO₃)₂ and Mg(NO₃)₂ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are:



With increasing voltage, the sequence of deposition of metals on the cathode will be

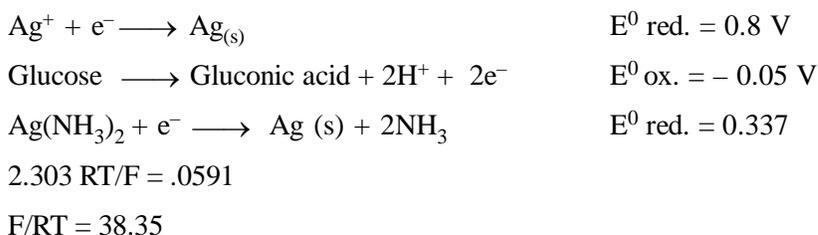
- (a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag (c) Ag, Hg, Cu (d) Cu, Hg, Ag
4. The electric charge for electrode deposition of one gram equivalent of substance is
- (a) one ampere for one second (b) 96500 coulombs per second
- (c) charge on one mole of electrons (d) one ampere for one hour
5. The reaction $\frac{1}{2} \text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \rightarrow \text{H}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) + \text{Ag}(\text{s})$ occurs in the galvanic cell
- (a) Ag | AgCl(s) | KCl(aq) | AgNO₃(aq) | Ag (b) Pt | H₂(g) | HCl(aq) | AgNO₃(aq) | Ag
- (c) Pt | H₂(g) | HCl(aq) | AgCl(s) | Ag (d) Pt | H₂(g) | KCl(aq) | AgCl(s) | Ag
6. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.
- (a) H₂, O₂ (b) O₂, H₂ (c) O₂, Na (d) O₂, SO₂
7. When a lead storage battery is discharged
- (a) SO₂ is evolved (b) lead sulphate is consumed
- (c) lead is formed (d) sulphuric acid is consumed
8. Of the following metals that cannot be obtained by electrolysis of the aqueous solution of their salts
-

are

- (a) Ag and Mg (b) Ag and Al (c) Mg and Al (d) Cu and Cr

9. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y⁻ and 1 MZ⁻ at 25° C. If the reduction potential is Z > Y > X, then
- (c) Y will oxidise both X and Z (d) Y will reduce both X and Z
10. For the electrochemical cell, M |M⁺ |X⁻ | X, E°(M⁺/M) = 0.33 V. From this data, one can deduce that
- (a) M + X → M⁺ + X⁻ is the spontaneous reaction
(b) M⁺ + X⁻ → M + X is the spontaneous reaction
(c) E_{cell} = 0.77 V
(d) E_{cell} = - 0.77 V

Comprehension (Q. 11 to 13)



11. Calculate lnK for equilibrium cell reaction by redox 1 and 2
- $$2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag}(s) + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$$
- (a) 66.13 (b) 57.52 (c) 28.30 (d) 46.29
12. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?
- (a) E_{oxd} will increase by a factor of 0.65 from E_{oxd}
(b) E_{oxd} will decrease by a factor of 0.65 from E_{oxd}
(c) E_{red} will increase by a factor of 0.65 from E_{red}
(d) E_{red} will decrease by a factor of 0.65 from E_{red}
13. Ammonia is always added in this reaction. Which of the following must be incorrect?
- (a) NH₃ combines with Ag⁺ to form a complex
(b) Ag(NH₃)₂⁺ is a stronger oxidising reagent than Ag⁺
(c) In absence of NH₃ silver salt of gluconic acid is formed.
(d) NH₃ has affected the standard reduction potential of glucose/gluconic acid electrode.

Paragraph (Q. 14 to 16)

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs).

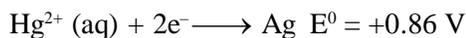
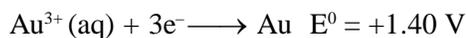
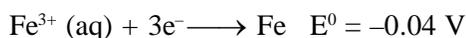
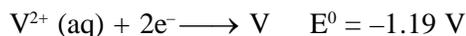
14. The total number of moles of chlorine gas evolved is
(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0
15. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is
(a) 200 (b) 225 (c) 400 (d) 446
16. The total charge (coulombs) required for complete electrolysis is
(a) 24125 (b) 48250 (c) 96500 (d) 193000

Paragraph (Q. 17 to 19)

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions 36-38



17. Among the following, identify the correct statement
(a) Chloride ion is oxidised by O_2 (b) Fe^{2+} is oxidised by iodine
(c) Iodide ion is oxidised by chlorine (d) Mn^{2+} is oxidised by chlorine
18. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2
19. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of
(a) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (b) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ (c) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$ (d) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$
20. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol⁻¹)
(a) 9.65×10^4 sec (b) 19.3×10^4 sec (c) 28.95×10^4 sec (d) 38.6×10^4 sec
21. For the reduction of NO_3^- ion in an aqueous solution, E^0 is + 0.96V. Values of E^0 for some metal ions are given below
-

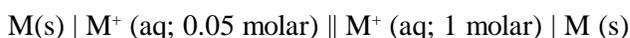


The pair(s) of metals that is (are) oxidized by NO_3^- in aqueous solution is (are)

- (a) V and Hg (b) Hg and Fe (c) Fe and Au (d) Fe and V

Paragraph (Q. 22 to 24)

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:



For the above electrolytic cell the magnitude of the cell potential $|E_{\text{cell}}| = 70 \text{ mV}$.

22. For the above cell

- (a) $E_{\text{cell}} < 0; \Delta G > 0$ (b) $E_{\text{cell}} > 0; \Delta G < 0$ (c) $E_{\text{cell}} < 0; \Delta G^{\circ} > 0$ (s) $E_{\text{cell}} > 0; \Delta G^{\circ} < 0$

23. If the 0.05 solution of M^{+} is replaced by a 0.0025 molar M^{+} solution, then the magnitude of the cell potential would be

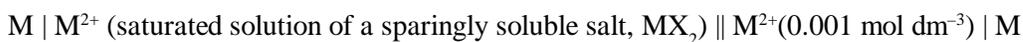
- (a) 35 mV (b) 70 mV (c) 140 mV (d) 700 mV

24. Consider the following cell reaction : $2\text{Fe}_{(\text{s})} + \text{O}_{2(\text{g})} + 4\text{H}^{+}_{(\text{aq})} \rightarrow 2\text{Fe}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}(\text{l})$ $E^{\circ} = 1.67 \text{ V}$ [IIT 2011]

- (a) 1.47 V (b) 1.77 V (c) 1.87 V (d) 1.57 V

Paragraph for Question 25 to 26

The electrochemical cell shown below is a concentration cell.



The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

25. The value of ΔG (kJ mol^{-1}) for the given cell is (take $1\text{F} = 96500 \text{ C mol}^{-1}$)

- (a) -5.7 (b) 5.7 (c) 11.4 (d) -11.4

26. The solubility product ($K_{\text{sp}} \text{ mol}^3 \text{ dm}^{-9}$) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/\text{F} = 0.059 \text{ V}$)

- (a) 1×10^{-15} (b) 4×10^{-15} (c) 1×10^{-12} (d) 4×10^{-12}

27. The standard reduction potential data at 25°C is given below.

$$E^0 (\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77\text{V};$$

$$E^0 (\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V};$$

$$E^0 (\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V};$$

$$E^0 (\text{Cu}^+, \text{Cu}) = +0.52 \text{ V};$$

$$E^0 [\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}] = +1.23 \text{ V};$$

$$E^0 [\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-] = +0.40 \text{ V};$$

$$E^0 (\text{Cr}^{3+}, \text{Cr}) = -0.74 \text{ V};$$

$$E^0 (\text{Cr}^{2+}, \text{Cr}) = -0.91\text{V}$$

Match E^0 of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists:

List I

List II

P. $E^0 (\text{Fe}^{3+}, \text{Fe})$

1. -0.18 V

Q. $E^0 (4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$

2. -0.4 V

R. $E^0 (\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+)$

3. -0.04 V

S. $E^0 (\text{Cr}^{3+}, \text{Cr}^{2+})$

4. -0.83 V

(a) P-4; Q-1; R-2; S-3

(b) P-2; Q-3; R-4; S-1

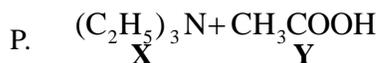
(c) P-1; Q-2; R-3; S-4

(d) A-3; B-4; R-1; R-2

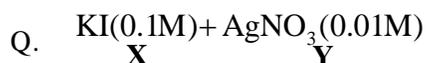
28. An aqueous solution of **X** is added slowly to an aqueous solution of **Y** as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists:

List I

List II



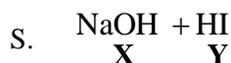
1. Conductivity decreases and then increases



2. Conductivity decreases and then does not change much



3. Conductivity increases and then does not change much



4. Conductivity does not change much and then increases

(a) P-3; Q-4; R-2; S-1

(b) P-4; Q-3; R-2; S-1

(c) P-2; Q-3; R-4; S-1

(d) A-1; B-4; R-3; R-2

29. In a galvanic cell, the salt bridge
-

- (a) does not participate chemically in the cell reaction
- (b) stops the diffusion of ions from one electrode to another.
- (c) is necessary for the occurrence of the cell reaction
- (d) ensures mixing of the two electrolytic solutions

DCE QUESTIONS

1. The standard reduction potentials of Sn^{2+}/Sn , Zn^{2+}/Zn and Fe^{2+}/Fe are respectively -0.14V , -0.76V and -0.44V . Pick out the correct statement.
 - (a) Corrosion of zinc can be prevented by coating with iron
 - (b) Corrosion of tin can be prevented by coating with zinc
 - (c) Corrosion of zinc can be prevented by coating with tin
 - (d) Corrosion of iron can be prevented by coating with tin

2. The standard reduction potential $E_{\text{Zn}^{2+}/\text{Zn}}$ is -0.76V and $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ is 0.34V . The EMF of the Daniel cell is
 - (a) $+1.10\text{ V}$
 - (b) -0.42 V
 - (c) -1.10 V
 - (d) -0.76 V

3. Cu^+ ion is not stable in aqueous solution because of disproportionation reaction. E° value of for disproportionation of Cu^+ is
 [Given: $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15\text{ V}$; $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{ V}$]
 - (a) -0.38 V
 - (b) -0.19 V
 - (c) -0.49 V
 - (d) -0.38 V

4. On passing 0.3 Faraday of electricity through aluminium chloride, the amount of aluminium metal deposited on cathode is ($\text{Al} = 27$)
 - (a) 0.27 g
 - (b) 0.3 g
 - (c) 2.7 g
 - (d) 0.9 g

5. What is wrongly stated about electrochemical series?
 - (a) It is the representation of element in order of increasing or decreasing standard electrode reductional potential
 - (b) It does not compare the relative reactivity of metals
 - (c) It compares relative strengths of oxidising agents
 - (d) H_2 is centrally placed element

6. The electrode potential of hydrogen electrode in neutral solution and 298 K is
 - (a) -0.41 V
 - (b) zero
 - (c) -0.49 V
 - (d) $+0.41\text{ V}$

7. $\text{Sn}^{4+} + 3e^- \longrightarrow \text{Sn}^{2+}$ $E^{\circ} = 0.13\text{ V}$, $\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^-$ $E^{\circ} = 1.08\text{ V}$
 Calculate K_{eq} for the cell reaction for the cell formed by two electrodes.
 - (a) 10^{41}
 - (b) 10^{32}
 - (c) 10^{-32}
 - (d) 10^{-42}

8. Molar conductance of electrolytic solution Λ_m is
 - (a) $\propto l$
 - (b) $\propto (1/A)$
 - (c) $\propto (1/C)$
 - (d) $\propto (\sqrt{C})$

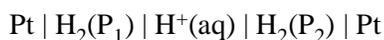
9. Small quantities of solution of compounds TX, TY and TZ are put into separate test tubes containing X, Y & Z solutions. TX does not react with any of these. TY reacts with both X & Z. TZ reacts with X. The decreasing order of oxidation of the anions X^- , Y^- , Z^- is
- (a) Y^-, Z^-, X^- (b) Z^-, X^-, Y^- (c) Y^-, X^-, Z^- (d) X^-, Z^-, Y^-

AIEEE/JEE-MAINS QUESTIONS

1. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is

- (a) $S\ m\ mol^{-1}$ (b) $S\ m^2\ mol^{-1}$ (c) $S^{-2}\ m^2\ mol^{-1}$ (d) $S^2\ m^2\ mol^{-1}$

2. What will be the emf for the given cell



- (a) $\frac{RT}{F} \ln \frac{P_1}{P_2}$ (b) $\frac{RT}{2F} \ln \frac{P_1}{P_2}$ (c) $\frac{RT}{F} \ln \frac{P_2}{P_1}$ (d) none of these

3. Which of the following reaction is possible at anode?

- (a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$ (b) $F_2 \rightarrow 2F^-$
 (c) $\frac{1}{2}O_2 + 2H^+ \rightarrow H_2O$ (d) none of these

4. When a sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are

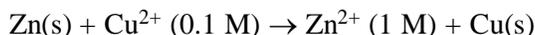
- (a) *Cathode* – Pure zinc, *Anode* – Pure copper
 (b) *Cathode* – Impure sample, *Anode* – Pure copper
 (c) *Cathode* – Impure zinc, *Anode* – Impure sample
 (d) *Cathode* – Pure copper, *Anode* – Impure sample

5. For the reaction



- (a) Carbon can oxidise zinc (b) Oxidation of carbon is not possible
 (c) Oxidation of zinc is not feasible (d) Zinc can oxidise carbon

6. For the redox reaction



taking place is a cell, E°_{cell} is 1.10 volt. E_{cell} for the cell will be $\left(2.303 \frac{RT}{F} = 0.0591\right)$

- (a) 1.80 volt (b) 1.07 volt (c) 0.82 volt (d) 2.14 volt

7. For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be

- (a) 29.5×10^2 (b) 10 (c) 1×10^{10} (d) 1×10^{-10}

1

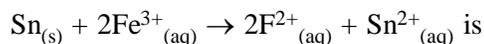
- (a) produce high purity water
- (b) create potential difference between the two electrodes
- (c) generate heat
- (d) remove absorbed oxygen from electrode surfaces

9. Consider the following E° values

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$$

$$E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$$

Under standard conditions the potential for the reaction



- (a) 0.91 V (b) 1.40 V (c) 1.68 V (d) 0.63 V
10. The standard e.m.f. of a cell, involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is ($F = 96,500 \text{ C mol}^{-1}$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)
- (a) 1.0×10^{10} (b) 1.0×10^5 (c) 1.0×10^1 (d) 1.0×10^{30}
11. The limiting molar conductivities Λ° for NaCl, KBr and KCl are 126, 152 and 150 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. The Λ° for NaBr is
- (a) 278 $\text{S cm}^2 \text{ mol}^{-1}$ (b) 176 $\text{S cm}^2 \text{ mol}^{-1}$ (c) 128 $\text{S cm}^2 \text{ mol}^{-1}$ (d) 302 $\text{S cm}^2 \text{ mol}^{-1}$
12. In a cell that utilises the reaction $\text{Zn}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_{2(g)}$ addition of H_2SO_4 to cathode compartment, will
- (a) increase the E & shift equilibrium to the right (b) lower the E & shift equilibrium to the right
 - (c) lower the E & shift equilibrium to the left (d) increase the E & shift equilibrium to the left
13. The highest electrical conductivity of the following aqueous solutions is of
- (a) 0.1 M acetic acid (b) 0.1 M chloroacetic acid
 - (c) 0.1 M fluoroacetic acid (d) 0.1 M difluoroacetic acid
14. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (at. mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is



To prepare 5.12 kg of aluminium metal by this method would require

- (a) $5.49 \times 10^7 \text{ C}$ of electricity (b) $1.83 \times 10^7 \text{ C}$ of electricity
- (c) $5.49 \times 10^4 \text{ C}$ of electricity (d) $5.49 \times 10^1 \text{ C}$ of electricity

15.

Electrolyte	KCl	KNO3	HCl	NaOAc	NaCl
$\Lambda^\circ (\text{S cm}^2 \text{ mol}^{-1})$	149.9	145.0	426.2	91.0	126.5

Calculate $\Delta_{\text{HOAc}}^\infty$ using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C

- (a) 517.2 (b) 552.7 (c) 390.7 (d) 217.5

16. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct?
- Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol.
 - Sodium sulphate solution causes coagulation in both sols
 - Mixing the sols has no effect
 - Coagulation in both sols can be brought about by electrophoresis

17. Excess of KI reacts with CuSO_4 solution and then $\text{Na}_2\text{S}_2\text{O}_3$ solution is added to it. Which of the statements is *incorrect* for this reaction?

- $\text{Na}_2\text{S}_2\text{O}_3$ is oxidised
- CuI_2 is formed
- Cu_2I_2 is formed
- Evolved I_2 is reduced

18. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100Ω . The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell when filled with 0.2 M of the same solution is 520Ω . The molar conductivity of 0.02 M solution of the electrolyte will be

- $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
- $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
- $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
- $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

19. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below:

$$\Lambda^\circ_{\text{CH}_3\text{COONa}} = 91.0 \text{ S cm}^2/\text{equiv}$$

$$\Lambda^\circ_{\text{HCl}} = 426.2 \text{ S cm}^2/\text{equiv}$$

What additional information/ quantity one needs to calculate Λ° of an aqueous solution of acetic acid?

- The limiting equivalent conductance of H^+ ($\lambda^\circ_{\text{H}^+}$)
- Λ° of chloroacetic acid (ClCH_2COOH)
- Λ° of NaCl
- Λ° of CH_3COOK

20. The cell, $\text{Zn} | \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+} (1\text{M}) | \text{Cu}$ ($E^\circ_{\text{cell}} = 1.10\text{V}$), was allowed to be completely discharged at

298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$ is

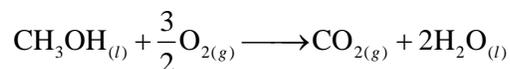
- $10^{37.3}$
- 9.65×10^4
- antilog (24.08)
- 37.3

21. Given $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.72 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.42 \text{ V}$. The potential for the cell

$\text{Cr} | \text{Cr}^{3+} (0.1 \text{ M}) || \text{Fe}^{2+} (0.01 \text{ M}) | \text{Fe}$ is

- 0.339 V
- 0.339 V
- 0.26 V
- 0.26 V

22. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is



At 298 K standard Gibb's energies of formation for $\text{CH}_3\text{OH}(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are -166.2 , -237.2 and -394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is 726 kJ mol^{-1} , efficiency of the fuel cell will be:

- (a) 87% (b) 90% (c) 97% (d) 80%
23. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows:
- $$\frac{2}{3}\text{Al}_2\text{O}_3 \longrightarrow \frac{4}{2}\text{Al} + \text{O}_2, \Delta_r G = +966\text{kJmol}^{-1}$$
- The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least
- (a) 2.5V (b) 5.0V (c) 4.5V (d) 3.0V
24. The reduction potential of hydrogen half-cell will be negative if:
- (a) $p(\text{H}_2) = 1$ atm and $[\text{H}^+] = 2.0$ M (b) $p(\text{H}_2) = 1$ atm and $[\text{H}^+] = 1.0$ M
(c) $p(\text{H}_2) = 2$ atm and $[\text{H}^+] = 1.0$ M (d) $p(\text{H}_2) = 2$ atm and $[\text{H}^+] = 2.0$ M
25. The standard reduction potentials for $\text{Zn}^{2+} / \text{Zn}$, $\text{Ni}^{2+} / \text{Ni}$, and $\text{Fe}^{2+} / \text{Fe}$ are -0.76 , -0.23 and -0.44V respectively. The reaction $\text{X} + \text{Y}^{2+} \rightarrow \text{X}^{2+} + \text{Y}$ will be spontaneous when:

- (a) $\text{X} = \text{Ni}$, $\text{Y} = \text{Fe}$ (b) $\text{X} = \text{Ni}$, $\text{Y} = \text{Zn}$ (c) $\text{X} = \text{Fe}$, $\text{Y} = \text{Zn}$ (d) $\text{X} = \text{Zn}$, $\text{Y} = \text{Ni}$

26. Given $E_{\text{Cr}^{3+}/\text{Cr}}^0 = -0.74\text{V}$; $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.51\text{V}$

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0 = 1.33\text{V}; E_{\text{Cl}_2/\text{Cl}^-}^0 = 1.36\text{V}$$

Based on the data given above, strongest oxidising agent will be:

27. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E_{\text{M}^{3+}/\text{M}^{2+}}^0$ value?
- (a) Fe ($Z = 26$) (b) Co ($Z = 27$) (c) Cr ($Z = 24$) (d) Mn ($Z = 25$)
28. The coagulating power of electrolytes having ions Na^+ , Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order:
- (a) $\text{Ba}^{2+} < \text{Na}^+ < \text{Al}^{3+}$ (b) $\text{Al}^{3+} < \text{Na}^+ < \text{Ba}^{2+}$
(c) $\text{Al}^{3+} < \text{Ba}^{2+} < \text{Na}^+$ (d) $\text{Na}^+ < \text{Ba}^{2+} < \text{Al}^{3+}$
29. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is [JEE-Mains 2014]
- (a) Cu (b) Cr (c) Ag (d) Ca
30. Resistance of 0.2 M solution of an electrolyte is 50Ω . The specific conductance of the solution is

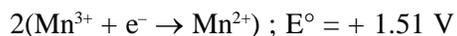
1.4 S m⁻¹. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5M solution of the electrolyte in S m² mol⁻¹ is

- (a) 5×10^3 (b) 5×10^2 (c) 5×10^{-4} (d) 5×10^{-3}

31. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_c and λ_∞ , respectively. The correct relationship between λ_c and λ_∞ is given as (where the constant B is positive)

- (a) $\lambda_c = \lambda_\infty - (B) \sqrt{C}$ (b) $\lambda_c = \lambda_\infty + (B) \sqrt{C}$ (c) $\lambda_c = \lambda_\infty + (B)C$ (d) $\lambda_c = \lambda_\infty - (B)C$

32. Given below are the half-cell reaction:



The E° for $3\text{Mn}^{2+} \rightarrow \text{Mn} + 2\text{Mn}^{3+}$ will be

- (a) -0.33 V ; the reaction will not occur (b) -0.33 V ; the reaction will occur
(c) -2.69 V ; the reaction will not occur (d) -2.69 V ; the reaction will occur
-

SUBJECTIVE PROBLEMS

1. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes ? What is the area of the tray if thickness of the silver plating is 0.00254 cm ? Density of silver is 10.5 g/cm³.
2. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 %. If the potential drop across the cell is 3.0 volts, how much energy will be consumed ?
3. After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time 600 ml of the solution was left which was found to be 1 N sodium hydroxide. During the same time 31.8 g of copper was deposited in a copper voltameter in series with the electrolytic cell. Calculate the percentage of the theoretical yield of sodium hydroxide obtained.

4. An aqueous solution of NaCl on electrolysis gives H₂(g), Cl₂(g) and NaOH according to the reaction :



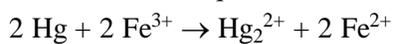
A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1 kg of Cl₂ ? What will be the molarity of the solution with respect to hydroxide ion? (Assuming no loss due to evaporation).

5. Calculate the quantity of electricity that will be required for liberating 710 g of chlorine gas by the electrolysis of a concentrated solution of NaCl. What

(a) weight of NaOH, and

(b) what volume of hydrogen measured at 27°C and 1 atm. pressure will be obtained during the process?

6. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe³⁺. It is found that 5% of Fe³⁺ remains at equilibrium at 25°C. Calculate E°_(Hg₂²⁺), assuming that the only reaction that occurs is



(Given E°_(Fe³⁺/Fe²⁺) = 0.77 V)

7. For the galvanic cell



Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

$$[K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}; K_{sp}(\text{AgBr}) = 3.3 \times 10^{-13}]$$

8. Find the solubility product of a saturated solution of Ag₂CrO₄ in water at 298 K if the e.m.f. of the cell Ag/Ag⁺ (satd. Ag₂CrO₄ soln.) // Ag⁺ (0.1 M)/Ag is 0.164 V at 298 K.

9. Calculate the maximum work that can be obtained from the cell



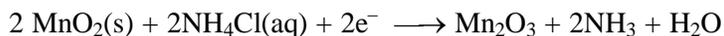
Given that E°_{Zn²⁺/Zn} = -0.76 V; E°_{Ag⁺/Ag} = +0.80 V

-
10. A cell, $\text{Ag} | \text{Ag}^+ || \text{Cu}^{2+} | \text{Cu}$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 hour.
11. The density of copper is 8.94 g ml^{-1} . Find out the number of coulombs needed to plate an area of $10 \text{ cm} \times 10 \text{ cm}$ to a thickness of 10^{-2} cm using CuSO_4 solution as electrolyte.
12. When 8040 coulombs of electricity is passed through a molten metal fluoride of the formula MF_2 , 3.652 g of metal was deposited. What is the atomic weight of metal ? How much electrons have passed through the cell in deposition of the metal ?
13. Evaluate the standard potential of $\text{Zn} | \text{Zn}^{2+}$ electrode if e.m.f. of
- (a) $\text{Zn} | \text{Zn}^{2+} || \text{Ni}^{2+} | \text{Ni} = 0.51 \text{ V}$ and that of

$$\frac{a}{a=1} \quad \frac{a}{a=1}$$
- (b) $\text{Ni} | \text{Ni}^{2+} || \text{KCl (saturated)} | \text{Hg}_2\text{Cl}_2, \text{Hg} = 0.49 \text{ V}$ ($E^\circ_{\text{cathode}} = 0.24 \text{ V}$)

$$\frac{a}{a=1}$$
14. Calculate the dissociation constant of water at 25°C from the following data :
- Specific conductance of $\text{H}_2\text{O} = 5.8 \times 10^{-8} \text{ mho cm}^{-1}$
 $\lambda^\circ_{\text{H}^+} = 350.0$ and $\lambda^\circ_{\text{OH}^-} = 198.0 \text{ mho cm}^2$
15. The specific conductance of a saturated solution of AgCl at 25°C after subtracting the specific conductance of conductivity of water is $2.28 \times 10^{-6} \text{ mho cm}^{-1}$. Find the solubility product of AgCl at 25°C . ($\Lambda^\circ_{\text{AgCl}} = 138.3 \text{ mho cm}^2$)
16. For H^+ and Na^+ the values of λ° are 349.8 and 50.11 respectively. Calculate the mobilities of these ions and their velocities if they are in a cell in which the electrodes are 5 cm apart and to which a potential of 2 volts is applied.
17. Calculate K_a of acetic acid if its 0.05 N solution has equivalent conductance of 7.36 mho cm^2 at 25°C . ($\Lambda^\circ_{\text{CH}_3\text{COOH}} = 390.7$)
18. A big irregular shaped vessel contained water, the specific conductance of which was $2.56 \times 10^{-5} \text{ mho cm}^{-1}$. 500 g of NaCl was then added to the water and the specific conductance after the addition of NaCl , was found to be $3.10 \times 10^{-5} \text{ mho cm}^{-1}$. Find the capacity of the vessel if it is fully filled with water. ($\Lambda^\circ_{\text{NaCl}} = 149.9$)
19. The resistance of a solution 'A' is 50 ohms and that of solution 'B' is 100 ohms, both solutions being taken in the same conductivity cell. If equal volumes of solution A and B are mixed, what will be the resistance of the mixture using the same cell. (Assume that there is no increase in the degree of dissociation of A and B on mixing).
20. Silver is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0.2 A for 3 hours. Calculate the thickness of silver deposited. Given $\rho_{\text{Ag}} = 10.47 \text{ g/cm}^3$.
21. Given that
- $$\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}; E^\circ = 0.77 \text{ V}$$
- $$\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}; E^\circ = -0.44 \text{ V}$$
- What will be the E° value for the following half cell ?
- $$\text{Fe}^{3+} + 3e \rightleftharpoons \text{Fe}$$
-

22. In a zinc manganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of MnO_2 , carbon, NH_4Cl and ZnCl_2 in aqueous base. The cathodic reaction may be represented as



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

23. Calculate the current required to deposit 0.50 g of elemental Pt from a solution containing $(\text{PtCl}_6)^{2-}$ ion within a time period of 5 h.

24. A constant current was passed through a solution of AuCl_4^{-1} ions between gold electrodes. After a period of 5 minutes the cathode increased in mass by 3.942 g. How much charges q , was passed? What was the current I ?

25. An electric current is passed through three cells in series containing respectively solutions of copper sulphate, silver nitrate, and potassium iodide. What masses of silver and iodine will be liberated while 1.25 g of copper is deposited?

26. 0.3605 g of a metal is deposited on the electrode by passing 1.2 A for 15 minutes through its salt. What will be its valency? (At. wt. of metal = 96).

27. Given: $E^\circ_{(\text{Ag}^+/\text{Ag})} = 0.8$ V; $K_{\text{sp}}(\text{AgI}) = 8.7 \times 10^{-17}$

Calculate the potential of Ag^+/Ag electrode in a saturated solution of AgI. Also calculate $E^\circ_{(\text{I}^-, \text{AgI}/\text{Ag})}$.

28. What pressure of H_2 gas would be required to make the emf of the hydrogen electrode zero in pure water at 25°C ?

29. Consider the cell $\text{Ag}|\text{Ag}^+||\text{Cu}^{2+}|\text{Cu}$

The cell initially contains 1 M Ag^+ & 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65A for 1 hour.

30. Calculate the reduction potential at pH = 14 for the Cu^{2+}/Cu couple. Given : $E^\circ_{(\text{Cu}^{2+}/\text{Cu})} = 0.34$ V and $K_{\text{sp}} [\text{Cu}(\text{OH})_2] = 10^{-19}$.

ANSWERS

Objective Questions

- | | | | | |
|-------------|---------------|-------------|-------------|-------------|
| 1. (d) | 2. (c) | 3. (c) | 4. (d) | 5. (a) |
| 6. (c) | 7. (d) | 8. (d) | 9. (a) | 10. (a) |
| 11. (d) | 12. (b) | 13. (c) | 14. (d) | 15. (d) |
| 16. (c) | 17. (b) | 18. (b) | 19. (a) | 20. (d) |
| 21. (a) | 22. (d) | 23. (b) | 24. (b) | 25. (d) |
| 26. (b) | 27. (d) | 28. (b) | 29. (c) | 30. (a) |
| 31. (a,c) | 32. (a,b,d) | 33. (b,c,d) | 34. (b,c,d) | 35. (b,c,d) |
| 36. (a,b,c) | 37. (a,b,c,d) | 38. (b,c) | 39. (a,b,c) | 40. (a,b) |

Miscellaneous Assignment

- | | | | | |
|--|--|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (c) | 4. (a) | 5. (a) |
| 6. (c) | 7. (c) | 8. (a) | 9. (d) | 10. (a) |
| 11. (d) | 12. A-(p),(q),(s); B-(r),(s); C-(p),(q); D-(p),(q),(s) | | | |
| 13. A-(p),(q),(r); B-(p),(q),(r),(s); C-(p),(q),(r),(s); D-(r),(s) | | | | |
| 14. (1) | 15. (4) | 16. (8) | 17. (6) | 18. (8) |
| 19. (2) | 20. (4) | 21. (6) | 22. (9) | 23. (5) |

Previous Year Questions

IIT-JEE/JEE-ADVANCE QUESTIONS

- | | | | | |
|-------------|---------|---------|-------------|---------|
| 1. (a) | 2. (c) | 3. (c) | 4. (c) | 5. (c) |
| 6. (a) | 7. (d) | 8. (c) | 9. (a) | 10. (b) |
| 11. (b) | 12. (a) | 13. (d) | 14. (b) | 15. (d) |
| 16. (d) | 17. (c) | 18. (d) | 19. (a) | 20. (b) |
| 21. (a,b,d) | 22. (b) | 23. (c) | 24. (d) | 25. (d) |
| 26. (b) | 27. (d) | 28. (a) | 29. (a,b,c) | |

DCE QUESTIONS

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (b) | 2. (a) | 3. (c) | 4. (c) | 5. (b) |
| 6. (a) | 7. (b) | 8. (c) | 9. (a) | |
-

MAINS QUESTIONS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (a) | 2. (b) | 3. (a) | 7. (d) | 5. (a) |
| 6. (b) | 7. (c) | 8. (c) | 9. (a) | 10. (c) |
| 11. (c) | 12. (a) | 13. (d) | 14. (a) | 15. (c) |
| 16. (c) | 17. (b) | 18. (b) | 19. (c) | 20. (a) |
| 21. (d) | 22. (c) | 23. (a) | 24. (c) | 25. (d) |
| 26. (b) | 27. (b) | 28. (d) | 29. (d) | 30. (c) |
| 31. (a) | 32. (c) | | | |

Subjective Problems

- | | | |
|---|--|-----------------------------------|
| 1. $1.02 \times 10^4 \text{ cm}^2$ | 2. 347.4 kJ | 3. 60% |
| 4. 1.408 M | 5. (a) 800 g, (b) 246.1 litres | 6. 0.792 V |
| 7. -0.037 V | 8. 2.44×10^{-12} | 9. -301.08 kJ |
| 10. -0.01355 V | 11. 27171.97 coulombs | 12. 49.66, 5.01×10^{22} |
| 13. -0.76 V | 14. 1×10^{-14} | 15. 2.7×10^{-10} |
| 16. Velocity of $\text{H}^+ = 1.45 \times 10^{-3} \text{ cm/sec}$ | 17. $1.76 \times 10^{-5} \text{ mole/litre}$ | 18. $2.37 \times 10^5 \text{ cc}$ |
| 19. 66.67 ohms | 20. $2.89 \times 10^{-4} \text{ cm}$ | 21. -0.04 V |
| 22. 25.675 days | 23. 0.055 A | 24. 19.30 A |
| 25. 4.26 g | 26. 3 | 27. 0.325 V, 0.149 V |
| 28. 10^{-14} atm | 30. -0.22 V | |
-