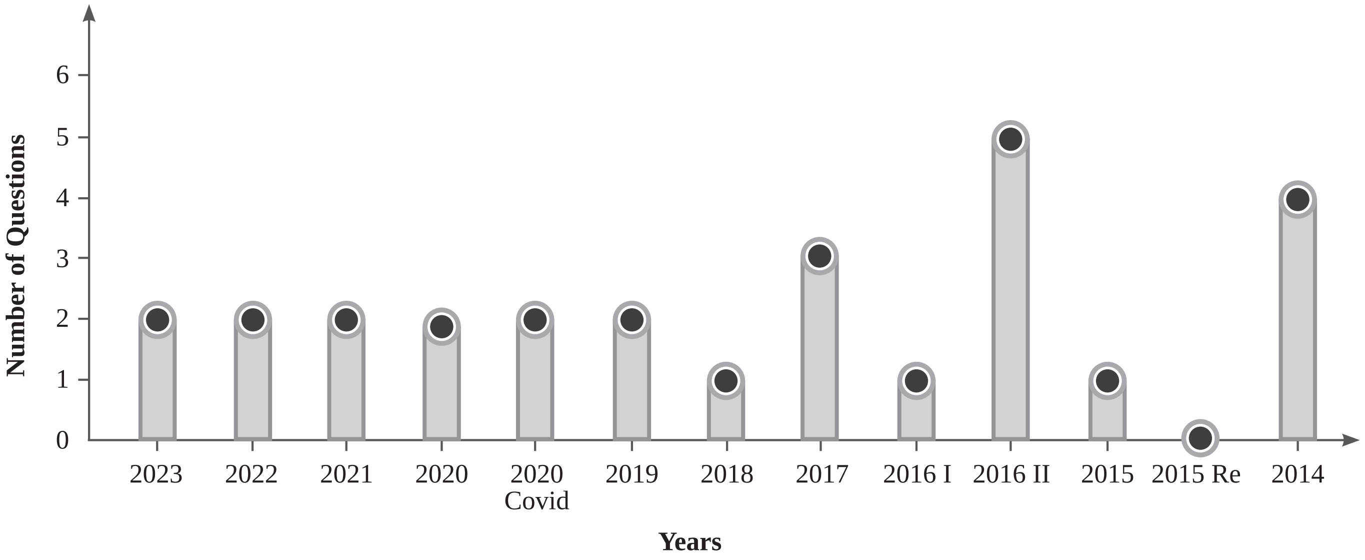
CHAPTER

2

# Electrochemistry

## Year Wise Number of Questions Analysis (2023-2014)



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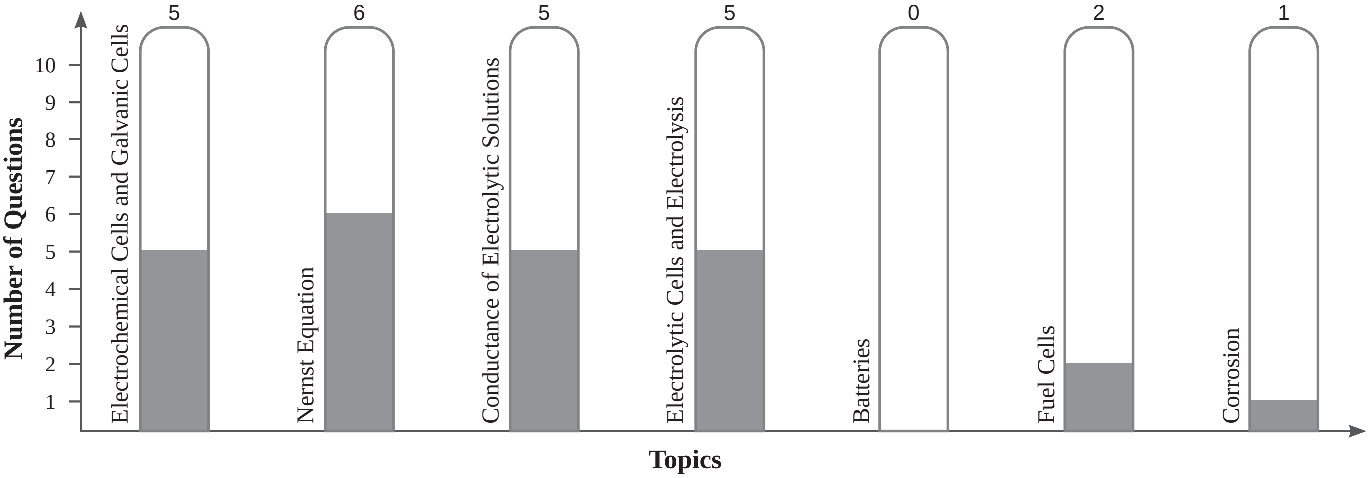


## INTRODUCTION

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformation.

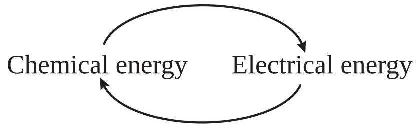
**It deals with:**

- The use of electrical energy for the dissociation of chemical compounds (electrolysis).
- The use of chemical reactions for the production of electrical energy (Galvanic cells).

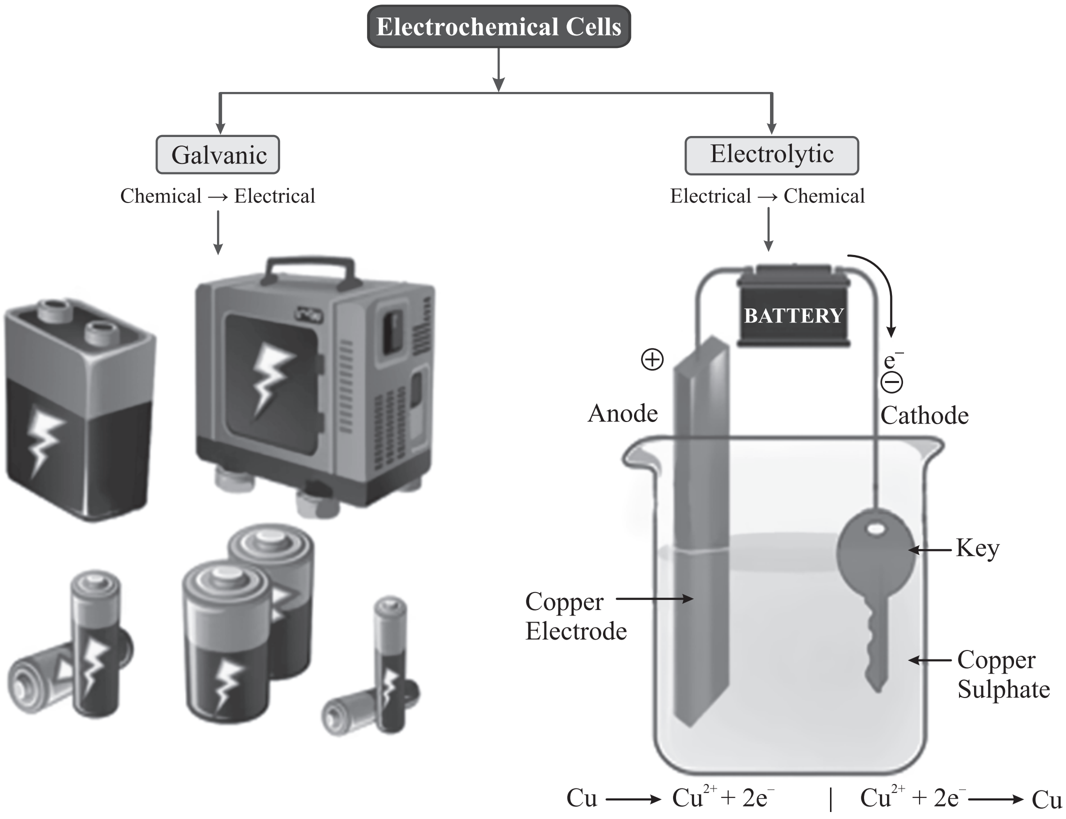
## ELECTROCHEMICAL CELL

Cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge.

- Electrochemistry is a study of interconversion of



- It is a study of **qualitative as well as quantitative aspects** of electrochemical reactions.



**Key Note**

The two types of cells are therefore reverse of each other.

## GALVANIC OR VOLTAIC CELL

### Working Principle

The cell in which **chemical energy** is converted into **electrical energy** is called **Galvanic cell**.

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

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

**3D Model**

Scan this QR code to understand Galvanic or Voltaic Cell through 3D model. To learn more download the Physics Wallah App

### Construction of Galvanic Cell

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

## Half Cell Electrodes

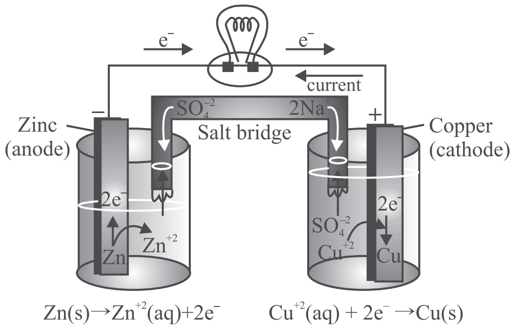
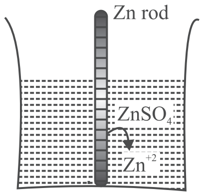


**Fig.:** Galvanic Cell

### (I) Anode

Zn rod is placed in $ZnSO_4$ solution.



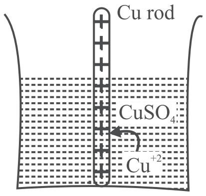
The Zn atom will move in the solution to form $Zn^{2+}$. After some time, following equilibrium will be established.

$Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$

This particular electrode is known as anode:

- On anode, oxidation will take place (release of electron).
- Act as source of electrons.
- It is of negative polarity.
- The electrode potential is represented by $E_{Zn(s) / Zn^{2+}\,(aq)}$

### (II) Cathode



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

The following equilibrium will be established:

$Cu^{2+}\,(aq) + 2e^- \rightleftharpoons Cu(s).$

This will be known as cathode.

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

**Key Note**

Anode: $\begin{cases}\text{Is where oxidation occurs}\\ \text{Is where electrons are produced}\\ \text{Has a negative sign}\end{cases}$

Cathode: $\begin{cases}\text{Is where reduction occurs}\\ \text{Is where electrons are consumed}\\ \text{Has a positive sign}\end{cases}$

### Salt bridge and its Functions

- A salt bridge is a U–shaped inverted tube that contains a gel permitted with an inert electrolyte.
- It connects the solution of two half cells to complete the circuit.
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.

## Selection of Electrolyte for Salt Bridge

- The electrolyte should be inert.
- The electrolyte in salt bridge should be such that speed of it's cation equals to speed of its anion in electrical field.
- Electrolyte should not disturb the cell reaction.

## Danniell Cell

- In Danniell cell instead of salt bridge, porous pot (or) porous diaphragm is used.

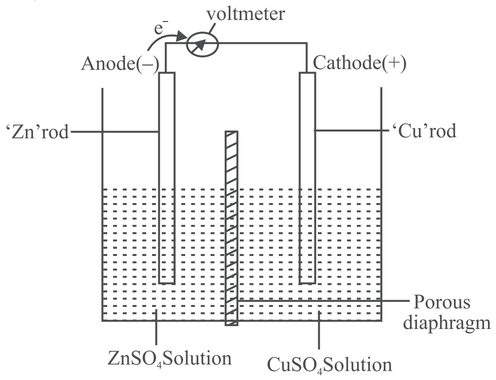


**Fig.:** Danniell cell having electrodes of zinc and copper dipping in the solution of their respective salts

**Key Note**

- ❍ Danniell cell is also called an electrochemical cell.

## Representation of an Electrochemical Cells

We require two half cells to produce an electrochemical cell, which can be represented by following few rules:

- The anode half-cell is always written on the left followed on the right by cathode half cell.
- The separation of two phases (state of matter) is shown by a vertical line.
- The various materials present in the same phase are shown together using semi-colon.
- The salt bridge is represented by a double slash (||).
- The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
- For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode (i.e. $Pt|H_2|\ H^+$ or $H^+|H_2|\ Pt$)

Direction of e⁻ flow →

$$\overbrace{Cu(s)\ |\ Cu^{2+}\,(aq,\ 1M)}^{\text{Anode half-cell}}\ \|\ \overbrace{Cl_2(g,\ 1\ atm)\ |\ Cl^-\,(aq,\ 1M)\ |\ C(s)}^{\text{Cathode half-cell}}$$

Phase boundary

Salt bridge

Phase boundary

- If it is Daniell cell then,
  $Zn | Zn^{2+} (aq)||Cu^{2+} (aq) | Cu$
- In case of a Galvanic cell with a non-metal electrode, inert metal like Pt rod (wire) is introduced in solution which acts as electrode. A Galvanic cell containing $H_2$ and $Cl_2$ gases as electrodes in an HCl solution is represented as**:**
  $Pt|H_2(g)\ (P_1\ atm)\ |\ HCl(aq)\ (c\ mol\ /\ L)\ |\ Cl_2\ (P_2\ atm)|Pt$

**Table:** Difference between Galvanic and Electrolytic Cells

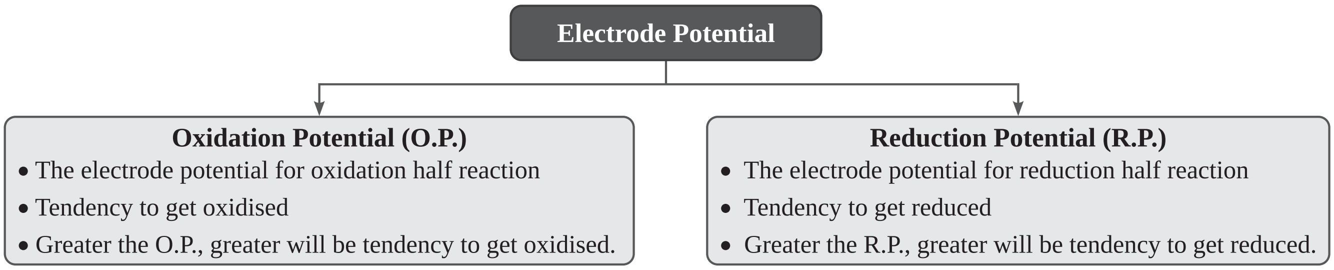
| S. No | Galvanic Cell | Electrolytic Cell |
|---|---|---|
| 1. | It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes. | It is a single cell containing the same electrodes present in the same electrolyte. |
| 2. | Anode is negative, Cathode is positive. | Anode is positive, Cathode is negative. |
| 3. | It converts chemical energy into electrical energy, produced as a result of redox reaction. | It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction. |
| 4. | Cell reaction is spontaneous $\Delta G < 0$. | Cell reaction is non-spontaneous $\Delta G > 0$. |
| 5. | Salt bridge is required. | No salt-bridge is required. |
| 6. | It is source of EMF. | It require EMF. |
| 7. | It is reversible and spontaneous. | It is irreversible and non-spontaneous. |

## ELECTRODE POTENTIAL

The potential difference developed between metal electrode and its ions in solution is known as electrode potential.

Electrode potential depends upon:

- Concentration of the solution
- Nature of the metal
- Nature of the electrolyte
- Pressure and temperature conditions



**Electrode Potential**

**Oxidation Potential (O.P.)**

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

**Reduction Potential (R.P.)**

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

**Table:** Different types of electrode and their reaction in standard condition

| | Type of Electrode | Electrode reaction in standard condition | Representation |
|---|---|---|---|
| **1.** | Metal electrode<br>(Zn electrode, Cu electrode etc) | Reduction: $Zn^{2+} + 2e^- \rightarrow Zn(s)$<br>Oxidation: $Zn(s) \rightarrow Zn^{2+} + 2e^-$ | $E^0_{Zn(s)/Zn^{2+}}$ (SOP)<br>$E^0_{Zn^{2+}/Zn(s)}$ (SRP) |
| **2.** | Hydrogen peroxide electrode | Reduction: $2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$<br>Oxidation: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ | $E^0_{H_2O_2/H_2O}$<br>$E^0_{H_2O_2/O_2}$ |
| **3.** | Redox electrode | Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | $E^0_{MnO_4^-/Mn^{2+}}$ |
| **4.** | Metal-Metal salt (insoluble electrode) | Reduction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$<br>Oxidation : $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$ | $E^0_{AgCl(s)/Ag(s)/Cl^-}$<br>$E^0_{Ag(s)/AgCl(s)/Cl^-}$ |

### Standard Electrode Potential (E°)

The potential difference developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is **known as standard electrode potential** or standard **reduction potential (old name).**

**Key Note**

- According to IUPAC, the given value of electrode potential is regarded as reduction potential unless it is specifically mentioned.
- The **reduction potential** of an electrode is exactly equal in magnitude but opposite in sign to its **oxidation potential.**

## Measurement of Electrode Potential

The difference in electrode potentials of the two half cell reactions (oxidation half cell and reduction half cell) is known as emf of the **cell or cell potential.**

- $E^o_{cell} = E^o_{oxd}(\text{anode}) + E^o_{red}(\text{cathode})$ [where, $E^o_{oxd}$ (anode) = oxidation potential of anode & $E^o_{red}$(cathode) = reduction potential of cathode]
- $E^o_{cell} = E^o_{cathode} - E^o_{anode}$ (both are either reduction potential or oxidation potential).

### Train Your Brain

**Example 1:** Write shorthand notation for the following reaction, $Sn^{2+}$ (aq) + $2Ag^+$ (aq) → $Sn^{4+}$ (aq) + 2Ag(s).

**Sol.** The cell consists of a platinum wire anode dipping into an $Sn^{+2}$ solution and a silver cathode dipping into an $Ag^+$ solution therefore Pt(s) | $Sn^{2+}$(aq), $Sn^{4+}$ (aq) || $Ag^+$ (aq) | Ag(s).

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

(1) Zn | $Zn^{2+}$ || $Br^-$, $Br_2$ | Pt
(2) Cr | $Cr^{3+}$ || $I^-$, $I_2$ | Pt
(3) Pt | $H_2$, $H^+$ || $Cu^{2+}$ | Cu
(4) Cd | $Cd^{2+}$ || $Cl^-$, AgCl | Ag

**Sol.**

| | | |
|---|---|---|
| (1) | Oxidation half cell, | $Zn \rightarrow Zn^{2+} + 2e^-$ |
| | Reduction half cell, | $Br_2 + 2e^- \rightarrow 2Br^-$ |
| | **Net cell reaction** | $Zn + Br_2 \rightarrow Zn^{2+} + 2Br^-$ |
| | +ve terminal : cathode Pt | |
| (2) | Oxidation half cell | $[Cr \rightarrow Cr^{3+} + 3e^-] \times 2$ |
| | Reduction half cell | $[I_2 + 2e^- \rightarrow 2I^-] \times 3$ |
| | **Net cell reaction** | $2Cr + 3I_2 \rightarrow 2Cr^{3+} + 6I^-$ |
| | +ve terminal : cathode Pt | |
| (3) | Oxidation half reaction, | $H_2 \rightarrow 2H^+ + 2e^-$ |
| | Reduction half reaction | $Cu^{2+} + 2e^- \rightarrow Cu$ |
| | **Net cell reaction** | $H_2 + Cu^{2+} \rightarrow Cu + 2H^+$ |
| | +ve terminal : cathode Cu | |
| (4) | Oxidation half cell, | $Cd \rightarrow Cd^{2+} + 2e^-$ |
| | Reduction half cell, | $[AgCl + e^- \rightarrow Ag + Cl^-] \times 2$ |
| | **Net cell reaction** | $Cd + 2AgCl \rightarrow Cd^{2+} + 2Ag + 2Cl^-$ |
| | +ve terminal : cathode Ag | |

**Example 3:** The standard emf of the cell, Ni | $Ni^{2+}$ (1.0 M) || $Ag^+$ (1.0M) | Ag [E° for $Ni^{2+}$ / Ni = – 0.25 volt, E° for $Ag^+$/Ag = 0.80 volt] is given by

(1) –0.25 + 0.80 = 0.55 volt
(2) –0.25 – (+0.80) = –1.05 volt
(3) 0 + 0.80 – (–0.25) = + 1.05 volt
(4) –0.80 – (–0.25) = – 0.55 volt

**Sol.** $E_{cell} = E^\circ_{Ni/Ni^{2+}} + E^\circ_{Ag^+/Ag}$

$= 0.25 + 0.80 = 1.05$ Volt.

### Concept Application

**1.** A gas X at 1 atm is bubbled through a solution containing a mixture of 1 $MY^-$ and 1 $MZ^-$ at 25°C. If the reduction potential of Z > Y > X then

(1) Y will oxidize X and not Z
(2) Y will oxidize Z and not X
(3) Y will oxidize both X and Z
(4) Y will reduce both X and Z

**2.** $E^0$ for $F_2 + 2e^- \rightarrow 2F^-$ is 2.8 V,

$E^0$ for $\frac{1}{2}F_2 + e^- \rightarrow F^-$ is

(1) 2.8 V (2) 1.4 V
(3) –2.8 V (4) –1.4 V

**3.** The standard emf for the cell reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ is 1.10 volt at 25°C. The emf for the cell reaction when 0.1 M $Cu^{2+}$ and 0.1 M $Zn^{2+}$ solutions are used at 25°C is

(1) 1.10 volt
(2) 0.110 volt
(3) –1.10 volt
(4) –0.110 volt

## Standard Hydrogen Electrode

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode (Fig.) represented by $Pt(s)|H_2(g)|H^+(aq)$, is assigned a zero potential at all temperatures corresponding to the reaction

$$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$$

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity (Fig.). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

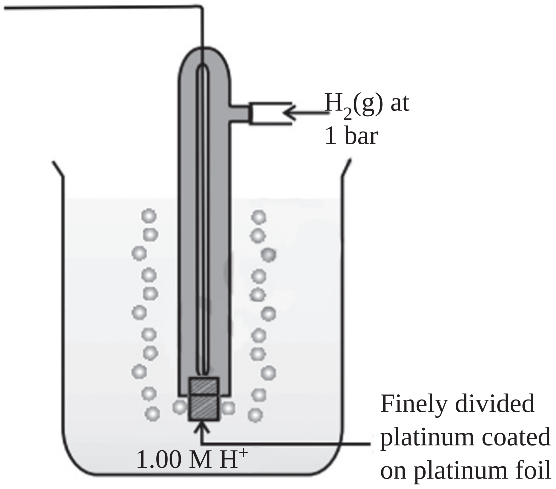


**Fig. :** Standard Hydrogen Electrode (SHE).

At 298 K the emf of the cell, standard hydrogen electrode || second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, $E_R^\ominus$ of the given half-cell.

$$E^\ominus = E_R^\ominus - E_L^\ominus$$

As $E_L^\ominus$ for standard hydrogen electrode is zero.

$$E^\ominus = E_R^\ominus - 0 = E_R^\ominus$$

In an electrolytic cell external source of voltage is used to bring about a chemical reaction. The electrochemical processes are of great importance in the laboratory and the chemical industry. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then $Cu^{2+}$ ions discharge at the cathode (negatively charged) and the following reaction takes place:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Copper metal is deposited on the cathode. At the anode, copper is converted into $Cu^{2+}$ ions by the reaction:

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

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at the cathode. Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

## Electrochemical Series

In the electrochemical series, the metals are arranged in the **increasing order of reduction potentials.**

High reduction potential, metal ions undergo reduction first on cathode or it acts as cathode in the electrochemical cell.

Low reduction potential metal (high negative value) undergo oxidation (or) it acts as anode. It is more reactive (or) more electropositive.

In the electrochemical series, **metal placed above** can displace the **below metal ions** from their solution.

### Train Your Brain

**Example 4:** Calculate $E^o_{cell}$ of (at 298 K),

$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

Given that

$E^o_{Zn/Zn^{2+}(aq)} = 0.76\,V$ ; E 0.34 V

$E^o_{Cu(s)/Cu^{2+}(aq)} = -0.34\ V$

**Sol.** $E^o_{cell} = (S.R.P)_{cathode} - (S.R.P)_{anode}$

$= 0.34 - (-0.76) = 1.1\ V$

**Example 5:** Given the cell Ag |AgCl(s) | NaCl (0.05 M) || $AgNO_3$ (0.3 M) | Ag

(1) Write half reaction occurring at the anode.
(2) Write half reaction occurring at the cathode.
(3) Write the net ionic equation of the reaction.
(4) Calculate $E^o_{cell}$ at 25°C.
(5) Does the cell reaction go spontaneous as written?

(Given $E^o_{Ag/AgCl/Cl^-}$ = + 0.22 V); $E^o_{Ag^+/Ag}$ = + 0.80 V)

**Sol.**

(1) LHS electrode is anode and half reaction is oxidation.
$Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$ ...(*i*)
(2) RHS electrode is cathode and half reaction is reduction.
$Ag^+ + e^- \rightarrow Ag(s)$ ...(*ii*)
(3) From equation (i) and (ii) cell reaction is:
$Cl^-$ (0.05 M) + $Ag^+$ (0.30 M) $\rightarrow$ AgCl(s)
(4) $E^o_{cell} = E^o_{right} - E^o_{left}$ = (0.80 – 0.22)volt = 0.58 volt
(5) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell reaction.

**Table:** Electrochemical Series

| Electrode | Reaction | SRP (at 298 K) |
|---|---|---|
| *Li | $Li^+ + e^- \rightarrow Li(s)$ | –3.05 V |
| K | $K^+ + e^- \rightarrow K$ | –2.93 V |
| Ca | $Ca^{2+} + 2e^- \rightarrow Ca(s)$ | –2.87 V |
| Na | $Na^+ + e^- \rightarrow Na(s)$ | –2.71 V |
| Mg | $Mg^{2+} + 2e^- \rightarrow Mg(s)$ | –2.37 V |
| Al | $Al^{3+} + 3e^- \rightarrow Al(s)$ | –1.66 V |
| * Electrolytes ($H_2O$) | $H_2O(l) + e^- \rightarrow \frac{1}{2}H_2 + OH^-$ | –0.83 V |
| *Zn | $Zn^{2+} + 2e^- \rightarrow Zn(s)$ | –0.76 V |
| Cr | $Cr^{3+} + 3e^- \rightarrow Cr(s)$ | –0.74 V |
| * Fe | $Fe^{2+} + 2e^- \rightarrow Fe(s)$ | –0.44 V |
| Cd | $Cd^{2+} + 2e^- \rightarrow Cd(s)$ | –0.40 V |
| Co | $Co^{2+} + 2e \rightarrow Co(s)$ | –0.277 V |
| Ni | $Ni^{2+} + 2e^- \rightarrow Ni(s)$ | –0.24 V |
| Sn | $Sn^{2+} + 2e^- \rightarrow Sn(s)$ | –0.14 V |
| Pb | $Pb^{2+} + 2e^- \rightarrow Pb(s)$ | –0.13 V |
| *** $H_2$** | **$2H^+ + 2e^- \rightarrow H_2(g)$** | **0.00 V** |
| Cu | $Cu^{2+} + 2e^- \rightarrow Cu(s)$ | 0.34 V |
| $I_2$ | $I_2 + 2e^- \rightarrow 2I^-$ | 0.54 V |
| Fe | $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | 0.77 V |
| Hg | $Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$ | 0.79 V |
| Ag | $Ag^+ + e^- \rightarrow Ag(s)$ | 0.80 V |
| Hg | $Hg^{2+} + 2e^- \rightarrow Hg(l)$ | 0.85 V |
| $Br_2$ | $Br_2 + 2e^- \rightarrow 2Br^-$ | 1.06 V |
| * Electrolytes $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O(\ell)$ | | 1.23 V |
| * $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$ | | 1.33 V |
| * $Cl_2 + 2e^- \rightarrow 2Cl^-$ | | 1.36 V |
| * $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | | 1.51 V |
| * $F_2(g) + 2e^- \rightarrow 2F^-$ | | 2.87 V |

## Concept Application

**4.** The two aqueous solutions; A ($AgNO_3$) and B(LiCl) were electrolysed using Pt. electrodes. The pH of the resulting solutions will

(1) Increase in A and decrease in B
(2) Decrease in both
(3) Increase in both
(4) Decrease in A and increase in B

**5.** Using the standard potential values given below, decide which of the statements I, II, III, IV are correct. Choose the right answer from (1), (2), (3) and (4)

$Fe^{2+} + 2e^- = Fe$, $E^o = -0.44$ V
$Cu^{2+} + 2e^- = Cu$, $E^o = +0.34$ V
$Ag^+ + e^- = Ag$, $E^o = +0.80$ V

I. Copper can displace iron from $FeSO_4$ solution
II. Iron can displace copper from $CuSO_4$ solution
III. Silver can displace Cu from $CuSO_4$ solution
IV. Iron can displace silver from $AgNO_3$ solution

(1) I and II
(2) II and III
(3) II and IV
(4) I and IV

## Important points about Electrochemical Series

Metals near the top of the series are strongly electropositive (or weakly electronegative). They lose electrons readily to give cations.

Weakly electronegative metals displaces metal below them from their salts. For example, iron displaces copper from $CuSO_4$ solution, Cu displaces silver from silver salt solution, silver displaces gold from gold salt solution as in photography during gold toning process.

Hydroxides of metals in the upper part of the series are strongly basic and their salts do not undergo hydrolysis. On the other hand, hydroxides of the metals in the lower part of the series are weakly basic and their salts undergo hydrolysis.

Metals lying above hydrogen are easily rusted. Those situated below are not rusted.

Metals above hydrogen displace hydrogen from dilute acids.

More electropositive metals like K, Na, Ca, etc. displace hydrogen from water.

Iron and other metals above it decompose steam and liberate hydrogen.

Oxides of iron and other metals below it can be reduced easily.

Oxides of manganese and other metals above it are reduced when heated in a current of hydrogen.

Oxides of mercury and other metals below it are decomposed on heating.

## NERNST EQUATION

Cell potentials depend on temperature and on the composition of the reaction mixtures.

It depends upon the concentration of the solute and the partial pressure of the gas, if any.

The dependence upon the concentration can be derived from thermodynamics.

From thermodynamics

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

$$-nFE_{cell} = -nFE^\circ_{cell} + 2.303\ RT \log Q$$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log Q$$

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

Now we get, $\boxed{E_{cell} = E^o_{cell} - \frac{0.059}{n}\log Q}$

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

Nernst equation can be used to calculate cell potentials for non standard conditions also.

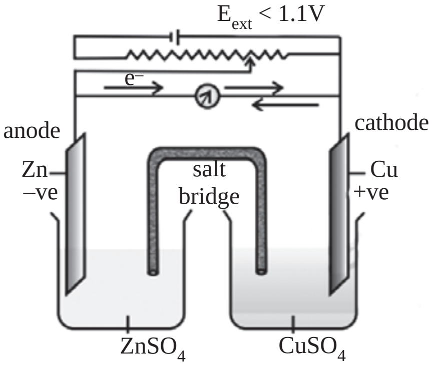
Nernst equations can be applied to half cell reactions also.

### Effect of opposing potential on the cell reaction

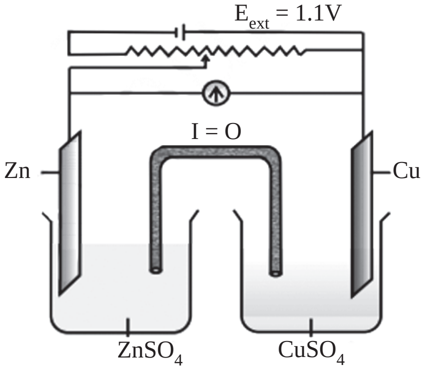
A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied, by coupling it to another cell $E_{(external)}$ through rheostat and galvanometer and increased slowly, what will happen to the cell reaction and current flowing through the cell?

The effect of opposing potential applied to a galvanic cell is as follows:

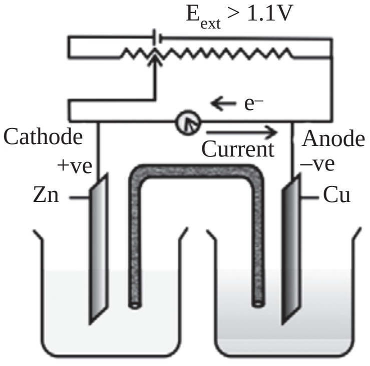
1. When $E_{(external)} < 1.1V$ In a galvanic cell, if an external opposite potential is applied and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V.



2. When $E_{(external)} = 1.1V$ When the external voltage is 1.1V the reaction stops altogether and no current flows through the cell.



3. When $E_{(external)} > 1.1V$ Any further increase in the external potential again starts the reaction but in the opposite direction. It now functions as an electrolytic cell, a device for using electrical energy to carry non-spontaneous chemical reactions



## Applications of Nernst Equation

### Nernst equation for electrode reduction potential

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

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

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

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

$$\Rightarrow E_{Red} = E^o_{Red} + \frac{0.059}{n}\log\left[M^{n+}\right]$$

**Hydrogen electrode**

$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$

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

**Metal–metal soluble salt electrode**

$Zn^{2+} + 2e^- \rightarrow Zn(s)$

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

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

**Gas electrode – hydrogen electrode**

$2H^+ + 2e^- \rightarrow H_2(g)$

$$E_{Red} = E^o_{red} - \frac{0.059}{2}\log\left(\frac{P_{H_2}}{\left[H^+\right]^2}\right)$$

**Redox electrode**

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

$$E_{ox} = E^o_{ox} - \frac{0.059}{5}\log\frac{\left[MnO_4^-\right]\left[H^+\right]^8}{\left[Mn^{+2}\right]}$$

**Nernst equation for cell potential**

$aA + bB \rightleftharpoons cC + dD$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ell n\,Q$$

n = no. of electrons exchanged during the reaction.

$$E_{cell} = E^o_{red}\left(\text{cathode}\right) - E^o_{red}\left(\text{anode}\right)$$

$$-\frac{0.059}{n}\log\left[\frac{\text{conc. of anode}}{\text{conc. of cathode}}\right]$$

**For example:** In the cell $Cu|Cu^{2+}||Ag^+|Ag$, the cell reaction is:

$Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

$$E_{cell} = \left(E^o_{red\ Ag^+|Ag} - E^o_{red\ Cu^{2+}|Cu}\right) - \frac{0.059\log}{2}\frac{\left[Cu^{2+}\right]}{\left[Ag^+\right]^2}$$

## Train Your Brain

**Example 6:** Given that

$E^o_{Cu^{2+}/Cu} = 0.337$ V and $E^o_{Cu^+/Cu^{2+}} = -0.153$ V

then calculate $E^\circ_{Cu^+/Cu}$

**Sol.** $(i)$ $Cu^{2+} + 2e^- \rightarrow Cu \quad \Delta G_1^0$

$(ii)$ $\underline{Cu^+ \rightarrow Cu^{2+} + e^- \quad \Delta G_2^0}$

after adding $Cu^+ + e^- \rightarrow Cu$

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

$-2FE_1^0 - FE_2^0 = -FE_3^0$

$E_3 = 2E_1^0 + E_2^0 = 2 \times 0.337 - 0.153$

$= 0.674 - 0.153 = 0.521$ V

**Example 7:** $Fe^{3+} + 3e^- \xrightarrow{\quad} Fe \qquad E^o_{Fe^{3+}/Fe} = -0.036$ V

$Fe^{2+} + 2e^- \xrightarrow{\quad} Fe \qquad E^o_{Fe^{2+}/Fe} = -0.44$ V

The standard $E^o_{Fe^{3+}/Fe^{2+}}$ is

(1) – 0.476

(2) – 0.404

(3) + 0.44 V

(4) + 0.772 V

**Sol.** $Fe^{3+} + 3e^- \rightarrow Fe$

$Fe^{2+} + 2e^- \rightarrow Fe$

$\Delta G_1 = -nFE^0_{cell} = -3 \times -0.036\ V \times F = 0.108\ F$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

$\Delta G_2 = -nFE^0_{cell} = -2 \times -0.44\ V \times F = 0.88\ F$

$\Delta G_3 = -nFE^0_{cell} = -1 \times E^o \times F = (+0.108 - 0.88)F\ V$

$E^o = 0.772$ V

**Example 8:** If $E_1^0$ is standard electrode potential for $Fe/Fe^{2+}$ and $E_2^0$ is for $Fe^{2+}/Fe^{3+}$ and $E_3^0$ for $Fe/Fe^{3+}$. Derive a relation between $E_1^0$, $E_2^0$ and $E_3^0$.

**Sol.** $Fe \xrightarrow{\quad} Fe^{2+} + 2e^-;\ \Delta G_1^0 = 2E_1^0F$ …(*i*)

$Fe^{2+} \rightarrow Fe^{3+} + e^-;\ \Delta G_2^0 = E_2^0F$ …(*ii*)

$Fe \xrightarrow{\quad} Fe^{3+} + 3e^-;\ \Delta G_3^0 = E_3^0F$ …(*iii*)

Subtracting eqs. (*i*) from (*iii*),

$Fe \xrightarrow{\quad} Fe^{3+} + 3e^-;\ \Delta G_3^0 = E_3^0F$

$Fe \xrightarrow{\quad} Fe^{2+} + 2e^-;\ \Delta G_1^0 = 2E_1^0F$

$- \ - \ - \ + \ -$

$Fe^{2+} \rightarrow Fe^{3+} + e^-;\ \Delta G_3^0 + \Delta G_1^0 = 3E_3^0F - 2E_1^0F$ …(*iv*)

Comparing eqs. (*ii*) and (*iv*)

$-\Delta G_2^0F = -\Delta G_3^0 + \Delta G_1^0 = 3E_3^0F - 2E_1^0F$

$+E_2^0F = 3E_3^0F - 2E_1^0F$

$$\therefore \quad E_3^0 = \frac{2E_1^0 + E_2^0}{3} \text{ or } 3E_3^0 = 2E_1^0 + E_2^0$$

## Concept Application

6. Estimate the cell potential of a Daniell cell having 1.0M $Zn^{++}$ and originally having 1.0M $Cu^{++}$ after sufficient $NH_3$ has been added to the cathode compartment to make $NH_3$ concentration 2.0M at equilibrium. Given $K_f$ for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, E° for the reaction, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ 1.1V.

(1) E = 0.36 V

(2) E = 0.17 V

(3) E = 0.71 V

(4) E = –0.71 V

**7.** $Cu^+ + e^- \longrightarrow Cu$, E° = $x_1$ volt;
$Cu^{2+} + 2e^- \longrightarrow Cu$, E° = $x_2$ volt, then for
$Cu^{2+} + e^- \longrightarrow Cu^+$, E° (volt) will be
(1) $x_1 - 2x_2$ (2) $x_1 + 2x_2$
(3) $x_1 - x_2$ (4) $2x_2 - x_1$

## ELECTROCHEMICAL CELL AND FREE ENERGY

### Electrochemical Cell and Gibbs Energy of the reaction

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

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

It may be remembered that $E_{(cell)}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on *n*. Thus, if we write the reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

$$\Delta_r G = -2FE_{(cell)}$$

but when we write the reaction

$$2\,Zn(s) + 2\,Cu^{2+}(aq) \rightarrow 2\,Zn^{2+}(aq) + 2Cu(s)$$

$$\Delta_r G = -4FE_{(cell)}$$

If the concentration of all the reacting species is unity, then $E_{(cell)} = E°_{(cell)}$ and we have

$$\Delta_r G° = -nFE°_{(cell)}$$

Thus, from the measurement of $E°_{(cell)}$ we can obtain an important thermodynamic quantity. ΔG°, standard $\Delta_r G°$, energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G° = RT \ln K.$$

### Calculation of equilibrium constant (Keq) from Nernst equation

$$\Delta G^0 = -nFE^o_{cell}$$

$$\Delta G = -nFE_{cell}$$

From thermodynamics,

$$\Delta G = \Delta G^0 + RT\ln Q$$

At chemical equilibrium, ΔG = 0

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

so, $\Delta G^0 = -RT \ln K_{eq}$

At equilibrium, $-nF\,E^o_{cell} = -2.303\,RT \log(K_{eq})$

$$\log K_{eq} = \frac{nF}{2.303RT}E^o_{cell}$$

At 298 K and R = 8.314 J/mol K

$$\log K_{eq} = \frac{n}{0.059}E^o_{cell}$$

$$\boxed{K_{eq} = 10^{nE^o_{cell}/0.059}}$$

## Train Your Brain

**Example 9:** Determine the standard equilibrium constant of the following reaction at 298 K.

$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$

**Sol.** In the given reaction, $Fe^{3+}$ is reduced to $Fe^{2+}$ (and hence constitutes right half-cell) and $Sn^{2+}$ is oxidized to $Sn^{4+}$ (constitutes left half-cell). Hence, the cell producing the given reaction is:

$Pt \mid Sn^{2+}, Sn^{4+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$

Its standard potential is

$$E^o_{cell} = E^o_{Fe^{3+},Fe^{2+}|Pt} - E^0_{Sn^{4+},Sn^{2+}|Pt}$$
$$= 0.771\,V - 0.150\,V = 0.621\,V$$

Therefore

$$\log K^o_{eq} = \frac{nFE^o_{cell}}{2.303\,RT} = \frac{2(96\,500\ C\ mol^{-1})\,(0.621\ V)}{2.303\times(8.314\ JK^{-1}mol^{-1})(298\ K)}$$
$$= 21.005$$

Hence, $K^o_{eq} = 1.0\times10^{21}$

The above calculations show that the equilibrium constant of the given reaction has a very large value. It implies that $Sn^{2+}$ can reduce $Fe^{3+}$ quantitatively.

**Example 10:** How would you use the arrangement Ag | AgI (sat. soln.) | AgI(s) | Ag to measure the solubility product of silver iodide at 298 K?

**Sol.** The half-cell reactions are

Right half-cell (**Reduction**) $AgI + e^- = Ag + I^-(aq)$

Left half-cell (**Oxidation**) $Ag = Ag^+(aq) + e^-$

The cell reaction is

$AgI = Ag^+(aq) + I^-(aq)$

The cell potential is given as

$$E_{cell} = E^o_{cell} - \frac{RT}{F}\ln(a_{Ag^+})(a_{1^-}) = E^o_{cell} - \frac{RT}{F}\ln K_{sp}(AgI)$$

At equilibrium, we will have

$$\frac{RT}{F}\ln K^o_{sp}(AgI) = E^o_{cell}$$

At 298 K, we have

$$\log K^o_{sp}(AgI) = \frac{E^o_{cell}}{(2.303\,RT/F)}$$
$$= \frac{(-0.151\ V)-(0.799\ V)}{0.059\,13} = \frac{-0.950\ V}{0.059\,13\ V}$$
$$= -16.07$$

Thus $K^o_{sp}(AgI) = 8.58\times10^{-17}$

**Concept Application**

**8.** Consider the cell $\begin{matrix} H_2(Pt) \\ 1\text{ atm} \end{matrix}\left|\begin{matrix} H_3O^+(aq) \\ pH = 5.03 \end{matrix}\right|\left|\begin{matrix} Ag^+ \\ x\text{ M} \end{matrix}\right|$ Ag. The measured EMF of the cell is 1.0 V. What is the value of x? $E^0_{Ag^+, Ag} = + 0.8$ V. [T = 25°C]

(1) $2.26 \times 10^{-2}$ M (2) $2 \times 10^{-3}$ M

(3) $1.5 \times 10^{-3}$ M (4) $1.5 \times 10^{-2}$ M

**9.** The standard potential of the reaction $H_2O + e^- \rightarrow H_2 + OH^-$ at 298 K by using $K_w$ $(H_2O) = 10^{-14}$, is:

(1) – 0.828 V (2) 0.828 V

(3) 0 V (4) – 0.5 V

## ELECTROLYTIC CELL & ELECTROLYSIS

In an electrolytic cell external source of voltage is used to bring about a chemical reaction.

Electrolyte is a combination of cations and anions which in fused state or in aqueous solution can conduct electricity.

This is possible due to the movement of ions from which it is made up of.

The process of using an electric current to bring about chemical change is called electrolysis.

Electrolysis is a process of oxidation and reduction due to current flow.

The product obtained during electrolysis depends on following factors:

(*i*) The nature of the electrolyte

(*ii*) The concentration of electrolyte

(*iii*) The charge density flowing during electrolysis.

(*iv*) The nature of the electrode

### Quantitative aspects of electrolysis and Faraday's law

#### Faraday's Law of Electrolysis

(***i***) **$1^{st}$ Law:** The mass deposited/released/produced at any substance during electrolysis is proportional to the amount of charge passed into the electrolyte.

$W \propto Q$

$W = ZQ$

Where,

Z = electrochemical equivalent of the substance.

Q = charge

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

**Z** is defined as mass deposited when 1 C of charge is passed into the solution.

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

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

e.g. $Ag^+ + e^- \rightarrow Ag$ $\quad E = \frac{M}{1}$

$Al^{3+} + 3e^- \rightarrow Al(s)$ $\quad E = \frac{M}{3}$

We know that,

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

i.e. 96500 C of charge deposits E gram metal

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

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

$$\boxed{W = \frac{i \times t}{96500} \times E}$$

(***ii***) **$2^{nd}$ Law:** When equal charge is passed through 2 electrolytic cells and these cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

$$W = ZQ = \frac{EQ}{96500}; \quad \boxed{\frac{W_1}{W_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2}(Q = \text{same})}$$

**3D Model**

Scan this QR code to understand Faradays's second Law through 3D model. To learn more download the Physics Wallah App

### Products of Electrolysis

Products of electrolysis depend on:

(*i*) Nature of material

(*ii*) Type of electrodes

(*iii*) In the case of an inert electrode, it will not participate in the reaction, while in the case of a reactive electrode, it will participate in the reaction.

For example, if we use molten NaCl, the products of electrolysis are sodium metal and $Cl_2$ gas. Here we have only one cation ($Na^+$) which is reduced at the cathode ($Na^+ + e^- \rightarrow Na$) and one anion ($Cl^-$) which is oxidised at the anode ($Cl^- \rightarrow 1/2Cl_2 + e^-$). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, $Cl_2$ and $H_2$. In this case besides $Na^+$ and $Cl^-$ ions we also have $H^+$ and $OH^-$ ions along with the solvent molecules, $H_2O$.

The reaction at anode with lower value of $E^0$ is preferred.

**Example:**

(*a*) Electrolysis of molten NaCl

Cathode: $Na^+ + e^- \rightarrow Na$

Anode: $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

(*b*) Electrolysis of aqueous NaCl

Cathode: $H_2O\ (l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-\ (aq)$

Anode: $Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$

**Net reaction:**

$$NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$$

## Train Your Brain

**Example 11:** The time required to coat a metal surface of 80 $cm^2$ with 0.005 mm thick layer of silver (density = 10.5 gm $cm^{-3}$) with the passage of 3A current through silver nitrate solution is

**Sol.** $\because$ Volume of layer of silver $= 0.005 \times 10^{-1} \times 80$
$= 0.04\ cm^3$

$\therefore$ Mass = Density × volume = 10.5 × 0.04 = 0.42 gm

$$\text{So, } w = \frac{E}{96500} \times it \qquad 0.42 = \frac{108}{96500} \times 3 \times t$$

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds}$$

**Example 12:** Calculate the quantity of electricity that will be required to liberate 710 g of $Cl_2$ gas by electrolyzing a conc. Solution of NaCl. What weight of NaOH and what volume of $H_2$ at 27°C and 1 atm pressure is obtained during this process?

**Sol.** $$w = \frac{E.i.t}{96500} \qquad 2Cl^- \longrightarrow Cl_2 + 2e^-$$

$$\because\ Q = i.t \qquad \because\ E_{Cl_2} = \frac{M.wt.}{2}$$

$$\therefore\ Q = \frac{96500\ w}{E} = \frac{96500 \times 710}{35.5} = 20\ F$$

Q = 1930000 coulomb

$\because$ 1 F gives 1g eq. or 40 g NaOH

$\therefore$ 20 F gives 20 g eq. or 40 × 20 g NaOH = 800 g NaOH

Also $\because$ 1 F gives 1 g eq. or 1 g $H_2$

$\therefore$ 20 F gives 20 g eq. or 20 g $H_2$

From $PV = \frac{w}{m} RT$

$$1 \times V = \frac{20}{2} \times 0.0821 \times 300$$

$$\therefore\ V_{H_2} = 246.3 \text{ litre}$$

**Example 13:** How long will it take for uniform current of 6.0 ampere to deposit 78.0g gold from a solution of $AuCl_4^-$?

What mass of chlorine gas will be formed simultaneously at the anode of the electrolytic cell?

**Sol.** $$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$$

$$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$$

$$\therefore\ w_{Au} = \frac{E.i.t.}{96500} \Rightarrow 78 = \frac{197 \times 6 \times t}{3 \times 96500}$$

$\Rightarrow$ *t* = 19104.06 sec

Also, Eq. of Au = Eq. of $Cl_2$

$$\frac{78}{197/3} = \frac{w}{71/2}$$

$$\therefore\ w_{Cl_2} = 42.16g$$

## Concept Application

**10.** Calculate the quantity of ferrous and ferric ions that would be deposited by 1 Faraday. (Fe = 56)

**11.** 0.2864 g of Cu was deposited on passage of a current of 0.5 ampere for 30 minutes through a solution of copper sulphate. What is the electrochemical equivalent of copper? (1F = 96500 coulombs)

**12.** An electric current is passed through three cells connected in series containing $ZnSO_4$, acidified water and $CuSO_4$ respectively. What amount of Zn and $H_2$ are liberated when 6.25 g of Cu is deposited? Eq. wt. of Cu and Zn are 31.70 and 32.6 respectively.

## ELECTROLYTIC CONDUCTANCE

### Difference between metallic conductors and Electrolytic Conductors

**Conductors**

| Metallic Conductors | Electrolytic Conductors |
|---|---|
| 1. Charge carriers are $e^-$ | 1. Charge carriers are ions (cations/anion) |
| 2. No chemical changes | 2. Decomposition of electrolyte takes place. |
| 3. No transfer of mass | 3. Transfer of mass |
| 4. Resistance is due to collision between electrons. | 4. Resistance is because of collision of ions with solvent molecules & because of interionic force of attraction. |
| 5. Temp ↑ R ↑ | 5. Temp ↑ R ↓ |
| 6. Low resistance generally good conductor. | 6. High resistance generally bad Conductor. |

### Resistance

$$R = \frac{V}{I} \left(\text{ohm's law}\ (\Omega)\right)$$

$$R = \frac{\rho \ell}{A}$$

ρ– resistivity/specific resistance (constant).

SI unit is Ω m

$$\boxed{\rho = \frac{RA}{\ell}}$$

Resistivity of a solution is defined as the resistance of the solution between two electrodes of 1 $cm^2$ area of cross section and 1 cm apart.

*or*

Resistance of 1 $cm^3$ of solution will be it's resistivity.

### Conductance

$$G = \frac{1}{R} = \text{mho} = \Omega^{-1} = S \text{ (Siemens)}$$

Conductivity/specific conductance:

$$\kappa = \frac{1}{\rho} = \frac{\ell}{RA} = G\frac{\ell}{A} \text{ where } \frac{\ell}{A} = x \text{ is cell constant}$$

unit: $\Omega^{-1}\ cm^{-1}$

= conductivity of 1 $cm^3$ of solution $\propto$ concentration of ions

$$\kappa = \frac{1}{\rho} \quad \text{and} \quad G = \frac{1}{R}$$

$\kappa \propto$ (no. of ions) no. of charge carriers

Since conductivity or resistivity of the solution is dependent on its concentration, so two more type of conductivities are defined for the solution.

## Factors Affecting Conduction & Resistance

1. Solute– Solute interactions (Inter – ionic force of attraction): Greater the force of attraction, lower is dissociation of solutes.

   $$\boxed{\text{Force} \propto \text{Charge}}$$

2. Solute– Solvent interaction (Hydration/Solvation of ions):

   Greater the solvation, lower is mobility of ion, greater will be resistance.

   $$\boxed{\text{Solvation} \propto \text{Charge on cation} \propto \frac{1}{\text{size}}}$$

   **Example**

   $Li^+$ (Hydrated largest); $Cs^+$ (Hydrated smallest)

   Resistance of LiCl > resistance of CsCl

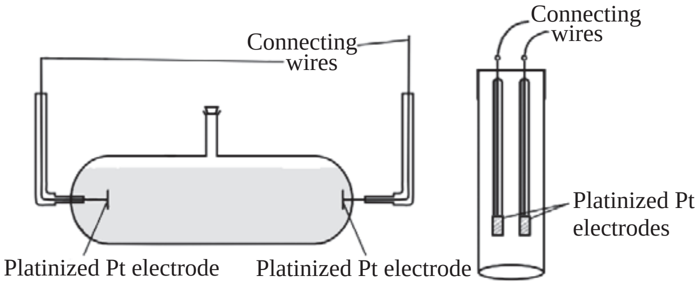
3. Solvent-solvent interaction (Viscosity); Greater the viscosity, greater will be resistance lower will be conduction.
4. Temperature: $T \propto \frac{1}{R}$
5. Nature of electrolyte:

   Weak electrolyte – low conductance due to less dissociation of electrolyte

   Strong electrolyte – High conductance due to complete dissociation.

## Determination of cell Constant

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called conductivity cell. It is available in several designs and two simple ones are shown in Fig.



Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to '*A*' and are separated by distance '*l*'. Therefore, solution confined between these electrodes is a column of length *l* and area of cross section *A*. The resistance of such a column of solution is then given by the equation:

$$R = \rho\frac{l}{A} = \frac{l}{\kappa A}$$

## Molar Conductivity/Molar Conductance ($\Lambda_m$)

Conductivity of a solution containing 1 mole of an electrolyte between 2 electrodes which are 1cm apart.

Let the molarity of the solution be 'C'.

$\therefore$ C moles of electrolyte are present in 1 L of solution.

So, molar conductance

$$\Lambda_m = \kappa V \Rightarrow \Lambda_m = \frac{\kappa \times 1000}{C} \Rightarrow \boxed{\Lambda_m = \frac{\kappa \times 1000}{\text{molarity}}}$$

Its unit is $Ohm^{-1}\ cm^2\ mol^{-1}$.

## Equivalent Conductance ($\Lambda_{eq}$)

Conductivity of a solution containing 1 g equivalent of the electrolyte.

$\Lambda_{eq}$ – equivalent conductivity/conductance

$$\boxed{\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}}$$

Its units is $Ohm^{-1}\ cm^2\ eq^{-1}$.

Relationship between molar conductivity and equivalent conductivity.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{n_f \times \text{Molarity}} = \frac{\lambda_M}{n_f}$$

### Train Your Brain

**Example 14:** If resistivity of 0.8 M KCl solution is $2.5 \times 10^{-3}\ \Omega$ cm, calculate $\Lambda_m$ of the solution.

**Sol.** $\rho = 2.5 \times 10^{-3}\ \Omega$ cm

$$\kappa = \frac{10^3}{2.5} = 4 \times 10^2$$

$$\Lambda_m = \frac{4 \times 10^2 \times 1000}{0.8} = 5 \times 10^5 \Omega^{-1} cm^2 mole^{-1}$$

**Example 15:** The resistance of an 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.

**Sol.** Cell constant $=\frac{l}{a}=\frac{4}{7}\text{ cm}^{-1}$.

Specific conductance = conductance × cell constant

$$=\frac{1}{\text{resistance}}\times\frac{l}{a}=\frac{1}{245}\times\frac{4}{7}=2.332\times10^{-3}\text{mho cm}^{-1}.$$

$$\wedge_{eq}=\frac{\kappa\times1000}{N}$$

$$=\frac{2.332\times10^{-3}\times1000}{\frac{1}{10}}=23.32\ \Omega^{-1}\text{ cm}^{2}\text{ eq}^{-1}$$

**Concept Application**

**13.** In a conductivity cell, the two platinum electrodes, each of area 10 sq cm, are fixed 1.5 cm apart. The cell contained 0.05 N solution of a salt. If the two electrodes are just half dipped into the solution, which has a resistance of 50 ohms, find equivalent conductance of the salt solution.

**14.** The resistance of conductivity cell containing M/10 NaCl solution at 298 K is 2000 Ω. What is the cell constant if conductivity of solution is $0.15\times10^{-2}$ S $\text{cm}^{-1}$?

### Electrolytes

Electrolytes are the substances that dissociate into in aqueous solution.

## Variation of Conductivity and Molar Conductivity with Concentration

Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.

The number of ions per unit volume that carry the current in a solution decreases on dilution.

Molar conductivity increases with decrease in concentration. This is because the total volume, V of solution containing one mole of electrolyte also increases.

Molar conductivity is the conductance of solution.

When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ°.

## STRONG ELECTROLYTES

For strong electrolytes, Λ increases slowly with dilution and can be represented by the equation $\Lambda=\Lambda^{\circ}-A\sqrt{c}$

The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e. the charges on the cations and anions produced on the dissociation of the electrolyte in the solution.

**Example:** NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 1-2 and 2-2 electrolyte respectively.

All electrolytes of a particular type have the same value for 'A'

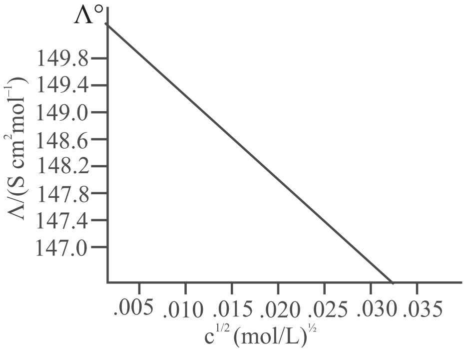


**Fig.:** Variation of Λ against $c^{1/2}$

### Debye - Huckel Onsager Equation

The equivalent conductance at large dilution (or) at very low concentration is known as equivalent conductance at infinite dilution ($\Lambda_\infty$) or zero concentration ($\Lambda_0$).

The equivalent conductance of an electrolytic solution at any concentration (C) is related to $\Lambda_o$ for solutions is given by the following Debye-Huckel - Onsager equation.

$$\Lambda_C=\Lambda_o-\left[\frac{82.4}{(DT)^{1/2}_{\eta}}+\frac{8.2\times10^{5}}{(DT)^{3/2}}\Lambda_o\right]\sqrt{c}$$

Where

D = Dielectric constant of water

T = Temperature in kelvin scale

$\Lambda_c$ = Equivalent conductance at conc 'c'

$\Lambda_o$ = equivalent conductance at almost zero concentration or infinite dilution.

η = viscosity co-efficient of solvent.

In short form, this equation is represented as:

$$\boxed{\Lambda_c=\Lambda_0-b\sqrt{c}}$$

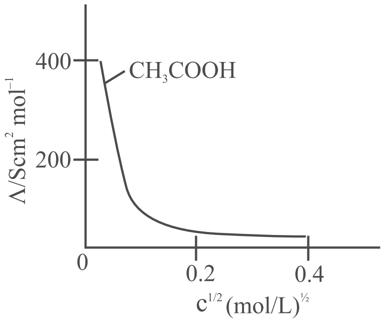
Where *b* is constant and depends on the nature of the solvent and temperature.

## WEAK ELECTROLYTES

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

At infinite dilution (i.e. concentration $c \rightarrow$ zero), electrolyte dissociates completely ($\alpha = 1$), but at such low concentration, the conductivity of the solution is so low that it cannot be measured accurately.

Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) is given as:



## Effect of Dilution

- With dilution, "Λ" as well as "$\Lambda_m$" of both weak/strong electrolytes increases.
- Specific conductivity (κ) decreases with dilution because of decrease in no. of ions per $cm^3$ of electrolyte.
- The molar (or) equivalent conductance of an electrolyte at infinite dilution (or) zero concentration is known as limiting molar conductance (or) limiting equivalent conductance.
- $\Lambda_0$ value for any strong electrolyte is calculated graphically but for weak electrolyte it is determined by **Kohlrausch's law**.
- The magnitude of increase in molar conductance for weak electrolyte is much larger than that for a strong electrolyte because strong electrolytes are almost completely ionised in all concentration and increase in $\Lambda_{eq}$ (or) $\Lambda_m$ with dilution is only due to decrease in interionic attractions.

## Effect of Temperature

The conductivity of all electrolytes increases with increase in temperature.

## Conductance Ratio (α)

The ratio of the equivalent conductance at any concentration ($\Lambda_c$) to that at infinite dilution ($\Lambda_0$) is called conductance ratio (α).

$$\boxed{\alpha = \frac{\Lambda_c}{\Lambda_o}}$$

For weak electrolytes, α = degree of ionisation.

**Key Note**

α is high for 0.01 M $CH_3COOH$ solution when compared to that of 0.1 M $CH_3COOH$, because $\Lambda_c$ is high in case of 0.01 M $CH_3COOH$

## KOHLRAUSCH'S LAW

Based on κ (specific conductance) value, electrolytes are of two types.

(*i*) Weak electrolytes: These have low 'κ' value
Eg : Weak acids, Weak bases.

(*ii*) Strong electrolytes: These have high 'κ' value
Eg : Strong acids, Strong bases, Salt solutions.

The conductance of an electrolyte is due to its ionisation.

The ionisation extent reaches maximum for weak electrolytes as dilution reaches maximum.

**Key Note**

$ClCH_2COOH$ has higher 'κ' value than $CH_3COOH$ since $ClCH_2COOH$ is stronger acid than $CH_3COOH$.

### Statement of Kohlrausch's Law

"The equivalent conductance at infinite dilution ($\Lambda_0$) of an electrolyte is equal to the algebraic sum of equivalent condutances (or) mobilities of anion ($\lambda_0^-$) and cation ($\lambda_0^+$) of the electrolyte at infinite dilution"

$$\boxed{\Lambda_0\left(\text{electrolyte}\right) = \lambda_0^+ + \lambda_0^-\left(\text{ions}\right)}$$

$$\boxed{\Lambda_{eq}^0 = \frac{1}{n^+}\lambda_c^0 + \frac{1}{n^-}\lambda_a^0}$$

**Example**

(*i*) $\Lambda_{KCl}^0 = \lambda_{K^+}^0 + \lambda_{Cl^-}^0$

(*ii*) $\Lambda_{eq.(CaCl_2)}^0 = \frac{1}{2}\lambda_{Ca^{2+}}^0 + \lambda_{Cl^-}^0$

(*iii*) $\Lambda_{eq.(AlCl_3)}^0 = \frac{1}{3}\lambda_{Al^{3+}}^0 + \lambda_{Cl^-}^0$

(*iv*) $\Lambda_{eq.Fe_2(SO_4)_3}^0 = \frac{1}{3}\lambda_{Fe^{3+}}^0 + \frac{1}{2}\lambda_{SO_4^{2-}}^0$

Where $n^+$ and $n^-$ are charge on each ion furnished by electrolyte. This law is valid at any dilution but is applied only at infinite dilution. Whereas "molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of electrolyte" e.g. $A_xB_y$

$$\boxed{\Lambda_M^0 = x \times \lambda_A^0 + y \times \lambda_B^0}$$

**Example**

(*i*) $\Lambda_{BaCl_2}^0 = \lambda_{Ba^{2+}}^0 + 2\lambda_{Cl^-}^0$

(*ii*) $\Lambda_{Fe_2\left(SO_4\right)_3}^0 = 2\lambda_{Fe^{3+}}^0 + 3\lambda_{SO_4^{2-}}^0$

**Key Note**

Ionic conductance is more for hydrated $Cs^+$ than hydrated $Li^+$.

### Applications of Kohlarausch Law

Using Kohlrausch law of independent migration of ions, it is possible to calculate E for any electrolyte from the 2° of individual ions. Moreover, m for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the E and A, at a given concentration *c*.

**Determination of $\Lambda_0$ for weak electrolytes:**

Eg : $NH_4OH$ is a weak electrolyte, its $\Lambda_o$ is calculated as:

$\Lambda_0(NH_4OH) = \Lambda_0(NH_4Cl) + \Lambda_0(NaOH) - \Lambda_0(NaCl)$

Degree of ionisation of weak electrolyte

$$(\alpha) = \frac{\Lambda_c}{\Lambda_0}$$

where, $\Lambda_c$ = equivalent conductivity at given concentration

$\Lambda_0$ = limiting equivalent conductivity

Dissociation constant of weak electrolyte

$K = c\alpha^2$

$\Lambda_m^0 = \Lambda_{eq}^0 \times$ n-factor

$\Lambda^0{}_m = n \times \Lambda^0{}_{eq}$

Calculation of dissociation constant of weak electrolytes:

$$\boxed{K_a = \frac{c\alpha^2}{1-\alpha} \Rightarrow K_a = \frac{c\left(\frac{\Lambda_c}{\Lambda_0}\right)^2}{\left(1-\frac{\Lambda_c}{\Lambda_0}\right)} = \frac{c\Lambda_c^2}{\Lambda_0\left(\Lambda_0 - \Lambda_c\right)}}$$

## Train Your Brain

**Example 16:** At infinite dilution, the molar conductance of $Al^{3+}$ and $SO_4^{-2}$ ions are 189 and $160\Omega^{-1}$ $cm^2$ $mol^{-1}$ respectively. Calculate the equivalent and molar conductivity at infinite dilution of $Al_2(SO_4)_3$.

**Sol.** $\Lambda^0_{eq[Al_2(SO_4)_3]} = \frac{1}{3}\lambda^0_{Al^{+3}} + \frac{1}{2}\lambda^0_{SO_4^{2-}}$

$$= \frac{1}{3}\times 189 + \frac{1}{2}\times 160 = 143\Omega^{-1}cm^2eq^{-1}$$

Molar conductivity = $\Lambda^0_{eq}$ × n-factor

$= 143 \times 6 = 858\ \Omega^{-1}\ cm^2\ mol^{-1}$

**Example 17:** The equivalent conductance of an infinitely dilute solution of $NH_4Cl$ is 150 and the equivalent conductances of $OH^-$ and $Cl^-$ ions are 198 and 76 respectively. What will be the equivalent conductance of the solution of $NH_4OH$ at infinite dilution? If the equivalent conductance of a 0.01 N solution of $NH_4OH$ is 9.6, what will be its degree of dissociation?

**Sol.** $\Lambda^0_{NH_4Cl} = \lambda^0_{NH_4^+} + \lambda^0_{Cl^-}$

$\therefore \quad \lambda^0_{NH_4^+} = \Lambda^0_{NH_4Cl} - \lambda^0_{Cl^-} = 150 - 76 = 74$

$\therefore \quad \Lambda^0_{NH_4OH} = \lambda^0_{NH_4^+} + \lambda^0_{OH^-} = 74 + 198 = 272$

Further, degree of dissociation $= \frac{\Lambda_c}{\Lambda_o} = \frac{9.6}{272} = 0.0353.$

**Example 18:** The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho $cm^2$ $eq.^{-1}$ at 25°C. A cell with electrodes that are 1.50 $cm^2$ in surface area and 0.50 cm apart is filled with 0.1N $MgCl_2$ solution. How much current will flow when the potential difference between the electrodes is 5 volts?

**Sol.** $\Lambda_{eq} = 97.1\ Scm^2\ eq^{-1}$, C = 0.1 N

A = 1.5 $cm^2$, l = 0.5 cm

$$\Lambda_{eq} = \frac{1000\times\left(\frac{1}{R}\times\frac{\ell}{A}\right)}{C}$$

$$\Rightarrow 97.1 = \frac{1000}{0.1}\times\frac{1}{R}\times\frac{0.5}{1.5}$$

$R = 34.33\ \Omega \Rightarrow i = \frac{V}{R} = \frac{5}{34.33} = 0.1456$ A

## Concept Application

**15.** Calculate $K_a$ of $CH_3COOH$ if its 0.01 M solution has molar conductance 16.48 S $cm^2$ $mol^{-1}$. Given limiting molar conductivity is 400 S $cm^2$ $mol^{-1}$.

**16.** The specific cond. of a saturated solution of AgCl at 25°C after subtracting the sp. conductance of conductivity of water is $2.28 \times 10^{-6}$ mho $cm^{-1}$. Find the solubility product of AgCl at 25°C. [Given $\Lambda^\infty_{AgCl}$ = 150 $\Omega^{-1}$ $cm^2$ $mol^{-1}$]

## Variation of $\kappa$, $\Lambda_m$ & $\Lambda_{eq}$ of Solutions with Dilution

$\kappa \propto$ conc. of ions in the solution. In case of both strong and weak electrolytes on dilution, the concentration of ions will decrease hence, $\kappa$ will decrease.

($\kappa \propto c$) strong electrolyte

$$\Lambda_m = \frac{1000\times\kappa}{\text{molarity}} \Rightarrow \left(\kappa \propto \sqrt{K_a.c}\right) \text{ weak electrolyte}$$

$$\Lambda_{eq} = \frac{1000\times\kappa}{\text{normality}} \qquad [\text{Note: } \kappa = \text{Kappa}]$$

$K_a$ = dissociation constant

For strong electrolyte : $\Lambda_m \propto \frac{\kappa}{c} \propto \frac{c}{c}$ = constant

For weak electrolyte : $\Lambda_m \propto \frac{\kappa}{c} \propto \frac{1}{\sqrt{c}}$

## Absolute Ionic Mobility and Their Calculations

The ionic mobility ($\mu$) is defined as the velocity attained by an ion moving through a gas under unit electric field.

Ionic mobility or Ionic conductance is the conductivity of a solution containing 1 g ion, at infinite dilution, when two sufficiently large electrodes are placed 1 cm apart.

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

Unit of ionic mobility is $\text{Ohm}^{-1}\ \text{cm}^2$ or $\text{V}^{-1}\ \text{S}^{-1}\text{cm}^2$

Ionic mobility and transport number are related as,

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

Absolute ionic mobilityis the mobility with which the ion moves under unit potential gradient. It's unit is cm $\text{sec}^{-1}$.

Absolute ionic mobility = Ionic mobility/96,500.

## Conductometric Titrations

In this type of titration, upon the continuous addition of the titrant (and the continuous recording of the corresponding change in electrolytic conductivity), a sudden change in the conductivity implies that the equivalence point has been reached. The increase or decrease in the electrolytic conductivity in the conductometric titration process is linked to the change in the concentration of the hydroxyl and hydrogen ions (which are the two most conducting ions).

The principle of the conductometric titration process can be stated as follows – During a titration process, one ion is replaced with another and the difference in the ionic conductivities of these ions directly impacts the overall electrolytic conductivity of the solution.

### 1. Strong acid Add with a Strong Base, e.g. HCl with NaOH

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance decreases due to the replacement of hydrogen ions by the added cation as $H^+$ ions react with $OH^+$ ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only *NaCl*. After the equivalence point, the conductance increases due to the high conductivity of $OH^-$ ions (Fig. 1).

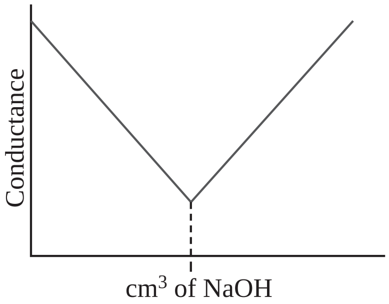


**Fig. 1:** Conductometric titration of strong acid (HCl) vs. strong base (NaOH).

### 2. Strong acid Add with a Weak Base, e.g. HCl with dilute ammonia

Initially the conductance is high and then it decreases due to the replacement of $H^+$. But after the endpoint has been reached, the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium chloride (Fig. 2). (Basic Buffer)

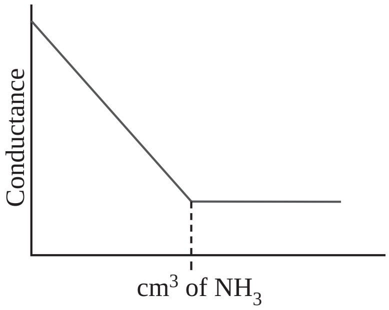


**Fig. 2:** Conductometric titration of strong acid (HCl) vs. weak base ($NH_4OH$).

### 3. Weak Acid with a Strong Base: e.g. $CH_3COOH$ with NaOH

Initially a slight decrease in the conductance is caused by binding a small amount of hydrogen ions, originating from dissociation of acetic acid, into waler molecules. Next, the gradual conductance increase is connected with the substitution of the weakly dissociated acetic acid by the well dissociated sodium acetate. After the equivalence point has been reached, the conductance increases significantly due to the increasing concentration of $OH^-$ ions (Fig. 3).

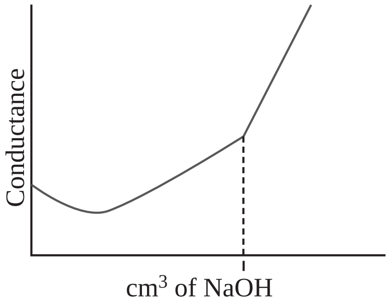


**Fig. 3:** Conductometric titration of weak acid ($CH_3COOH$) vs. strong base (NaOH).

### 4. Weak Acid with a Weak Base: e.g. $CH_3COOH$ with dilute ammonia

Initially a slight decrease in the conductance is caused by binding a small amount of hydrogen ions originating from dissociation of acetic acid into water molecules and next an increase is observed because of well dissociated salt - ammonium acetate formation. After the equivalence point the conductance increases but much less (Fig. 4).

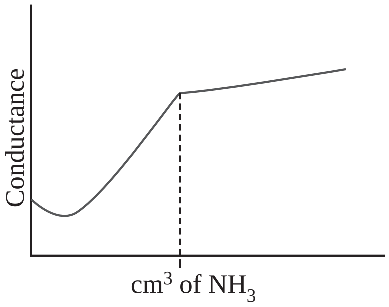


**Fig. 4:** Conductometric titration of weak acid ($CH_3COOH$) vs. weak base ($NH_4OH$).

## Advantages and Disadvantages of Conductometric Titration

Some advantages of the conductometric titration process are listed below.

- This process is very useful in the titrations of very dilute solutions and weak acids.
- The end-point of this method of titration is very sharp and accurate when compared to a few other titration processes.
- This type of titration is applicable for solutions that are coloured or turbid, and for which the endpoint of the titration with normal indicators cannot be observed easily by the human eye.
- Conductometric titration has numerous applications in acid-base titrations, redox titrations, precipitation titrations, and complex titrations.

**The two major disadvantages of this type of titration include:**

1. Only a few specific redox titrations can be done with the help of this process. This is because the conductivity of the solution is masked by relatively high hydronium ion concentration.
2. The accuracy of conductometric titration is low when the concentrations of the electrolyte are high, making the titration process unsatisfactory.

## CELL & BATTERIES

**3D Model**

Scan this QR code to understand Charging and Dischargin process of Cell & Batteries through 3D model. To learn more download the Physics Wallah App

### Primary Cells

(*i*) It is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current.

(*ii*) In which electrode reactions cannot be reversed by external source.

**Example:** Dry cell (leclanche cells), mercury cells

$E_{cell}$ = constant as all substances used are either pure solids or pure liquids.

### Secondary Cells

(*i*) Electrical energy from an external source is first converted into chemical energy (Electrolysis) and when the source is removed then the cell is made to operate in the reverse direction.

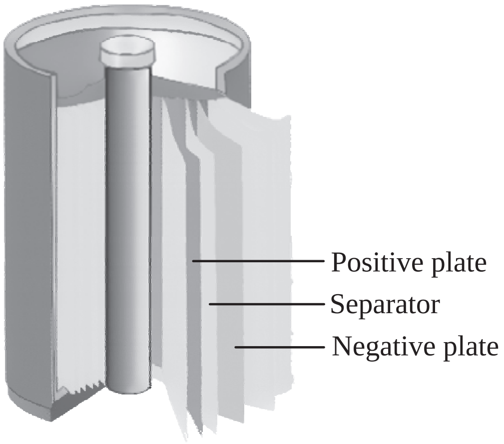
(*ii*) Secondary cells are those which are rechargeable and can be used again and again.

**Example:** Lead storage batteries used in automobiles (Cars/bikes), Li-ion battery, hydrogen oxygen fuel cell etc.

### Nickel-Cadmium Cell

- Has a jelly roll arrangement separated by a layer soaked in moist NaOH or KOH.
- Longer life than the lead storage cell, but more expensive to manufacture.
- The overall reaction during discharge:

  $Cd(s) + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

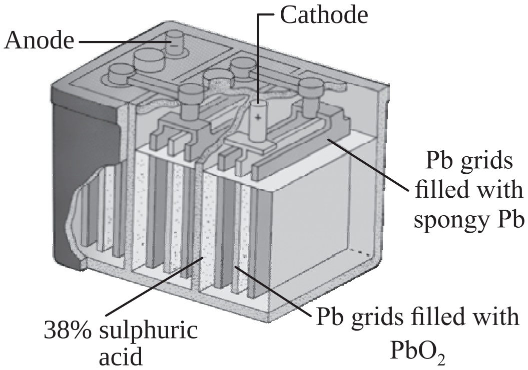


### The Lead Storage Battery

- **Anode:** Pb grids with spongy Pb

  Rxn. $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$
- **Cathode:** Pb grids filled with $PbO_2$

  Rxn. $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(1)$
- **Electrolyte:** 38% solution of $H_2SO_4$
- Cell rxn.: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(1)$
- On charging the battery, the reaction is reversed.
- Used commonly in **automobiles and inverters.**



### Fuel Cells

Galvanic cells which are designed to convert the energy of combustion of fuels like methane, hydrogen, methanol, etc. directly into electrical energy are known as fuel cells.

#### Hydrogen-Oxygen fuel cell

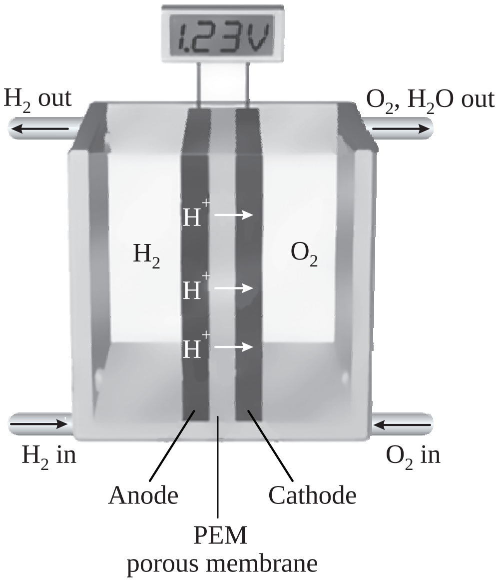
- **Electrodes:** C with finely divided Pt or Pd for increasing electrode reaction.

- **Electrolyte:** Conc. aq. NaOH

  **Cathode reaction:** $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

  **Anode reaction:** $2H_2(g) + 4OH^-\ (aq) \rightarrow 4H_2O(l) + 4e^-$

  **Overall:** $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- The cell was used for electrical power in the **Apollo space programme**. The water was used for drinking by astronauts.
- This cell runs continuously as long as the reactants are supplied.

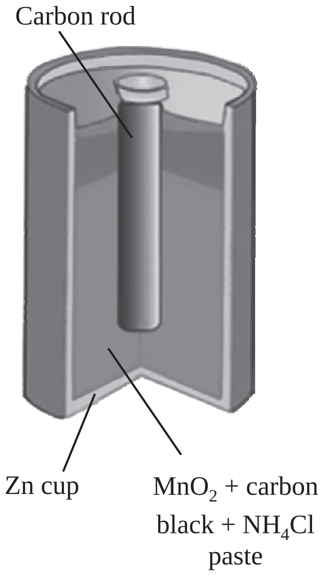


## Dry Cell or Leclanche Cell

- **Anode:** Zinc container

  Reaction: – $Zn(s) \rightarrow Zn^{2+}\ (aq) + 2e^-$
- **Cathode:** Carbon (graphite) rod surrounded by powdered manganese dioxide and carbon

  Reaction: – $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$
- **Electrolyte:** A moist paste of ammonium chloride ($NH_4Cl$) and zinc chloride ($ZnC1_2$)
- Ammonia forms a complex with $Zn^{2+}$ to give $[Zn\ (NH_3)_4]^{2+}$.
- Cell Potential ≈ **1.5 V**
- Used commonly in **transistors and clocks**.

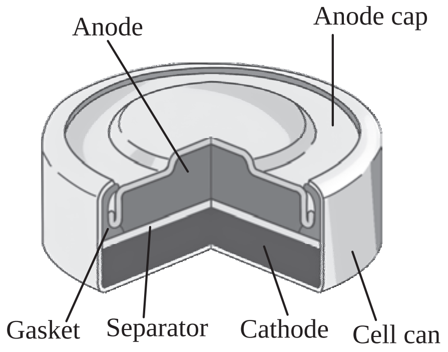


## Mercury Cell

- **Anode:** Zinc – mercury amalgam

  Reaction $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$
- **Cathode:** A paste of HgO and carbon

  Reaction: – $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$
- **Electrolyte:** A paste of KOH and ZnO
- Cell Reaction: $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
- Cell Potential ≈ **1.35 V** (remains constant during its life as ions are not involved)
- Used commonly in **low current devices** like **hearing aids, watches, etc.**



# SHORT NOTES

## Electrochemical Cells

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

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

Electrochemical cells can be classified as:

(*i*) Electrolytic Cells in which a non-spontaneous reaction is driven by an external source of current.

(*ii*) Galvanic Cells which produce electricity as a result of a spontaneous cell reaction.

## Electrolysis

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

## Electrolytic Cell

This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell.

## Electrodes

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

## Faraday's Laws of Electrolysis

(*i*) **First law of electrolysis:** $w \propto Q$

$w$ = weight liberated

$Q$ = charge in coluomb

$w = ZQ$

(*ii*) **Second law of electrolysis:** $w_1/w_2 = E_1/E_2$

## Conductance

**Introduction:** i.e. $V = IR$

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

$$\frac{1}{R} = \frac{1A}{\rho l} \quad \text{or} \quad G = \kappa\frac{A}{l}$$

where $G$ = conductance $\text{ohm}^{-1}$,

$\kappa$ = specific conductance $\text{ohm}^{-1}\ \text{cm}^{-1}$.

Mho and siemens are other units of conductance

$$\kappa = \frac{l}{A}G$$

Specific conductance = Cell constant – Conductance

**Specific conductance is conductance of 1 $\text{cm}^3$ of an electrolyte solution.**

1. **Equivalent Conductance:**

$$\Lambda = \kappa \times V$$

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

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

$$\text{Thus, } \Lambda_{eq} = \kappa \times \frac{1000}{N}$$

2. **Molar Conductance:**

$$\Lambda_m = \kappa V$$

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

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

## Application of Kohlrausch's Law

1. **Determination of $\Lambda_m^0$ of a weak electrolyte:**

In order to calculate $\Lambda_m^0$ of a weak electrolyte say $CH_3COOH$, we determine experimentally $\Lambda_m^0$ values of strong electrolytes:

2. **Determination of degree of dissociation ($\alpha$):**

$$\alpha = \frac{\text{Number of molecules ionised}}{\text{Total number of molecules dissovled}} = \frac{\Lambda_m}{\Lambda_m^0}$$

3. **Determination of solubility of sparingly soluble salt:**

$$\Lambda_m^0 = \frac{1000\kappa}{C}$$

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

## Relationship Between ΔG and Electrode Potential

Work done = Charge × Potential = nFE

$\therefore\ \Delta G = -nFE$

Under standard state

$\Delta G^0 = -nFE^0$

## Concept of Electromotive Force (emf) of a Cell

$E_{cell}$ = Reduction potential of cathode – Reduction potential of anode

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

$E°_{cell}$ = Standard reduction potential of cathode – Standard

## Nernst Equation

$$\Delta G = \Delta G° + RT \ln Q \qquad ...(i)$$

$$\therefore\ -\Delta G = nFE \qquad \text{and} \qquad -\Delta G° = nFE°$$

Thus from Eq. (i), we get $-nFE = -nFE° + RT \ln Q$

(*i*) **Determination of equilibrium constant:**

$$K_{eq} = \text{antilog}\left[\frac{nE^0}{0.0591}\right]$$

(*ii*) **Heat of Reaction inside the cell:**

$$\therefore\ \Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_P$$

(*iii*) **Entropy change inside the cell:**

$$\text{or}\ \ \Delta S = nF\left[\frac{\partial E}{\partial T}\right]_P$$

## Concentration Cell

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

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

$$E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$$

For spontaneity of such cell reaction, $p_1 > p_2$

(*ii*) **Electrolyte concentration cells:**

$$\text{or}\qquad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontaneity of such cell reaction, $C_2 > C_1$

## AARAMBH (SOLVED EXAMPLES)

**1.** Saturated solution of $KNO_3$ is used to make salt bridge because

(1) Velocity of $K^+$ is greater than that of $NO_3^-$

(2) Velocity of $NO_3^-$ is greater than that of $NO_3^-$

(3) Velocity of $K^+$ and $NO_3^-$ are nearly same

(4) $KNO_3$ is highly soluble in water

**Sol.** Velocity of $K^+$ and $NO_3^-$ are nearly same so that electroneutrality is maintained (1), (2) are ruled out and (4) is not correct reason for selecting $KNO_3$.

Therefore, option (1) is the correct answer.

**2.** What is the charge on tin if 7.42 g of metallic tin is deposited by passage of 24125 C through a solution containing the ion? [At. wt. of Sn = 118]

| | |
|---|---|
| (1) +1 | (2) + 3 |
| (3) + 2 | (4) + 4 |

**Sol.** $m = Z \times Q$

$$7.42 = \frac{118}{n \times 96500} \times 24125 \Rightarrow n = \frac{118}{7.42 \times 4} = 4$$

Therefore, option (4) is the correct answer.

**3.** A factory produces 40 kg of calcium in two hours by electrolysis. How much aluminium can be produced by same current in 2 hours if current efficiency is 50%?

| | |
|---|---|
| (1) 22 kg | (2) 18 kg |
| (3) 9 kg | (4) 27 kg |

**Sol.** $\frac{W_{Ca}}{E_{Ca}} = \frac{W_{Al}}{E_{Al}} \Rightarrow \frac{40}{20} = \frac{W_{Al}}{9} \Rightarrow W_{Al} = 18\text{ kg}$

If current efficiency is 100%, then

$W_{Al}$ = 9 kg because current efficiency is 50%.

Therefore, option (3) is the correct answer.

**4.** $Cu^{2+}(C_1) + Zn(s) \longrightarrow Zn^{2+}(C_2) + Cu(s)$

For a cell reaction of an electrochemical cell, the free energy change $\Delta G$ at a given temperature is a function of

| | |
|---|---|
| (1) $\ln C_1 \times C_2$ | (2) $\ln \frac{C_2}{C_1}$ |
| (3) $\ln C_1$ | (4) $\ln C_2$ |

**Sol.** $\Delta G = -RT\ln K$

$\Delta G$ is a function of ln K for a given temperature

$$K = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{C_2}{C_1} \Rightarrow \ln K = \ln\frac{C_2}{C_1}$$

Therefore, option (2) is the correct answer.

**5.** How much time is required for the complete decomposition of 2 moles of water using a current of 2 ampere?

**Sol.** Electrolysis of water takes place according to the equation:

$2H_2O \rightarrow 2H_2 + O_2$

$\because$ 1 equivalent of hydrogen is produced by $\frac{1}{2}$ mole of water

$\therefore$ No. of equivalents of $H_2O$ decomposed

= 2 × no. of moles of water = 2 × 2 = 4.

[Eqn. 6(ii), Chapter 7]

$\because$ 1 equivalent of $H_2O$ will be decomposed by 1 mole of electricity (1 F)

$\therefore$ Mole of electric charge = 4 faradays = 4 × 96500 coulombs

$$\therefore\ \text{Duration of electrolysis} = \frac{\text{change in coulombs}}{\text{current in amperes}}$$

$$= \frac{4 \times 96500}{2}\text{ seconds}$$

$$= \frac{4 \times 96500}{2 \times 60 \times 60}\text{ hours}$$

= 53.61 hours.

**6.** In an electrolysis experiment, current was passed from 5 hour through two cells connected in series. The first cell contains a solution of gold and the second contains $CuSO_4$ solution. 9.85g of gold was deposited in the first cell. If the oxidation no. of gold is + 3, find the amount of Cu deposited on cathode in second cell. Also, calculate the current strength in ampere. At. wt. of Au = 197 and at. wt. of Cu = 63.5.

**Sol.** Equivalent of gold formed = Eq. of Cu formed

$$\frac{9.85}{197/3}=\frac{w_{Cu}}{63.5/2} \quad \begin{array}{l} Au^{3+}+3e^{-}\to Au \\ Cu^{2+}+2e^{-}\to Cu \end{array}$$

$\therefore$ $w_{Cu}$ = 4.763g

$$\text{Also } w=\frac{E.i.t.}{96500}$$

$$\therefore 4.763=\frac{63.5\times i\times 5\times 60\times 60}{2\times 96500}$$

$\therefore$ $i$ = 0.804 ampere

**7.** Calculate the e.m.f. of cell

$$\begin{array}{c|c||c|c} Pt_{H_2} & CH_3COOH & NH_4OH & Pt_{H_2} \\ 1\,atm & 0.1\,M & 0.01\,M & 1\,atm \end{array}$$

$K_a$ for $CH_3COOH = 1.8 \times 10^{-5}$;

$K_b$ for $NH_4OH = 1.8 \times 10^{-5}$.

**Sol.** At L.H.S. :

From $CH_2COOH \rightleftharpoons CH_2COO^{-}+H^{+}$

$$[H^{+}]=c\times\alpha=c\sqrt{\left(\frac{K_a}{c}\right)}=\sqrt{(K_a.c)}$$

$$=\sqrt{(1.8\times10^{-5}\times0.1)} = 1.342 \times 10^{-3}\text{ mol L}^{-1}$$

At R.H.S. : From $NH_4OH \rightleftharpoons NH_4^{+}+OH^{-}$

$$[OH^{-}]=c\times\alpha=c\sqrt{\left(\frac{K_b}{c}\right)}$$

$$=\sqrt{(K_b.c)}=\sqrt{(1.8\times10^{-5}\times0.01)}$$

$$= 0.424 \times10^{-3}\text{ mol litre}^{-1}$$

$$\therefore [H^{+}]=\frac{10^{-14}}{0.424\times10^{-3}}=2.359\times10^{-11}\text{ mol L}^{-1}$$

Now for cell,

$\frac{1}{2}H_2 \to H^{+}+e^{-}$ At anode, i.e., L.H.S.

$H^{+}+e \to \frac{1}{2}H_2$ At cathode, i.e., R.H.S.

$$E_{cell}=E_{OP_{H/H^{+}}}+E_{RP_{H^{+}/H}}$$

$$=E^{0}_{OP_{H/H^{+}}}-\frac{0.059}{1}\log_{10}\frac{[H^{+}]_{L.H.S.}}{[P_{H_2}]^{1/2}}+E^{0}_{RP_{H^{+}/H}}$$

$$+\frac{0.059}{1}\log_{10}\frac{[H^{+}]_{R.H.S.}}{[P_{H_2}]^{1/2}}$$

$$=\frac{0.059}{1}\log_{10}\frac{[H^{+}]_{R.H.S.}}{[H^{+}]_{L.H.S.}}$$

($\because$ $P_{H_2}$ = 1 atm on both sides)

$$=\frac{0.059}{1}\log_{10}\frac{2.359\times10^{-11}}{1.342\times10^{-3}}$$

= – 0.4575 V

**8.** The reduction potential diagram for Cu in acid solution is

$$\begin{tikzcd} Cu^{+2} \arrow[r, "+0.15\text{ volt}"] \arrow[rr, bend right, "E^{0} = X\text{ volt}"'] & Cu^{+} \arrow[r, "+0.50\text{ volt}"] & Cu \end{tikzcd}$$

Calculate X. Does $Cu^{+}$ disproportionate in solution?

**Sol.** Given, $Cu^{2+}+e^{-}\longrightarrow Cu^{+};\ E^{0}_{1}=0.15\text{ V};\ \Delta G^{0}_{1}$ …($i$)

$Cu^{+}+e^{-}\longrightarrow Cu;\ E^{0}_{2}=0.5\text{ V};\ \Delta G^{0}_{2}$ …($ii$)

$Cu^{2+}+2e^{-}\longrightarrow Cu;\ E^{0}_{3}=?;\ \Delta G^{0}_{3}$ …($iii$)

For Eq. ($i$), $+\Delta G^{0}_{1}=-nE^{0}_{1}F=-1\times0.15\times F=-0.15\text{ F}$

For Eq. ($ii$), $+\Delta G^{0}_{2}=-nE^{0}_{2}F=-1\times0.5\times F=-0.5\text{ F}$

$\therefore$ Adding $\Delta G^{0}_{1}+\Delta G^{0}_{2}=\Delta G^{0}_{3}$

$-0.15F+(0.5F)=\Delta G^{0}_{3}$

$\Delta G^{0}_{3}=-0.65\text{ F}$

$-nE^{0}_{3}F=-0.65\text{ F}$

$$\text{or } E^{0}_{3}=\frac{-0.65F}{-2F}=0.325\text{ V}$$

$\therefore$ X = + 0.325 V

Now for disproportionation,

$Cu^{+}\longrightarrow Cu^{2+}+e^{-};\ E^{0}_{OP}$

$Cu^{+}+e^{-}\longrightarrow Cu;\ E^{0}_{RP}$

---

$2Cu^{+}\longrightarrow Cu^{2+}+Cu$ ...($iv$)

$$\therefore\ E^{0}_{cell}=E^{0}_{OP_{Cu^{+}/Cu^{+2}}}+E^{0}_{RP_{Cu^{+}/Cu}}=-0.15+0.5$$

= + 0.35 V (yes, it disproportionates)

**9.** A current of 3.7 ampere is passed for 6 hr between Ni electrodes in 0.5 litre of 2 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

**Sol.** The electrolysis of $Ni(NO_3)_2$ in presence of Ni electrode will bring in following changes:

At anode: $Ni \longrightarrow Ni^{2+} + 2e^{-}$

At cathode: $Ni^{2+} + 2e^{-} \longrightarrow Ni$

$\because$ Eq of $Ni^{2+}$ formed = Eq. of $Ni^{2+}$ lost

Thus, there will be no change in conc. of $Ni(NO_3)_2$ solution during electrolysis i.e., it will remain 2 M.

**10.** Which of the following is not a redox reaction?

(1) $2Na + Cl_2 \to 2NaCl$

(2) $Cu + 2AgNO_3 \to Cu(NO_3)_2 + 2Ag$

(3) $2H_2 + O_2 \to 2H_2O$

(4) $Zn + CuSO_4 \to ZnSO_4 + Cu$

**Sol.** This is a synthesis reaction where two hydrogen molecules combine with one oxygen molecule to form two water molecules. There is no change in oxidation states, indicating that it is not a redox reaction.

Therefore, option (3) is the correct answer.

**11.** Which of the following is the strongest reducing agent?

(1) Na (2) Mg

(3) Al (4) Zn

**Sol**. The reducing power of an element is determined by its ability to lose electrons. Sodium (Na) has a lower ionization energy and readily loses electrons, making it a strong reducing agent compared to the other elements listed.

Therefore, option (1) is the correct answer.

**12.** In which of the following half-reactions is reduction taking place?

(1) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

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

(3) $Cl_2 + 2e^- \rightarrow 2C1^-$

(4) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

**Sol**. Reduction involves gaining electrons. In the given half-reaction, $MnO_4^-$ gains 5 electrons to form $Mn^{2+}$, indicating a reduction process.

Therefore, option (2) is the correct answer.

**13.** Which of the following is a non-spontaneous redox reaction?

(1) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

(2) $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

(3) $2Na + Cl_2 \rightarrow 2NaCI$

(4) $2Al + 3Pb(NO_3)_2 \rightarrow 2AI(NO_3)_3 + 3Pb$

**Sol**. A non-spontaneous redox reaction is one that does not occur naturally without an external energy source. In this reaction, copper (Cu) displaces silver (Ag) from silver nitrate ($AgNO_3$), which is not spontaneous.

Therefore, option (1) is the correct answer.

**14.** For the given cell.

$Cd(s)/Cd^{2+}$ (0.1 M) || $AgNO_3$ (0.2 M)/Ag(s)

the ($E$) of the cell at 298 K equals

Given: $E°_{(Cd^{2+}/Cd)} = – 0.40V$, $E°_{(Ag/Ag)} = – 10.80$ V

(1) 2.96 V (2) 1.18 V

(3) 1.08 V (4) 2.08 V

**Sol**. Anode : $Cd(s) \rightarrow Cd^{2+} + 2e^-$

Cathode : $2Ag^+ + 2e^- \rightarrow 2Ag(s)$

Cell reaction : $Cd(s) + 2Ag^+ \rightarrow Cd^{2+} + 2Ag$

$E°_{Cell} = E°_{(cathode)} - E°_{(anode)}$

$= 0.80 – (– 0.40) = 1.2$ V

$$E_{cell} = E°_{Cell} - \frac{0.059}{n}\log\frac{[Cd^{2+}]}{[Ag^+]^2}$$

$$= 1.2 - \frac{0.059}{n}\log\frac{0.1}{(0.2)^2}$$

$= 1.2 – 0.012 = 1.18$ V

Therefore, option (2) is the correct answer.

**15.** The solution of $AgNO_3$ in which Ag red is dipped is diluted to 10 times, the reduction electrode potential will:

(1) Decrease by 0.059 V (2) Decrease by 0.03

(3) Increase by 0.059 V (4) Increase by 0.03

**Sol**. $Ag^+$ (aq) + $e^- \rightarrow$ Ag(s)

Initially, $E_{cell(Initial)} = E°_{(Ag^+/Ag)} - \frac{0.059}{1}\log\frac{1}{[Ag^+]_{initial}}$

After dilution,

$$E_{cell(final)} = E°_{(Ag^+/Ag)} - \frac{0.059}{1}\log\frac{1}{[Ag^+]_{final}}$$

$$E_{cell(final)} - E_{cell(initial)} = 0.059\log\frac{[Ag^+]_{final}}{[Ag^+]_{Initial}}$$

$$= 0.059\log\left(\frac{1}{10}\right) = – 0.059 \text{ V}$$

Reduction potential decreases by 0.059 V.

Therefore, option (1) is the correct answer.

**16.** For the given reaction, the value of equilibrium conetant is

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(Ag) + Cu(s)$

(1) $10^{34}$ (2) $10^{10}$

(3) $10^{19}$ (4) $10^{37}$

**Sol**. $E°_{Cell} = \frac{0.059}{n}\log K_{eq}$

$$K_{eq} = \frac{nE°}{0.059}$$

$$\text{or } K_{eq} = 10\left(\frac{nE°}{0.059}\right)$$

$$= 10\left(\frac{2\times1.1}{0.059}\right) = 10^{37}$$

Therefore, option (4) is the correct answer.

# BOARD LEVEL PROBLEMS

## MULTIPLE CHOICE QUESTIONS

**1.** In a galvanic cell, the salt bridge is used to:

(1) To produce current at a constant strength
(2) Facilitate continuity of the cell reaction
(3) Prevent accumulation of charges around the electrodes
(4) All of these

**2.** A cell from the following which converts electrical energy into chemical energy:

(1) Dry cell (2) Electrochemical cell
(3) Electrolytic cell (4) None of these

**3.** Three faradays electricity was passed through an aqueous solution of iron (II) bromide. The weight of iron metal (at. wt. = 56) deposited at the cathode (in gm) is:

(1) 56 (2) 84 (3) 112 (4) 168

**4.** $E^0 = \frac{RT}{nF}\ln K_{eq}$. That is called:

(1) Gibb's equation
(2) Gibb's–Helmholtz equation
(3) Nernst's equation
(4) Vander Waal's equation

**5.** Which among the given is incorrectly matched?

(1) Molar conductance – $Sm^2\ mol^{-1}$
(2) Conductivity – $Sm^{-1}$
(3) Specific conductance – $Sm^2$
(4) Equivalent conductance – $Sm^2\ (eq)^{-1}$

**6.** The molar conductivity is maximum for the solution of concentration:

(1) 0.001 M (2) 0.005 M
(3) 0.002 M (4) 0.004 M

**7.** Calculate the electrode potential (in volt) at 25°C for the following electrode at $Ni^{2+}_{(0.1M)} \mid Ni_{(s)}$

$[E^0_{[Ni2+|Ni]} = -0.25V,\ \frac{2.303\,RT}{F} = (0.06)]$

(1) –0.28 V (2) –0.91 V
(3) –0.54 V (4) –0.22 V

**8.** $E^0$ for the cell Zn | $Zn^{2+}$ (aq) || $Cu^{2+}$(aq) | Cu is 1.10 V at 25°C, the equilibrium constant for the reaction,

$Zn + Cu^{2+}(aq) \rightleftharpoons Cu + Zn^{2+}(aq)$ is of the order of:

(1) $10^{-28}$ (2) $10^{37}$ (3) $10^{+18}$ (4) $10^{+17}$

## ASSERTION AND REASON QUESTIONS

**Directions:** These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(1) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.
(2) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.
(3) Assertion is True but the Reason is False.
(4) Assertion is False but Reason is True.

**1.** **Assertion (A):** Conductivity of all electrolytes decreases on dilution.

**Reason (R):** On dilution number of ions per unit volume decreases.

**2.** **Assertion (A):** $\Lambda_m$ for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

**Reason (R):** For weak electrolytes degree of dissociation increases with dilution of solution.

## MATCH THE COLUMN TYPE QUESTIONS

**1.** Match the following species with the corresponding conjugate acid

| List-I | | List-II | |
|---|---|---|---|
| A. | $\Lambda_m$ | P. | $S\ cm^{-1}$ |
| B. | $E_{cell}$ | Q. | $m^{-1}$ |
| C. | $\kappa$ | R. | $S\ cm^2 mol^{-1}$ |
| D. | G° | S. | V |

(1) A-(Q); B-(R); C-(S); D-(P)
(2) A-(Q); B-(S); C-(R); D-(P)
(3) A-(R); B-(S); C-(P); D-(Q)
(4) A-(Q); B-(P); C-(R); D-(S)

**2.** Match the List-I with List-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | $\Lambda_m$ | P. | intensive property |
| B. | $E^{\ominus}_{cell}$ | Q. | depends on number of ions/volume |
| C. | k | R. | extensive property |
| D. | $\Delta_r G_{cell}$ | S. | Increases with dilution |

(1) A-(P); B-(Q); C-(R); D-(S)
(2) A-(S); B-(P); C-(Q); D-(R)
(3) A-(P); B-(S); C-(R); D-(Q)
(4) A-(R); B-(Q); C-(P); D-(S)

## VERY SHORT ANSWER QUESTIONS

**1.** Determine the values of equilibrium constant ($K_c$) and ΔG° for the following reaction:

$Ni(s) + 2Ag^+ (aq) \rightarrow Ni^{2+} (aq) + 2Ag(s)$,

E° = 1.05 V

($1F = 96500\ C\ mol^{-1}$)

**2.** (1) The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm-1. Calculate its molar conductivity.

(2) The standard electrode potential (E°) for Daniel cell is +1.1 V. Calculate the ΔG° for the reaction

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

($1\ F = 96500\ C\ mol^{-1}$).

**3.** The conductivity of 0.001 M acetic acid is $4 \times 10^{-5}$ S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S $cm^2$/mol.

**4.** State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution?

**5.** Calculate the time to deposit 1.27 g of copper at cathode when a current of 2A was passed through the solution of $CuSO_4$.

(Molar mass of Cu = 63.5 g $mol^{-1}$,1 F = 96500 C $mol^{-1}$)

**6.** Why on dilution the Λm of $CH_3COOH$ increases drastically, while that of $CH_3COONa$ increases gradually?

## LONG ANSWER QUESTIONS

**1.** (1) What is limiting molar conductivity? Why is there a steep rise in the molar conductivity of weak electrolyte on dilution?

(2) Calculate the emf of the following cell at 298 K:

$Mg\ (s) \mid Mg^{2+}\ (0.1\ M) \parallel Cu^{2+}\ (1.0 \times 10^{-3}M) \mid Cu\ (s)$

[Given = $E^0_{Cell}$ = 2.71 V].

**2.** (1) What are fuel cells? Give an example of a fuel cell.

(2) Calculate the equilibrium constant (log $K_c$) and $\Delta_r G°$ for the following reaction at 298 K.

$Cu(s) + 2Ag^+\ (aq) \rightleftharpoons Cu^{2+}\ (aq) + 2Ag\ (s)$

Given $E^0_{cell}$ = 0.46 V and IF = 96500 C $mol^{-1}$

**3.** (1) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of $Cu^{2+}$ to Cu.

(2) Estimate the minimum potential difference needed to reduce $Al_2O_3$ at 500°C. The Gibbs energy change for the decomposition reaction

$2/3\ Al_2O_3 \rightarrow 4/3\ Al + O_2$ is 960 kJ

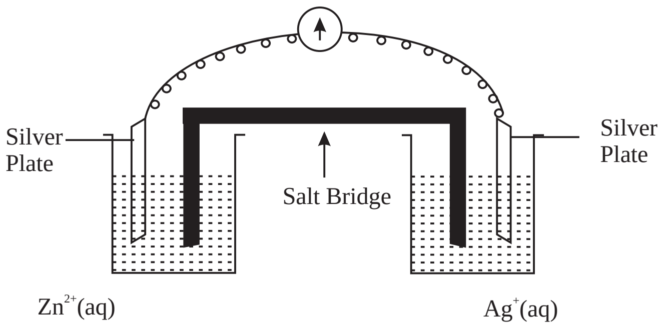
($F = 96500\ C\ mol^{-1}$)

**4.** Consider the figure given and answer the following questions:

(*i*) What is the direction of flow of electrons?

(*ii*) Which is anode and which is cathode?

(*iii*) What will happen if the salt bridge is removed?



(*iv*) How will concentration of $Zn^{2+}$ and $Ag^+$ ions be affected when the cell functions?

(*v*) How will concentration of these ions be affected when the cell becomes dead?

**5.** (1) The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.

(2) Why does mercury cell give constant voltage?

(3) Explain the term electrolysis. Discuss electrolysis of molten NaCl briefly?

## CASE BASED STUDY TYPE

Resistance is the property of a conductor due to which it opposes the flow of current through it. Electrical resistance of any object is directly proportional to its length and inversely proportional to its area of cross section. Inverse of resistance is known as conductance. Inverse of resistivity is known as conductivity. Molar conductivity is the conductance property of a solution containing one mole of the electrolyte.

Both conductivity and molar conductivity change with the concentration of the electrolyte. The molar conductivity of a solution at infinite dilution, i.e., when concentration approaches zero is called limiting molar conductivity. The Kohlrausch law Independent migration of ions states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

**1.** Which of the following is the SI unit of conductivity?

(1) $Sm^{-1}$ (2) $Ohm^{-1}$

(3) S (4) Ohm

**2.** Which of the following equations represents the correct relationship between conductivity and molar conductivity of the solution?

(1) $\Lambda m = (\kappa \times m) / c$ (2) $\Lambda m = \kappa/c$

(3) $\Lambda m = m / \kappa$ (4) $\Lambda m = \kappa + cm$

**3.** The unit of molar conductivity is:

(1) S (2) $Sm^{-1}$

(3) $Sm^2\ mol^{-1}$ (4) $Sm^{-1}mol^{-2}$

**4.** $\Lambda_m$ for NaCl, HCl, HCl and NaAc are 126.4, 425.9 and 91.0 S $cm^2 mol^{-1}$ respectively. Calculate Λ° for HAc.

(1) 284.1 S $cm^2\ mol^{-1}$

(2) 390.5 S $cm^2\ mol^{-1}$

(3) 162.7 S $cm^2\ mol^{-1}$

(4) 132.8 S $cm^2\ mol^{-1}$

# PRARAMBH EXERCISE-1 (TOPICWISE)

## ELECTROCHEMICAL CELLS AND GALVANIC CELL

**1.** In a galvanic cell, electron flow will be from:

(1) Negative electrode to positive electrode
(2) Positive electrode to negative electrode
(3) There will be no flow of electrons
(4) Cathode to anode in the external circuit

**2.** In a galvanic cell, the reactions taking place in the anodic half cell and the cathodic half cell will be:

(1) Reduction
(2) Oxidation
(3) Oxidation and reduction
(4) Reduction and oxidation

**3.** Which of the following is not true for a galvanic cell represented in IUPAC system?

(1) Right hand electrode is a +ve terminal.
(2) Right hand electrode acts as cathode.
(3) Electrons are given out in the external circuit from the anode.
(4) Electrons are given out in the external circuit from the cathode.

**4.** A half cell reaction is one that:

(1) Involves only half a mole of electrolyte
(2) Goes only half way to completion
(3) Takes place at one electrode
(4) Consumes half a unit of electricity

**5.** Which of the following energy changes occur in galvanic cell?

(1) Electrical energy → Chemical energy
(2) Chemical energy → electrical energy
(3) Chemical energy → Internal energy
(4) Internal energy → electrical energy

**6.** The purpose of the salt bridge in a galvanic cell is to

(1) Prevent accumulation of charges around the electrodes
(2) Facilitate continuity of the cell reaction
(3) To produce current at a constant strength
(4) All the above

**7.** Agar–Agar is used in salt bridge since it is:

(1) Electrolyte (2) Non–electrolyte
(3) Inert electrolyte (4) A solid

**8.** The thermodynamic efficiency of cell is given by:

(1) –nFE (2) –nFE/ΔG
(3) –nFE/ΔH (4) None of these

**9.** If a salt bridge is not used between two half cells, voltage:

(1) Drops to zero (2) Does not change
(3) Increases gradually (4) Increases rapidly

**10.** The electro-chemical cell stops working after some time because

(1) Electrode potentials of both electrodes become zero
(2) Electrode potentials of both electrodes become equal
(3) Temperature of the cell increases
(4) The reaction starts proceeding in opposite direction

**11.** The reaction ½ $H_2(g) + AgCl(s) \rightarrow H^+(aq) + Ag(s)$ can be represented in the galvanic cell as:

(1) Ag|AgCl(s) | KCl(sol) || $AgNO_3$(sol) | Ag
(2) Pt, $H_2$(g) | HCl(sol) || $AgNO_3$(sol) | Ag
(3) Pt, $H_2$(g) | HCl(sol) || AgCl(s) | Ag
(4) $H_2$(g) | HCl(sol) || AgCl(s) | Ag

**12.** In a Daniell cell,

(1) The chemical energy liberated during the redox reaction is converted to electrical energy.
(2) The electrical energy of the cell is converted to chemical energy.
(3) The energy of the cell is utilised in conduction of the redox reaction.
(4) The potential energy of the cell is converted into electrical energy.

**13.** For which of the following SOP and SRP are equal?

(1) SHE (2) Mg Electrode
(3) Ni electrode (4) Cu electrode

**14.** Cathodic standard reduction potential minus anodic standard reduction potential is equal to:

(1) Faraday (2) Coulomb
(3) Cell potential (4) Ampere

**15.** What will be standard cell potential of galvanic cell with the following reaction?

$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd(s)$

[Given : $E^0_{Cr^{3+}/Cr} = -0.74V$ and $E^0_{Cd^{2+}/Cd} = -0.4V$ ]

(1) 0.70 V (2) 1.14 V
(3) 0.34 V (4) –0.34 V

**16.** The electrode potential measures the:

(1) Tendency of the electrode to gain or lose electrons
(2) Electron affinity of elements
(3) Difference in the ionization potential of electrode and metal ion
(4) Heat of combustion

**17.** If $E^o_{Ni^{2+}|Ni} = 0.25V, E^o_{Cu^{2+}|Cu} = 0.34V, E^o_{Ag^{+}|Ag} = 0.8V$ and $E^o_{Zn^{2+}|Zn} = -0.76V$, then which of the following reactions under standard condition will not take place in the specified direction spontaneously?

(1) $Cu(s) + Ni^{2+}(aq) \rightarrow Cu^{2+}(aq) + Ni(s)$

(2) $Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

(3) $Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$

(4) Both (1) and (3)

**18.** Fluorine is the best oxidising agent because it has:

(1) Highest electron affinity

(2) Highest reduction potential

(3) Highest oxidising potential

(4) Lowest electron affinity

**19.** Which one of the following metal will not reduce $H_2O$?

(1) Ca (2) Fe

(3) Cu (4) Li

**20.** The cell reaction for the given cell is:

$Pt(H_2) \mid pH = 2 \parallel pH = 3 \mid Pt(H_2)$

$P_1 = 1$ atm $P_2 = 1$ atm

(1) Spontaneous (2) Non-spontaneous

(3) In equilibrium (4) Either of these

**21.** Which of the following is the cell reaction that occurs when the following half – cells are combined?

$I_2 + 2e^- \rightarrow 2I^-$ (1M) ; E = + 0.54 V

$Br_2 + 2e^- \rightarrow 2\ Br^-$ (1M) ; E = + 1.09 V

(1) $2Br^- + I_2 \rightarrow Br_2 + 2I^-$

(2) $I_2 + Br_2 \rightarrow 2I^- + 2Br^-$

(3) $2I^- + Br_2 \rightarrow I_2 + 2Br^-$

(4) $2I^- + 2Br^- \rightarrow I_2 + Br_2$

**22.** Arrange the following in the order of their decreasing electrode potentials: Mg, K, Ba, Ca

(1) K > Ba > Ca > Mg (2) Ba > Ca > K > Mg

(3) Ca > Mg > K > Ba (4) Mg > Ca > Ba > K

**23.** The emf of a galvanic cell, with electrode potential of $Zn^{2+} = -0.76$ V and that of $Cu^{2+} = 0.34$ V, is:

(1) 0.76 V (2) 1.1 V

(3) –1.1 V (4) 1.6 V

**24.** If the half - cell reactions are given as:

I. $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$, $E^0 = -0.44$ V

II. $2H^+(aq) + \frac{1}{2}O_2(g) + 2e^- \rightarrow H_2O_{(d)}$, $E^0 = +1.23$ V

The $E^0$ for the reaction,

$Fe(s) + 2H^+ + 1/2\ O_2(g) \rightarrow Fe^{2+} + H_2O(l)$

(1) + 1.67 V (2) –1.67 V

(3) + 0.79 V (4) –0.79 V

**25.** The EMF of a galvanic cell is determined by using a:

(1) Voltmeter (2) Spectrometer

(3) Coulometer (4) Ammeter

**26.** For cell reaction, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, cell representation is:

(1) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ (2) $Cu \mid Cu^{2+} \parallel Zn^{2+} \mid Zn$

(3) $Cu \mid Zn^{z+} \parallel Zn \mid Cu^{2+}$ (4) $Cu^{2+} \mid Zn \parallel Zn^{2+} \mid Cu$

**27.** The electrode potentials for:

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

and $Cu^+(aq) + e^- \rightarrow Cu(aq)$ are 0.15 V and + 0.50 V respectively. The value of $E^0_{Cu^{2+}|Cu}$ will be:

(1) 0.150 V (2) 0.500 V

(3) 0.325 V (4) 0.650 V

**28.** When Zn metal is added to $CuSO_4$ solution Cu is precipitated. It is due to:

(1) Oxidation of $Cu^{2+}$ (2) Reduction of $Cu^{2+}$

(3) Hydrolysis of $CuSO_4$ (4) Ionization of $CuSO_4$

**29.** Which of the following statements is true for the electrochemical Daniell cell?

(1) Electrons flows from copper electrode to zinc electrode

(2) Currents flows from zinc electrode to copper electrode

(3) Cations moves towards copper electrode

(4) Cations moves towards zinc electrode

## NERNST EQUATION

**30.** The relationship between free energy and electrode potential is:

(1) $\Delta G = -nFE$ (2) $\Delta G = nFE$

(3) $\Delta G = \frac{\Delta H}{nFE}$ (4) $\Delta G = \frac{nFE}{R}$

**31.** $\Delta G^0$ for the reaction, $Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$ is:

[given: $E^0_{Cu^{2+}/Cu} = +0.34V$ , $E^0_{Fe^{2+}/Fe} = -0.44V$ ]

(1) 11.44 KJ (2) 180.8 KJ

(3) 150.5 KJ (4) 28.5 KJ

**32.** $E^0_{cell}$ for the reaction, $2H_2O \rightarrow H_3O^+ + OH^-$ at 25°C is –0.8277 V. The equilibrium constant for the reaction is:

(1) $10^{-14}$ (2) $10^{-23}$

(3) $10^{-7}$ (4) $10^{-21}$

**33.** The Nernst equation giving dependence of electrode reduction potential on concentration is:

(1) $E = E^0 + \frac{2.303\ RT}{nF}\log\left[M^{n+}\right]$

(2) $E = E^0 - \frac{2.303\ RT}{nF}\log\frac{\left[M^{n+}\right]}{\left[M\right]}$

(3) $E = E^0 - \frac{2.303\ RT}{nF}\log\left[M^{n+}\right]$

(4) $E = E^0 + \frac{2.303\ RT}{nF}\log\frac{\left[M\right]}{\left[M^{n+}\right]}$

**34.** The chlorate ion can disproportionate in basic solution according to reaction, $2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$

What is the equilibrium concentration of perchlorate ions from a solution initially at 0.1 M in chlorate ions at 298 K?

Given

$$E^0_{ClO_4^-ClO_3^-} = 0.36\,V \text{ and } E^0_{ClO_3^-|ClO_2^-} = 0.33\,V \text{ at } 298\,K$$

(1) 0.019 M (2) 0.024 M

(3) 0.1 M (4) 0.19 M

**35.** The Gibb's energy for the decomposition of $Al_2O_3$ at 500°C is as follows:

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2; \Delta_rG = +966\,kJ/mol$$

The potential difference needed for electrolytic reduction of $Al_2O_3$ at 500°C is atleast:

(1) 5 V (2) 4.5 V

(3) 3 V (4) 2.5 V

**36.** Mark the correct Nernst equation for the given cell:

$$Fe_{(s)}\,|\,Fe^{2+}(0.001M)\,||\,H^+(1M)\,|\,H_{2(g)}(1bar)\,|\,Pt(s)$$

(1) $E_{cell} = E^0_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Fe^{2+}][H^+]^2}{[Fe][H_2]}$

(2) $E_{cell} = E^0_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Fe][H^+]^2}{[Fe^{2+}][H_2]}$

(3) $E_{cell} = E^0_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Fe^{2+}][H_2]}{[Fe][H^+]^2}$

(4) $E_{cell} = E^0_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Fe][H_2]}{[Fe^{2+}][H^+]^2}$

**37.** The oxidation potential of hydrogen half-cell will be negative if:

(1) $p(H_2)$ = 1 atm and $[H^+]$ = 1 M

(2) $p(H_2)$ = 1 atm and $[H^+]$ = 2 M

(3) $p(H_2)$ = 0.2 atm and $[H^+]$ = 1 M

(4) Both (2) and (3)

**38.** The potential of a single electrode depends upon:

(1) The nature of the electrode

(2) Temperature

(3) Concentration of the ion with respect to which it is reversible

(4) All the above

**39.** If the solution of the $CuSO_4$ in which copper rod is immersed is diluted to 10 times, the electrode potential:

(1) Increases by 0.295V (2) Decreases by 0.0295V

(3) Increases by 0.059V (4) Decreases by 0.059V

**40.** Calculate the emf of half cell:

$$\left.\begin{matrix} Pt, Cl_2(g) \\ (10\text{ atm}) \end{matrix}\right| \begin{matrix} HCl \\ (0.1)\,M \end{matrix}; E^o_{Cl_2|Cl^-} = 1.36V$$

(1) 1.45 V (2) 1.27 V

(3) –1.45 V (4) –1.27 V

**41.** During electrochemical process:

(1) Gibbs free energy increases

(2) Gibbs free energy remains constant

(3) No prediction can be made about Gibbs free energy

(4) Gibbs free energy decreases

**42.** Alkali metals have high oxidation potential, hence, they behave as good:

(1) Oxidising agent (2) Lewis bases

(3) Reducing agents (4) Electrolytes

**43.** Zn gives $H_2$ gas with $H_2SO_4$ and HCl but not with $HNO_3$ because:

(1) Zn act as oxidising agent when react with $HNO_3$

(2) $HNO_3$ is weaker acid than $H_2SO_4$ and HCl

(3) In electrochemical series, Zn is above hydrogen

(4) $NO_3^-$ is reduced in preference to hydronium ion

**44.** What is the electrode potential (in volt) of the following electrode at 25°C?

$$Ni^{2+}_{(0.1M)}\,|\,Ni_{(s)}$$

$$\left[E^0_{(Ni^{2+}|Ni)} = -0.25V, \frac{2.303RT}{F} = 0.06\right]$$

(1) –0.28 V (2) –0.34 V

(3) –0.82 V (4) –0.22 V

**45.** The relation between standard reduction potential of a cell and equilibrium constant is shown by:

(1) $E^0_{cell} = \dfrac{n}{0.059}\log K_c$ (2) $E^0_{cell} = \dfrac{0.059}{n}\log K_c$

(3) $E^0_{cell} = 0.059\,n\log K_c$ (4) $E^0_{cell} = \dfrac{\log K_c}{n}$

**46.** Emf of hydrogen electrode in terms of pH is: [at 1atm pressure]

(1) $E_{H_2} = \dfrac{RT}{F}pH$ (2) $E_{H_2} = \dfrac{RT}{F}\dfrac{1}{pH}$

(3) $E_{H_2} = \dfrac{2.303RT}{F}pH$ (4) $E_{H_2} = -0.0591\,pH$

**47.** The equilibrium constant of the reaction,

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

$E^0$ = 0.46 V at 298 K is:

(1) $2.4 \times 10^{10}$ (2) $2.0 \times 10^{10}$

(3) $4.0 \times 10^{10}$ (4) $4.0 \times 10^{15}$

**48.** For $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$,

$E^0$ = + 1.33V at $[Cr_2O_7^{2-}]$ = 4.5 millimole per ltr, $[Cr^{3+}]$ = 15 millimole per ltr, E is 1.06 V. The pH of the solution is nearly equal to:

(1) 2 (2) 3

(3) 5 (4) 4

**49.** For a cell reaction involving a two-electron exchange, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be:

(1) $1 \times 10^{-10}$ (2) $29.5 \times 10^{-2}$

(3) 10 (4) $1 \times 10^{10}$

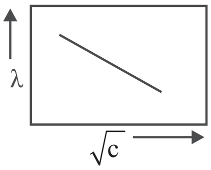
## CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

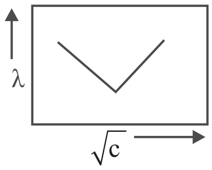
**50.** Molar conductance of KCl increases slowly with decrease in concentration because of:
(1) Increase in degree of ionisation
(2) Increase in total number of current carrying species
(3) Weakening of interionic attractions and increase in ionic mobilities
(4) Increase in hydration of ions

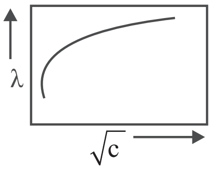
**51.** The reason for increase in electrical conduction of a weak electrolyte with increase in temperature:
(1) Increase in the number of ions
(2) Increase in the speed of ions
(3) Increase in the degree of dissociation of electrolytes
(4) All the above

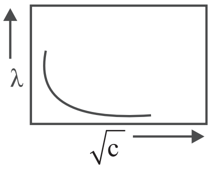
**52.** The molar conductance of acetic acid at infinite dilution is $\infty$. If the conductivity of 0.1M acetic acid is S, the apparent degree of ionisation is:
(1) $\frac{10000S}{\lambda_\infty}$ (2) $\frac{10S}{\lambda_\infty}$
(3) $\frac{\lambda_\infty}{100S}$ (4) $\frac{100000}{\lambda_\infty S}$

**53.** The variation of equivalent conductance of strong electrolyte with (concentration) is represented by:

(1)


(2)


(3)


(4)


**54.** The specific conductivity of N/10 KCl solution at 20°C is 0.0212 $\Omega^{-1}$ cm$^{-1}$ and the resistance of the cell containing this solution at 20°C is 55 Ω. The cell constant is:
(1) 3.324 cm$^{-1}$ (2) 1.166 cm$^{-1}$
(3) 2.372 cm$^{-1}$ (4) 3.682 cm$^{-1}$

**55.** Pure water does not conduct electricity because it is:
(1) Neutral (2) Readily decomposed
(3) Almost unionised (4) Completely ionised

**56.** In aqueous solution, strong electrolytes ionize and yield:
(1) Ions (2) Electrons
(3) Acids (4) Oxides

**57.** NaCl, $MgCl_2$ and $CaSO_4$ are known as:
(1) 1-1, 2-1, 2-2 types electrolyte respectively
(2) Strong, weak and strong electrolytes respectively
(3) Electrolytes with different value of A
(4) Electrolytes with same molar conductivity

**58.** Calculate molar conductivity of 0.15 M solution of KCl at 298 K if its conductivity is 0.0152 S cm$^{-1}$:
(1) 124 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ (2) 204 $\Omega^{-1}$ cm$^2$ mol$^{-1}$
(3) 101 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ (4) 300 $\Omega^{-1}$ cm$^2$ mol$^{-1}$

**59.** Specific conductance of 0.1 M NaCl solution is $1.01 \times 10^{-2}$ $\Omega^{-1}$ cm$^{-1}$. Its molar conductance in $\Omega^{-1}$ cm$^2$ mol$^{-1}$ is:
(1) $1.01 \times 10^2$ (2) $1.01 \times 10^3$
(3) $1.01 \times 10^4$ (4) 1.01

**60.** Limiting molar conductivity of NaBr is:
(1) $\Lambda^0_m \text{NaBr} = \Lambda^0_m \text{NaCl} + \Lambda^0_m \text{KBr}$
(2) $\Lambda^0_m \text{NaBr} = \Lambda^0_m \text{NaCl} + \Lambda^0_m \text{KBr} - \Lambda^0_m \text{KCl}$
(3) $\Lambda^0_m \text{NaBr} = \Lambda^0_m \text{NaOH} + \Lambda^0_m \text{NaBr} - \Lambda^0_m \text{NaCl}$
(4) $\Lambda^0_m \text{NaBr} = \Lambda^0_m \text{NaCl} - \Lambda^0_m \text{NaBr}$

**61.** Which of the following is a poor conductor of electricity?
(1) $CH_3COONa$ (2) $C_2H_5OH$
(3) NaCl (4) KOH

**62.** The units of conductivity of solution are:
(1) ohm$^{-1}$ (2) ohms
(3) ohm$^{-1}$cm$^{-1}$ (4) ohm$^{-1}$eq$^{-1}$

**63.** Molar conductivity of 0.025 mol L$^{-1}$ methanoic acid is 46.1 Scm$^2$mol$^{-1}$ the dissociation constant will be:
(Given : $\lambda^0_{H^+}$ = 349.6 Scm$^2$ mol$^{-1}$ and $\lambda^0_{HCOO^-}$ = 54.6 Scm$^2$ mol$^{-1}$)
(1) 11.4% . $3.67 \times 10^{-4}$ mol L$^{-1}$
(2) 22.8% , $1.83 \times 10^{-4}$ mol L$^{-1}$
(3) 52.2% , $4.25 \times 10^{-4}$ mol L$^{-1}$
(4) 1.14 % , $3.67 \times 10^{-4}$ mol L$^{-1}$

**64.** Molar conductivity of $NH_4OH$ can be calculated by the equation:
(1) $\Lambda^0_{NH_4OH} = \Lambda^0_{Ba(OH)_2} + \Lambda^0_{NH_4Cl} - \Lambda^0_{BaCl_2}$
(2) $\Lambda^0_{NH_4OH} = \Lambda^0_{BaCl_2} + \Lambda^0_{NH_4Cl} - \Lambda^0_{Ba(OH)_2}$
(3) $\Lambda^0_{NH_4OH} = \frac{\Lambda^0_{Ba(OH)_2} + 2\Lambda^0_{NH_4Cl} - \Lambda^0_{BaCl_2}}{2}$
(4) $\Lambda^0_{NH_4OH} = \frac{2\Lambda^0_{NH_4Cl} - \Lambda^0_{Ba(OH)_2}}{2}$

**65.** Units of the properties measured are given below, which of the properties have not been matched correctly?
(1) Molar conductance = Sm$^2$ mol$^{-1}$
(2) Cell constant = m$^{-1}$
(3) Specific conductance = Sm$^2$
(4) Equivalent conductance = Sm$^2$ (eq)$^{-1}$

**66.** When water is added to an aqueous solution of an electrolyte, what is the change in specific conductivity of the electrolyte?
(1) Conductivity increases
(2) Conductivity decreases
(3) Conductivity remains same
(4) Conductivity does not depends on number of ions

**67.** The unit of cell constant is:
(1) $ohm^{-1}$ (2) ohm - cm
(3) $cm^{-1}$ (4) $ohm^{-1}cm^2eq^{-1}$

**68.** The cell constant is the product of resistance and:
(1) Conductance (2) Molar conductance
(3) Specific conductance (4) Specific resistance

**69.** What would be the equivalent conductivity of a cell in which 0.5 M salt solution offers a resistance of 40 Ω whose electrodes are 2 cm apart and 5 $cm^2$ in area?
(1) $10\Omega^{-1}\ cm^2\ eq^{-1}$ (2) $20\Omega^{-1}\ cm^2\ eq^{-1}$
(3) $30\Omega^{-1}\ cm^2\ eq^{-1}$ (4) $25\Omega^{-1}\ cm^2\ eq^{-1}$

**70.** The molar conductance of $Ba^{2+}$ and $Cl^-$ are respectively 127 and 76 $\Omega^{-1}\ cm^2\ eq^{-1}$ at infinite dilution. What will be the equivalent conductance of $BaCl_2$ at Infinite dilution?
(1) 139.5 $\Omega^{-1}\ cm^2\ eq^{-1}$ (2) 203 $\Omega^{-1}\ cm^2\ eq^{-1}$
(3) 279 $\Omega^{-1}\ cm^2\ eq^{-1}$ (4) 101.5 $\Omega^{-1}\ cm^2\ eq^{-1}$

**71.** Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on:
(1) The nature and structure of the metal
(2) The no. of valence electrons per atom
(3) Change in temperature
(4) All of these

**72.** What happens at infinite dilution in a given solution?
(1) The degree of dissociation is unity for the weak electrolytes
(2) The electrolyte is 100% ionised
(3) All interionic attractions disappear
(4) All the above

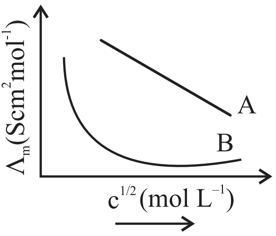
**73.** With increase in temperature, the electrical conduction of metallic conductor:
(1) Increases
(2) Decreases
(3) Remains the same
(4) Changes irregularly

**74.** During electric conduction, the composition of which of the following is changed?
(1) Graphite (2) Zinc wire
(3) Copper wire (4) $H_2SO_4$

**75.** What will be the molar conductivity of $Al^{3+}$ ions at infinite dilution if molar conductivity of $Al_2\ (SO_4)_3$ is 858 $Scm^2$ $mol^{-1}$ and ionic conductance of $SO_4^{2-}$ is 160 $Scm^2\ mol^{-1}$ at infinite dilution?
(1) 189 $Scm^2\ mol^{-1}$ (2) 698 $Scm^2\ mol^{-1}$
(3) 1018 $Scm^2\ mol^{-1}$ (4) 429 $Scm^2\ mol^{-1}$

**76.** How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7?
(1) Increase by 0.059 V (2) Decrease by 0.059 V
(3) Increase by 0.41 V (4) Decrease by 0.41 V

**77.** Mark the correct choice of electrolytes represented in the graph:



(1) $A \rightarrow NH_4OH,\ B \rightarrow NaCl$
(2) $A \rightarrow NH_4OH,\ B \rightarrow NH_4Cl$
(3) $A \rightarrow CH_3COOH,\ B \rightarrow CH_3COONa$
(4) $A \rightarrow KCl,\ B \rightarrow NH_4OH$

**78.** Fused NaCl has less electrical conductance than NaCl in the aqueous solution. This is due to:
(1) Fused NaCl has less number of ions
(2) Incomplete ionization occurs in the fused state
(3) $Na^+$, $Cl^-$ ions do not move freely in the fused salt
(4) Fused NaCl has no ions

**79.** The degree of dissociation of an electrolyte does not depend on:
(1) Nature of electrolyte (2) Catalytic action
(3) Dilution (4) Temperature

**80.** Match the list-I with list-II and mark the appropriate choice:

| List-I | | List-II | |
|---|---|---|---|
| A. | Kohlrausch's law | P. | $\Lambda^0_{eq} = \Lambda^0_c + \Lambda^0_a$ |
| B. | Molar conductivity | Q. | $\Lambda_m = \frac{K \times 1000}{Molarity}$ |
| C. | Degree of dissociation | R. | $\alpha = \frac{\Lambda_m}{\Lambda^0_m}$ |
| D. | Dissociation constant | S. | $K_a = \frac{c\alpha^2}{1-\alpha}$ |

(1) A-(R); B-(S); C-(P); D-(Q)
(2) A-(P); B-(Q); C-(R); D-(S)
(3) A-(S); B-(P); C-(Q); D-(R)
(4) A-(Q); B-(R); C-(S); D-(P)

**81.** Conductivity of a saturated solution of a sparingly soluble salt AB at 298 K is $1.85 \times 10^{-5}\ Sm^{-1}$. Solubility product of the salt AB at 298 K is:
[Given; $\Lambda^0_m$ (AB) = $140 \times 10^{-4}\ Sm^{-2}\ mol^{-1}$]
(1) $5.7 \times 10^{-12}$ (2) $1.32 \times 10^{-12}$
(3) $7.5 \times 10^{-12}$ (4) $1.74 \times 10^{-12}$

**82.** At 18°C, the conductance of $H^+$ and $CH_3COO^-$ at infinite dilution are 315 and 35 mho $cm^2\ eq^{-1}$ respectively. The equivalent conductivity of $CH_3COOH$ at infinite dilution is_____ (mho $cm^2\ eq^{-1}$)
(1) 350 (2) 280
(3) 30 (4) 315

**83.** The extent of ionization of weak electrolyte increases:

(1) With increase in concentration of the solute
(2) On addition of excess of water
(3) On decreasing the temperature
(4) On stirring the solution vigorously

**84.** The equivalent conductance of a 1 N solution of an electrolyte is nearly:

(1) 1000 times its specific conductance
(2) 10 times its specific conductance
(3) 100 times its specific conductance
(4) The same as its specific conductance

**85.** The specific conductance (κ) of an electrolyte of 0.1 N concentration is related to equivalent conductance Λ by the following formula:

(1) $\Lambda = \kappa$ (2) $\Lambda = 10\ \kappa$
(3) $\Lambda = 100\ \kappa$ (4) $\Lambda = 10000\ \kappa$

**86.** A current of 1.40 ampere is passed through 500 mL of 0.180 M solution of zinc sulphate for 200 seconds. What will be the molarity of $Zn^{2+}$ ions after deposition of Zinc?

(1) 0.154 M (2) 0.177 M
(3) 2 M (4) 0.180 M

**87.** The equivalent conductance at infinite dilution of a weak acid such as HF:

(1) Can be determined by extrapolation of measurements on dilute solutions of HCl, HBr and HI
(2) Can be determined by measurement on very dilute HF solutions
(3) Can be best determined from measurements on dilute solutions of NaF, NaCl and HCl
(4) Is an undefined quantity.

**88.** Which of the following statements is correct for an electrolytic solution upon dilution?

(1) Conductivity increases
(2) Conductivity decreases
(3) Molar conductance decreases but equivalent conductance increases
(4) Molar conductance increases while equivalent conductance decreases.

## ELECTROLYTIC CELL AND ELECTROLYSIS

**89.** Faraday's laws of electrolysis are related to the:

(1) Equivalent mass of the electrolyte
(2) Equivalent weight of the cation /anion
(3) Atomic weight of the electrolyte
(4) Atomic number of the cation/anion

**90.** The unit of electrochemical equivalent is:

(1) Gram
(2) Gram/Ampere sec
(3) Gram/Coulomb
(4) Coulomb/Gram

**91.** The number of faradays required to liberate 1 mole of any element indicates:

(1) Weight of the element
(2) Conductance of the electrolyte
(3) Charge on the ion of the element
(4) Isotopic number

**92.** $6.023 \times 10^{23}$ electrons are equal approximately to:

(1) 10 coulombs (2) 96500 coulombs
(3) 1electron volt (4) 0.1 Faraday

**93.** Dilute nitric acid on electrolysis using platinum electrodes yields:

(1) Both oxygen & hydrogen at cathode
(2) Both oxygen & hydrogen at anode
(3) $H_2$ at cathode and $O_2$ at anode
(4) $O_2$ at cathode and $H_2$ at anode

**94.** Which of the following occurs at cathode?

(1) $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$
(2) $Ag \rightarrow Ag^+ + e^-$
(3) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
(4) $Cu^{2+} + 2e^- \rightarrow Cu$

**95.** How much metal will be deposited when a current of 12 ampere with 75% efficiency is passed through the cell for 3 h?

[Given ; Z(electrochemical equivalent) = $4 \times 10^{-4}$]

(1) 32.4 g (2) 38.8 g
(3) 36.0 g (4) 22.4 g

**96.** If 54 g of silver is deposited during an electrolysis reaction, how much aluminium will be deposited by the same amount of electric current?

(1) 2.7 g (2) 4.5 g
(3) 27 g (4) 5.4 g

**97.** The quantity of electricity needed to separately electrolyse 1 M solution of $ZnSO_4$, $AlCl_3$, and $AgNO_3$ completely is in the ratio of:

(1) 2 : 3 : 1 (2) 2 : 1 : 1
(3) 2 : 1 : 3 (4) 2 : 2 : 1

**98.** Electrolysis of salt solution is due to the formation of:

(1) Electron (2) Ions
(3) Oxides (4) Acids

**99.** During the electrolysis of fused NaCl, which reaction occurs at anode?

(1) Chloride ions are oxidised
(2) Chloride ions are reduced
(3) Sodium ions are oxidised
(4) Sodium ions are reduced

**100.** What is the time required (in seconds) for depositing all the silver present in 125 mL of 1 M $AgNO_3$ solution by passing a current of 241.25 A [1F = 96500 C]?

(1) 10 sec (2) 50 sec
(3) 1000 sec (4) 100 sec

**101.** On passing 3A of electricity for 50 min, 1.8 g metal deposits, the equivalent mass of metal is:

(1) 9.3 (2) 19.3
(3) 38.3 (4) 39.9

**102.** 1C electricity deposits:

(1) 10.8 g of Ag
(2) 96500 g of Ag
(3) Electrochemical equivalent of Ag
(4) Half of electro-chemical equivalent of Ag

**103.** In an electrolytic cell, current flows from:

(1) Cathode to anode in outer circuit
(2) Anode to cathode outside the cell
(3) Cathode to anode inside the cell
(4) Current does not flow

**104.** During electrolysis, electrons flow from:

(1) Cations to cathode (2) Anode to cathode
(3) Cathode to anode (4) Anions to anode

**105.** When 9.65 coulomb of electricity is passed through a solution of silver nitrate (atomic mass of Ag 108 g $mol^{-1}$). The amount of silver deposited is:

(1) 16.2 mg (2) 21.2 mg
(3) 10.8 mg (4) 6.4 mg

**106.** A certain current liberated 0.50 gm of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution?

(1) 12.7 gm (2) 15.9 gm
(3) 31.8 gm (4) 63.5 gm

**107.** The cathode of an electrolytic cell and a reducing agent are similar because both:

(1) Are metals (2) Supply electrons
(3) Remove electrons (4) Absorb electrons

**108.** The cathode reaction in electrolysis of dilute sulphuric acid with platinum electrode is:

(1) Oxidation
(2) Reduction
(3) Both oxidation and reduction
(4) Neutralization

**109.** In electrolysis of dil. $H_2SO_4$ using platinum electrodes:

(1) $H_2$ is evolved at cathode
(2) $SO_2$ is produced at anode
(3) $O_2$ is obtained at cathode
(4) $SO_2$ is produced at cathode

## BATTERIES

**110.** When lead storages battery discharges

(1) $SO_2$ is evolved
(2) $PbSO_4$ is consumed
(3) Lead is formed
(4) $H_2SO_4$ is consumed

**111.** Lithium is generally used as an electrode in high energy density batteries. This is because

(1) Lithium is the lightest element
(2) Lithium has quite high negative reduction potential
(3) Lithium is quite reactive
(4) Lithium does not corrode easily

**112.** The reaction which is taking place in nickel-cadmium battery can be represented by which of the following equation?

(1) $Cd + NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$
(2) $Cd + NiO_2 + 2OH \rightarrow Ni + Cd(OH)_2$
(3) $Ni + Cd(OH)_2 \rightarrow Cd + Ni(OH)_2$
(4) $Ni(OH)_2 + Cd(OH)_2 \rightarrow Ni + Cd + 2H_2O$

**113.** In dry cell cathode is:

(1) Zn (2) Carbon rod
(3) $Zn+NH_4Cl$ (4) $C+MnO_2$

**114.** In Leclanche cell, Zinc rod is placed in:

(1) $10\%NH_4Cl$ (2) $20\%NH_4Cl$
(3) $30\%NH_4Cl$ (4) $40\%NH_4Cl$

**115.** Which of the following does not conduct electricity?

(1) Fused NaCl (2) Solid NaCl
(3) Brine solution (4) Copper

## FUEL CELLS

**116.** In fuel cell, oxidants used are:

(1) $O_2$ (2) $H_2O_2$
(3) $HNO_3$ (4) All

**117.** Theoretical efficiency of fuel cell is:

(1) Nearly 60%
(2) 50%
(3) 33%
(4) Nearly 100%

**118.** Which of the following statements is true for fuel cells?

(1) They are more efficient
(2) They are free from pollution
(3) They run till reactants are active
(4) All of the above

**119.** The efficiency of a fuel cell is given by:

(1) $\frac{\Delta H}{\Delta G}$ (2) $\frac{\Delta G}{\Delta S}$
(3) $\frac{\Delta G}{\Delta H}$ (4) $\frac{\Delta S}{\Delta G}$

**120.** The overall reaction of a hydrogen - oxygen fuel cell is:

(1) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
(2) $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O_{(2)} + 4e^-$
(3) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(eq)$
(4) $4OH^-(aq) + 4e^- \rightarrow 2H_2O(l)$

# PRABAL EXERCISE-2 (LEARNING PLUS)

**1.** The standard reduction potentials of $Cu^{+2}$, $Ag^{+}$, $Hg^{+2}$ and $Mg^{+2}$ are +0.34V, +0.80V, +0.79V and –2.37V respectively. With increasing voltage, the sequence of deposition of metals on the cathode from a molten mixture containing all those ions is:

(1) Ag, Hg, Mg, Cu
(2) Cu, Hg, Ag, Mg
(3) Ag, Hg, Cu, Mg
(4) Cu, Hg, Mg, Ag

**2.** Which metal pairs when coupled will get maximum emf for a voltaic cell?

(1) Fe and Cu
(2) Pb and Cu
(3) Cu and Au
(4) Ca and Cu

**3.** The standard reduction potentials of $Zn^{2+}|Zn, Cu^{2+}|Cu$ and $Ag^{+}|Ag$ are respectively -0.76, 0.34 and 0.8V. The following cells were constructed

A. $Zn|Zn^{2+}||Cu^{2+}|Cu$
B. $Zn|Zn^{2+}||Ag^{+}|Ag$
C. $Cu|Cu^{2+}||Ag^{+}|Ag$

What is the correct order emf of these cells?

(1) B > C > A
(2) C > B > A
(3) B > A > C
(4) C > A > B

**4.** Consider the following four electrodes:

$A = Cu^{2+}$ (0.0001M)|Cu(s)
$B = Cu^{2+}$(0.1M)|Cu (s)
$C = Cu^{2+}$(0.01M)|Cu (s)
$D = Cu^{2+}$(0.001M)|Cu (s)

If the standard reduction potential of $Cu^{+2}/Cu$ is +0.34V, then the reduction potentials (in volts) of the above electrodes follow the order:

(1) A > D > C > B
(2) B > C > D > A
(3) C > D > B > A
(4) A > B > C > D

**5.** Which of the following is always true regarding the spontaneity of reaction occuring in a galvanic cell?

(1) $E^0_{cell} > 0, \Delta G^0 < 0 \text{ and } Q > K_c$
(2) $E^0_{cell} > 0, \Delta G^0 > 0 \text{ and } Q < K_c$
(3) $E^0_{cell} > 0, \Delta G^0 > 0 \text{ and } Q > K_c$
(4) $E^0_{cell} > 0, \Delta G^0 < 0 \text{ and } Q < K_c$

**6.** The standard reduction potentials of $Zn^{2+}|Zn$ and $Cu^{2+}|Cu$ are -0.76V and +0.34 V respectively. What is the cell e.m.f (inV) of the following cell?

$$\left(\frac{RT}{F} = 0.059\right)$$

$Zn|Zn^{2+}$ (0.05M)$||Cu^{2+}$ (0.005M)|Cu

(1) 1.1295
(2) 1.0705
(3) 1.1
(4) 1.041

**7.** $I_2(s)|I^-$(0.1M) half cell is connected to a $H^+(aq)|H_2$(1 bar)|Pt half cell and e.m.f. is found to be 0.7714V. If $E_{I_2|I^-} = 0.535V$, find the pH of $H^+|H_2$ half-cell.

(1) 1
(2) 3
(3) 5
(4) 7

**8.** Given that $E_{H_2O|H_2|Pt} = 0$ at 298K. The pressure of $H_2$ gas would be:

(1) $10^{-7}$ atm
(2) $10^{-14}$atm
(3) $10^{-10}$atm
(4) $10^{-12}$atm

**9.** Which of the following will increase the voltage of the cell?
$Sn(s)+2Ag^+(aq) \rightarrow 2Ag(s) + Sn^{2+}$

(1) Increase in the concentration of $Sn^{2+}$ ions
(2) Increase in the concentration of $Ag^+$ ions
(3) Increase in the size of silver rod
(4) Removal of salt bridge

**10.** The potential of the cell containing two hydrogen electrodes as represented below Pt, $H_2(g)|H^+(10^{-6}M)||H^+(10^{-4}M)|H_2(g)$, Pt at 298 K is:

(1) –0.118 V
(2) –0.0591 V
(3) 0.118 V
(4) OV

**11.** The cell, $Zn|Zn^{+2}(1M)||Cu^{2+}(1M)|Cu$ $(E^0_{cell} = 1.10V)$, was allowed to be completely discharged at 298 K. The relative concentration of $Zn^{2+}$ to $Cu^{2+}$ is:

(1) 37.3
(2) $10^{37.3}$
(3) $9.65 \times 10^4$
(4) Antilog (24.04)

**12.** The e.m.f. of the cell, $Zn | Zn^{2+}(0.01M) || Fe^{2+}(0.001M) | Fe$ at 298 K is 0.2957, then the value of equilibrium constant for the cell reaction is:

(1) $e^{\left(\frac{0.32}{0.295}\right)}$
(2) $10^{\left(\frac{0.26}{0.0295}\right)}$
(3) $10^{\left(\frac{0.32}{0.0295}\right)}$
(4) $10^{\left(\frac{0.26}{0.0591}\right)}$

**13.** Deduce from the following E° values of half cells, what combination of two half cells would result in a cell with the largest potential?

| | | |
|---|---|---|
| I. | $A \rightarrow A^+ + e^-$; | E° = –0.24V |
| II. | $B^+ + e^- \rightarrow B$; | E° = –2.1V |
| III. | $C \rightarrow C^{2+} + 2e^-$; | E° = –0.38V |
| IV. | $D^{2-} \rightarrow D^- + e^-$; | E° = –0.59V |

(1) I and IV
(2) II and III
(3) III and IV
(4) I and II

**14.** Equivalent conductance of 1M of $CH_3COOH$ is 10 $ohm^{-1}$ $cm^2eq^{-1}$ and that at infinite dilution is 200 $ohm^{-1}cm^2eq^{-1}$. Hence the % ionization of $CH_3COOH$ is:

(1) 5% (2) 2%
(3) 4% (4) 1%

**15.** The equivalent conductivity of a solution containing 2.54g of $CuSO_4$ per litre is $91.0\Omega^{-1}cm^2eq^{-1}$. Its conductivity would be:

(1) $1.45 \times 10^{-3}\Omega^{-1}cm^{-1}$ (2) $2.17\times10^{-3}\Omega^{-1}cm^{-1}$
(3) $2.90\times10^{-3}\Omega^{-1}cm^2$ (4) $2.9\times10^{-3}\Omega^{-1}cm^{-1}$

**16.** Conductance of 0.1 M KCl (conductivity = X $ohm^{-1}$ $cm^{-1}$). filled in a conductivity cell is Y $ohm^{-1}$. If the conductance of 0.1M NaOH filled in the same cell is Z $ohm^{-1}$, the molar conductance of NaOH will be:

(1) $10^3\frac{XZ}{Y}$ (2) $10^4\frac{XZ}{Y}$
(3) $10\frac{XZ}{Y}$ (4) $0.1\frac{XZ}{Y}$

**17.** The charge required to reduce 1 mole $Cr_2O_7^{2-}$ to $Cr^{+3}$ ions is:

(1) 3F (2) 3 coulomb
(3) 6F (4) $2 \times 6.023 \times 10^{23}e^-$

**18.** A certain quantity of electricity is passed through an aqueous solution of $AgNO_3$ and cupric salt solution connected in series. The amount of silver deposited is 1.08g. The amount of copper deposited is (AW. of Cu = 63.54; Ag = 108)

(1) 0.6454g (2) 6.354g
(3) 0.3177g (4) 3.177g

**19.** The specific conductance of saturated solution of silver chloride is K ($ohm^{-1}cm^{-1}$). The limiting ionic conductance of $Ag^+$ and $Cl^-$ ions are x and y respectively. The solubility of AgCl in gm $litre^{-1}$ is: (Molar mass of AgCl = 143.5 $gmol^{-1}$ )

(1) $K\times\frac{1000}{x-y}$ (2) $\frac{K}{x+y}\times143.5$
(3) $\frac{K\times1000\times143.5}{x+y}$ (4) $\frac{x+y}{K}\times\frac{1000}{143.5}$

**20.** Which cell will measure standard electrode potential of copper electrode?

(1) $Pt(s)|H_2(g,0.1bar)|H^+(aq.,1M)||Cu^{2+}(aq.,1M)|Cu$

(2) $Pt(s)|H_2(g,1bar)|H^+(aq,1M)||Cu^{2+}(aq.,2M)|Cu$

(3) $Pt(s)|H_2(g,1bar)|H^+(aq,1M)||Cu^{2+}(aq.,1M)|Cu$

(4) $Pt(s)|H_2(g,0.1bar)|H^+(aq,0.1M)||Cu^{2+}(aq.,1M)|Cu$

**21.** Which of the following statement is correct?

(1) $E_{cell}$ and $\Delta_rG$ of cell reaction both are extensive properties
(2) $E_{cell}$ and $\Delta_rG$ of cell reaction both are intensive properties
(3) $E_{cell}$ is an intensive property while $\Delta_rG$ of cell reaction is an extensive property
(4) $E_{cell}$ is an extensive property while $\Delta_rG$ of cell reaction is an intensive property

**22.** The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called:

(1) Cell potential (2) Cell emf
(3) Potential difference (4) Cell voltage

**23.** Which of the following statement is not correct about an inert electrode in a cell?

(1) It does not participate in the cell reaction
(2) It provides surface either for oxidation or for reduction reaction
(3) It provides surface for conduction of electrons
(4) It provides surface for redox reaction

**24.** An electrochemical cell can behave like an electrolytic cell when:

(1) $E_{cell} = 0$ (2) $E_{cell} > E_{ext}$
(3) $E_{ext} > E_{cell}$ (4) $E_{cell} = E_{ext}$

**25.** Which of the statements about solutions of electrolytes is not correct?

(1) Conductivity of solution depends upon size of ions
(2) Conductivity depends upon viscosity of solution
(3) Conductivity does not depend upon solvation of ions present in solution
(4) Conductivity of solution increases with temperature

**26.** Using the data given below, find out the strongest reducing agent:

$$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V; E^0_{Cl_2/Cl^-} = 1.36V$$

$$E^0_{MnO_4^-/Mn^{2+}} = 1.51V; E^0_{Cr^{3+}/Cr} = -0.74\ V$$

(1) $Cl^-$ (2) Cr
(3) $Cr^{3+}$ (4) $Mn^{2+}$

**27.** Use the data given in Q. 26, find out which of the following is the strongest oxidising agent?

(1) $Cl^-$ (2) $Mn^{2+}$
(3) $MnO_4^-$ (4) $Cr^{3+}$

**28.** Using the data given in Q. 26, find out in which option the order of reducing power is correct.

(1) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$
(2) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$
(3) $Cr^{3+} < Cl^- < Cr_2O_7^{-2} < MnO_4^-$
(4) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$

**29.** Use the data given in Q. 26, find out the most stable ion in its reduced form:

(1) $Cl^-$ (2) $Cr^{3+}$
(3) $Cr^{2+}$ (4) $Mn^{2+}$

**30.** Use the data of Q. 26, find out the most stable oxidised species.

(1) $Cr^{3+}$ (2) $MnO_4^-$

(3) $Cr_2O_7^{2-}$ (4) $Mn^{2+}$

**31.** The quantity of charge required to obtain one mole of aluminium from $Al_2O_3$ is:

(1) 1 F (2) 6 F

(3) 3 F (4) 2 F

**32.** The cell constant of a conductivity cell:

(1) Changes with change of electrolyte

(2) Changes with change of concentration of electrolyte

(3) Changes with temperature of electrolyte

(4) Remains constant for a cell

**33.** While charging the lead storage battery:

(1) $PbSO_4$ anode is reduced to Pb

(2) $PbSO_4$ cathode is reduced to Pb

(3) $PbSO_4$ anode is oxidised to Pb

(4) $PbSO_4$ anode is oxidised to $PbO_2$

**34.** In the electrolysis of aqueous sodium chloride solution, which of the half cell reaction will occur at anode?

(1) $Na^+(aq) + e^- \to Na(s); E^\circ_{cell} = -2.71\,V$

(2) $2H_2O(l) \to O_2(g) + 4H^+(aq) + 4e^-; E^\circ_{cell} = -1.23\,V$

(3) $H^+(aq) + e^- \to \frac{1}{2}H_2(g); E^\circ_{cell} = 0.00\,V$

(4) $Cl^-(aq) \to \frac{1}{2}Cl_2(g) + e^-; E^\circ_{cell} = 1.36\,V$

**35.** The positive value of the standard electrode potential of $Cu^{2+}|Cu$ indicates that:

(1) This redox couple is a stronger reducing agent than the $H^+/H_2$ couple

(2) This redox couple is a stronger oxidising agent than $H^+/H_2$

(3) Both (2) and (4)

(4) Cu cannot displace $H_2$ from acid.

**36.** For the given cell, $|Mg|Mg^{2+}||Cu^{2+}|Cu$

(1) Mg is cathode

(2) Cu is anode

(3) The cell reaction is $Mg + Cu^{2+} \to Mg^{2+} + Cu$

(4) Mg is the oxidising agent

**37.** Conductivity of an electrolytic solution depends on:

(1) Nature of electrolyte

(2) Concentration of electrolyte

(3) Both (1) and (2)

(4) Distance between the electrodes

**38.** What will happen during the electrolysis of aqueous solution of $CuSO_4$ by using platinum electrodes?

(1) Copper will deposit at cathode

(2) Copper will deposit at cathode

(3) Oxygen will be released at anode

(4) Copper will dissolve at anode

**39.** What will happen during the electrolysis of aqueous solution of $CuSO_4$ by using the presence of Cu electrodes?

(1) Copper will deposit at cathode

(2) Copper will dissolve at anode

(3) Oxygen will be released at anode

(4) Copper will deposit at anode

**40.** Conductivity κ, is equal to:

(1) $\frac{1}{R}\frac{l}{A}$ (2) $\frac{G^*}{R}$

(3) $\Lambda_m$ (4) $\frac{l}{A}$

## PARIKSHIT EXERCISE-3 (MULTICONCEPT)

### MATCH THE COLUMN MCQs

**1.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Oxidising agent | P. | Disproportionation |
| B. | $Mn_3O_4$ | Q. | Redox reaction |
| C. | $C_6H_6$ | R. | Decreases its oxidation number |
| D. | $2Cu^+ \to Cu^{2+} + Cu^0$ | S. | Fractional oxidation number |
| E. | $H_2O_2 + O_3 \to H_2O + 2O_2$ | T. | Oxidation number of C, –1 |

(1) A-(R); B-(S); C-(T); D-(P); E-(Q)

(2) A-(S); B-(R); C-(T); D-(P); E-(Q)

(3) A-(R); B-(S); C-(Q); D-(T); E-(P)

(4) A-(T); B-(P); C-(Q); D-(R); E-(S)

**2.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Cell constant | P. | $E^0_{cathode} - E^0_{anode}$ |
| B. | Anode | Q. | $\ell/a$ |
| C. | Conductance | R. | Mass of product deposited by 1 columb of electricity. |

| | | | |
|---|---|---|---|
| D. | Electrochemical equivalent | S. | Resistance$^{-1}$ |
| E. | $E^0_{cell}$ | T. | Involve oxidation |

(1) A-(R); B-(T); C-(P); D-(Q); E-(S)
(2) A-(P); B-(S); C-(R); D-(Q); E-(T)
(3) A-(T); B-(S); C-(Q); D-(R); E-(P)
(4) A-(Q); B-(T); C-(S); D-(R); E-(P)

**3.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Cathode | P. | Primary cell |
| B. | 1 Coulomb | Q. | Secondary cell |
| C. | Dry cell | R. | $6.25 \times 10^{18}$ electrons |
| D. | Lead strong cell | S. | Concentration cell |
| E. | Zn $\|Zn^{2+}$ (0.01 M)$\|\|$ $Zn^{2+}$ (0.1 M)$\|$ Zn | T. | Positive terminal of electrochemical cell. |

(1) A-(T); B-(R); C-(P); D-(Q); E-(S)
(2) A-(T); B-(S); C-(Q); D-(R); E-(P)
(3) A-(Q); B-(R); C-(T); D-(S); E-(P)
(4) A-(S); B-(P); C-(Q); D-(R); E-(T)

**4.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Electrolytic cell | P. | $-\Delta G^0$ |
| B. | $nFE^0_{cell}$ | Q. | Concentration cell |
| C. | $E_{cell} = \frac{0.059}{n} \log \frac{C_{cathode}}{C_{anode}}$ | R. | 96500 Coulombs |
| D. | Diffusion of ions | S. | Device converting electrical energy into chemical energy |
| E. | 1 Faraday | T. | Salt bridge |

(1) A-(T); B-(R); C-(P); D-(Q); E-(S)
(2) A-(S); B-(P); C-(Q); D-(T); E-(R)
(3) A-(Q); B-(R); C-(T); D-(S); E-(P)
(4) A-(S); B-(P); C-(Q); D-(R); E-(T)

**5.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Conductance | P. | $cm^{-1}$ |
| B. | Specific conductance | Q. | $Ohm^{-1}$ $cm^2$ $mol^{-1}$ |
| C. | Cell constant | R. | $Ohm^{-1}$ |
| D. | Equivalent conductance | S. | $Ohm^{-1}$ $cm^{-1}$ |
| E. | Molar conductance | T. | $Ohm^{-1}$ $cm^2$ $equivalent^{-1}$ |

(1) A-(T); B-(R); C-(P); D-(Q); E-(S)
(2) A-(Q); B-(R); C-(T); D-(S); E-(P)
(3) A-(S); B-(P); C-(Q); D-(R); E-(T)
(4) A-(R); B-(S); C-(P); D-(T); E-(Q)

**6.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | $Hg_2Cl_2$ | P. | Used in salt-bridge |
| B. | Quinhydrone | Q. | Measurement of cell constant |
| C. | Lead acetate | R. | Redox electrode |
| D. | $NH_4NO_3$ | S. | Calomel electrode |
| E. | 0.1 N KCl | T. | Used in platinising solution |

(1) A-(T); B-(S); C-(Q); D-(R); E-(P)
(2) A-(Q); B-(R); C-(T); D-(S); E-(P)
(3) A-(S); B-(R); C-(T); D-(P); E-(Q)
(4) A-(T); B-(R); C-(P); D-(Q); E-(S)

**7.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Electrode reversible with respect to cation | P. | $Pt/Fe^{2+}$, $Fe^{3+}$ |
| B. | Electrode reversible with respect to anion | Q. | Pt, $H_2g$ (1 bar) $\|$ $H^+$ (a = 1) |
| C. | Redox electrode | R. | Ag $\|$ AgCl(s), HCl (aq.) |
| D. | Reference electrode | S. | Ag $\|$ $AgNO_3$ |

(1) A-(S); B-(R); C-(P); D-(Q)
(2) A-(R); B-(S); C-(Q); D-(P)
(3) A-(Q); B-(S); C-(R); D-(P)
(4) A-(P); B-(S); C-(R); D-(R)

**8.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Transport number | P. | $cm^2$ $V^{-1}$ $s^{-1}$ |
| B. | Ionic mobility | Q. | $ohm^{-1}$ $cm^2$ $mol^{-1}$ |
| C. | Ionic conductivity | R. | $ohm^{-1}$ $cm^{-1}$ |
| D. | Cell constant | S. | unit less |
| | | T. | $cm^{-1}$ |

(1) A-(S); B-(P); C-(Q); D-(T)
(2) A-(P); B-(S); C-(Q); D-(R)
(3) A-(S); B-(Q); C-(R); D-(P)
(4) A-(S); B-(P); C-(R); D-(T)

**9.** Match the list-I with list-II.

| List-I | | List-II | |
|---|---|---|---|
| A. | Conductance | P. | siemen $m^2$ $mol^{-1}$ |
| B. | Resistivity | Q. | $m^{-1}$ |
| C. | Conductivity | R. | volt per ampere |
| D. | Molar conductivity | S. | siemen |
| E. | Cell constant | T. | siemen $m^{-1}$ |
| F. | Resistance | U. | ohm metre |

(1) A-(U); B-(T); C-(S); D-(R); E-(Q); F-(P)

(2) A-(P); B-(R); C-(S); D-(U); E-(Q); F-(T)

(3) A-(S); B-(U); C-(T); D-(P); E-(Q); F-(R)

(4) A-(Q); B-(T); C-(P); D-(U); E-(R); F-(S)

**10.** Match the list-I with list-II.

| List-I | | List-II (Electrolysis product using inert electrode) | |
|---|---|---|---|
| A. | Dilute solution of HCl | P. | $O_2$ evolved at anode |
| B. | Dilute solution of NaCl | Q. | $H_2$ evolved at cathode |
| C. | Concentrated solution of NaCl | R. | $Cl_2$ evolved at anode |
| D. | $AgNO_3$ solution | S. | Ag deposition at cathode |

(1) A-(P, Q); B-(R, Q); C-(S, P); D-(Q, S)

(2) A-(P, Q); B-(P, Q); C-(Q, R); D-(P, S)

(3) A-(S, Q); B-(R, P); C-(R, S); D-(S, Q)

(4) A-(P, Q); B-(Q, S); C-(Q, R); D-(P, S)

## CORRECT-INCORRECT STATEMENT MCQs

**11.** Which of the following statements are not correct?

(1) Different quantity of electricity deposits more of iron from ferric sulphate solution than from ferrous sulphate solution

(2) Electrochemical equivalent of an element of an element can be obtained by dividing its equivalent weight by 96,500

(3) 1 Faraday always liberates 1 mole of the substance at the electrode

(4) A 60 watt bulb emits 60 Joules of energy per second

**12.** Which of the following relationships is correct?

(1) pH of solution in hydrogen electrode

$$= \frac{\text{Electrode potential}}{0.0591} \text{ at } 298 \text{ K}$$

(2) $E_{cell} = \frac{0.0591}{n} \log K_c$

(3) Cell constant = Conductivity/Conductance

(4) $\Delta G^o = nFE^o_{cell}$

**13.** Which of the following are false?

(1) Saline water slows down rusting.

(2) In Daniell cell, if concentrations of the solutions are doubled, the emf of the cell is constant.

(3) EMF of a cell is an intensive quantity whereas free energy change, ΔG is extensive.

(4) Galvanized iron sheets remain protected from rusting even if a crack is developed.

**14.** Which of the following is correct?

(1) Cathode is positive terminal in an electrolytic cell

(2) Cathode is negative terminal in a galvanic cell

(3) Reduction occurs at cathode in either of cells

(4) Oxidation occurs at cathode in either of cells

**15.** Which of the following statements is correct?

(1) Oxidation occurs at anode in both galvanic and electrolytic cells.

(2) Reduction occurs at anode in both galvanic and electrolytic cells.

(3) Reduction occurs at anode in electrolytic cell whereas oxidation occurs at cathode in a galvanic cell.

(4) Oxidation occurs at anode in electrolytic cell whereas reduction occurs at anode in a galvanic cell.

**16.** In a galvanic cell, which is wrong?

(1) Anode has negative polarity

(2) Cathode has positive polarity

(3) Reduction takes place at anode

(4) Reduction takes place at cathode

**17.** Which one is correct?

(1) Ni displaces zinc from its solution

(2) Zn displaces iron from its solution

(3) Ag displaces copper from its solution

(4) Cu displaces nickel from its solution

**18.** Which statement is not correct?

(1) Conductance of an electrolytic solution increases with dilution

(2) Conductance of an electrolytic solution decreases with dilution

(3) Specific conductance of an electrolytic solution decreases with dilution

(4) Equivalent conductance of an electrolytic solution increases with dilution

**19.** Which of the following is not correct?

(1) Aqueous solution of NaCl is an electrolyte

(2) The units of electrochemical equivalent are g-coulomb

(3) In the Nernst equation, n represents the number of electrons transferred in the electrode reaction

(4) Standard reduction potential of hydrogen electrode is zero volt

**20.** Which is not true for a standard hydrogen electrode?

(1) The hydrogen ion concentration is 1M

(2) Temperature is 25°C

(3) Pressure of hydrogen is 1 atmosphere

(4) It contains a metallic conductor which does not adsorb hydrogen

## STATEMENT BASED MCQs

(1) Both Statement-I and Statement-II are correct.

(2) Both Statement-I and Statement-II are incorrect.

(3) Statement-I is correct & Statement-II is incorrect.

(4) Statement-I is incorrect & Statement-II is correct.

**21.** **Statement-I:** Presence of $CO_2$ in the air accelerates corrosion.

**Statement-II:** $CO_2$ is poisonous gas.

**22.** **Statement-I:** Electrolysis of molten calcium hydride produces hydrogen gas at the anode.

**Statement-II:** Hydrogen in calcium hydride is present as $H^-$ ion.

**23.** **Statement-I:** Lead storage battery has almost constant cell potential.

**Statement-II:** Most of the reagent used are either solids of concentrated solutes.

**24.** **Statement-I:** Salt bridge is used generally in the electrochemical cells.

**Statement-II:** The ions of the electrolyte used in the salt bridge should have nearly same transport numbers.

**25.** **Statement-I:** The molar conductivity of strong electrolyte does not change with dilution at all.

**Statement-II:** At high concentration of electrolyte, the ions of opposite charge influence the speed of each other besides the viscosity of medium.

**26.** **Statement-I:** In the electrolytic reduction of alumina, cryolite is added to it.

**Statement-II:** Cryolite dissolves alumina readily.

**27.** **Statement-I:** Blocks of magnesium are often stapped to steel hulls of ocean going ships.

**Statement-II:** Magnesium causes cathodic protection of iron

**28.** **Statement-I:** In the reaction, $\frac{1}{2}O_2 + F_2 \longrightarrow OF_2$, fluorine is oxidant.

**Statement-II :** Fluorine cannot show positive oxidation state.

**29.** **Statement-I:** Lead storage battery does not require salt bridge.

**Statement-II:** The solid nature of each oxidising agent and reducing agent prevent direct contact.

**30.** **Statement-I:** Absolute value of $E^0_{red}$ of an electrode cannot be determined.

**Statement-II:** Neither oxidation nor reduction can take place alone.

## ASSERTION & REASON MCQs

(1) Assertion (A) is true, Reason (R) is true; Reason (R) is a correct explanation for Assertion (A).

(2) Assertion (A) is true, Reason (R) is true; Reason (R) is not a correct explanation for Assertion (A).

(3) Assertion (A) is true, Reason (R) is false.

(4) Assertion (A) is false, Reason (R) is true.

**31.** **Assertion (A):** When acidified zinc sulphate solution is electrolysed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.

**Reason (R):** The electrode potential of zinc is more negative than hydrogen as the over voltage for the hydrogen evolution on zinc is quite large.

**32.** **Assertion (A):** In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.

**Reason (R):** The molecular weights of silver and copper are different.

**33.** **Assertion (A):** Equivalent conductance of all electrolytes decreases with increasing concentration.

**Reason (R):** Lesser number of ions are available per gram equivalent at higher concentration.

**34.** **Assertion (A):** If an aqueous solution of NaCl is electroysed, the product obtained at the cathode is $H_2$ gas and not Na.

**Reason (R):** Gases are liberated faster than the metals.

**35.** **Assertion (A):** The cell constant of a cell depends upon the nature of the material of the electrodes.

**Reason (R):** The observed conductance of a solution depends upon the nature of the material of the electrodes.

**36.** **Assertion (A):** The ratio of specific conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.

**Reason (R):** Specific conductivity decreases with dilution whereas observed conductance increases with dilution.

**37.** **Assertion (A):** Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

**Reason (R):** Kohlrausch law help to find the molar conductivity of a weak electrolyte at infinite dilution.

**38.** **Assertion (A):** Gold chloride ($AuCl_3$) solution cannot be stored in a vessel made of copper, iron, nickel, chromium, zinc or tin.

**Reason (R):** Gold is very precious metal.

**39.** **Assertion (A):** In the Daniell cell, if concentrations of $Cu^{2+}$ and $Zn^{2+}$ ions are doubled, the e.m.f. of the cell will be doubled.

**Reason (R):** If the concentration of ions in contact with the metals is doubled, the electrode potential is doubled.

**40.** **Assertion (A):** $H_2 + O_2$ fuel cell gives a constant voltage throughout its life.

**Reason (R):** In this fuel cell, $H_2$ reacts with $OH^-$ ions, yet the overall concentration of $OH^-$ions does not change.

## PYQ's EXERCISE-4 (NEET PAST YEAR QUESTIONS)

**1.** Given below are two statements: one is labeled as **Assertion (A)** and the other is labeled as **Reason (R)**: **(2023)**

**Assertion (A):** In equation $\Delta_r G = -nFE_{\text{cell}}$ value of $\Delta_r G$ depends on n.

**Reasons (R):** $E_{\text{cell}}$ is an intensive property and $\Delta_r G$ is an extensive property.

In the light of the above statements, choose the correct answer from the options given below:

(1) A is false but R is true.

(2) Both A and R are true and R is the correct explanation of A.

(3) Both A and R are true and R is NOT the correct explanation of A.

(4) A is true but R is false.

**2.** The conductivity of centimolar solution of KCl at 25°C is 0.0210 $ohm^{-1}\ cm^{-1}$ and the resistance- of the cell containing the solution at 25°C is 60 ohm. The value of cell constant is - **(2023)**

(1) 3.34 $cm^{-1}$ (2) 0.34 $cm^{-1}$

(3) 3.28 $cm^{-1}$ (4) 1.26 $cm^{-1}$

**3.** Given below are half cell reactions: **(2022)**

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

$$E^o_{Mn^{2+}/MnO_4^-} = -1.510\,V$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$E_{O_2/H_2O} = +1.223\ V$$

Will the permanganate ion, $MnO^-{}_4$ liberate $O_2$ from water in the presence of an acid?

(1) No because $E^o_{cell} = -2.733\,V$

(2) Yes, because $E^o_{cell} = +0.287\,V$

(3) No, because $E^o_{cell} = -0.287\,V$

(4) Yes, because $E^o_{cell} = +2.733\ V$

**4.** Find the emf of the cell in which the following reaction takes place at 298 K **(2022)**

$Ni(s) + 2Ag^+\ (0.001\ M) \rightarrow Ni^{2+}\ (0.001\ M) + 2Ag(s)$

(Given that $E°_{cell} = 1.05\ V$, $\frac{2.303\ RT}{F} = 0.059$ at 298 K)

(1) 1.05 V (2) 1.0385 V

(3) 1.385 V (4) 0.9615 V

**5.** The molar conductance of NaCl, HCl and $CH_3COONa$ at infinite dilution are 126.45, 426.16 and 91.0 S $cm^2\ mol^{-1}$ respectively. The molar conductance of $CH_3COOH$ at infinite dilution is. Choose the right option for your answer. **(2021)**

(1) 390.71 S $cm^2\ mol^{-1}$ (2) 698.28 S $cm^2\ mol^{-1}$

(3) 540.48 S $cm^2\ mol^{-1}$ (4) 201.28 S $cm^2\ mol^{-1}$

**6.** The molar conductivity of 0.007 M acetic acid is 20 S $cm^2\ mol^{-1}$. What is the dissociation constant of acetic acid? Choose the correct option. **(2021)**

$$\begin{bmatrix} \Lambda^0_{H^+} = 350\ S\ cm^2 mol^{-1} \\ \Lambda^0_{CH_3COO^-} = 50\ S\ cm^2 mol^{-1} \end{bmatrix}$$

(1) $2.50 \times 10^{-4}$ mol $L^{-1}$ (2) $1.75 \times 10^{-5}$ mol $L^{-1}$

(3) $2.50 \times 10^{-5}$ mol $L^{-1}$ (4) $1.75 \times 10^{-4}$ mol $L^{-1}$

**7.** On electrolysis of dil sulphuric acid using Platinum (Pt) electrode, the product obtained at anode will be **(2020)**

(1) Oxygen gas (2) $H_2S$ gas

(3) $SO_2$ gas (4) Hydrogen gas

**8.** The number of Faradays (F) required to produce 20g of calcium from molten $CaCl_2$ (Atomic mass of Ca = 40g $mol^{-1}$) is **(2020)**

(1) 2 (2) 3

(3) 4 (4) 1

**9.** Identify the reaction from following having top position in EMF series (Std. red. potential) according to their electrode potential at 298 K. **(2020-Covid)**

(1) $Fe^{2+} + 2e^- \rightarrow Fe(s)$ (2) $Au^{3+} + 3e^- \rightarrow Au(s)$

(3) $K^+ + 1e^- \rightarrow K(s)$ (4) $Mg^{2+} + 2e^- \rightarrow Mg(s)$

**10.** In a typical fuel cell, the reactants (R) and product (P) are **(2020-Covid)**

(1) $R = H_{2(g)}, O_{2(g)}; P = H_2O_{(\ell)}$

(2) $R = H_{2(g)}, O_{2(g)}, Cl_{2(g)}; P = HClO_{4(aq)}$

(3) $R = H_{2(g)}, N_{2(g)}; P = NH_{3(aq)}$

(4) $R = H_{2(g)}, O_{2(g)}; P = H_2O_{2(\ell)}$

**11.** For a cell involving one electron E°cell = 0.59 V at 298 K, the equilibrium constant for the cell reaction is

$\left[\text{Given that } \frac{2.303RT}{F} = 0.059V \text{ at } T = 298K\right]$ **(2019)**

(1) $1.0 \times 10^2$ (2) $1.0 \times 10^5$

(3) $1.0 \times 10^{10}$ (4) $1.0 \times 10^{30}$

**12.** For the cell reaction

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

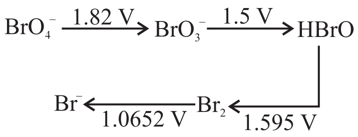
$E^{\ominus}_{cell} = 0.24$ V at 298 K. The standard Gibbs energy $(\Delta_r G^{\ominus})$ of the cell reaction is:

[Given that Faraday constant F = 96500 C $mol^{-1}$] **(2019)**

(1) –46.32 kJ $mol^{-1}$ (2) –23.16 kJ $mol^{-1}$

(3) 46.32 kJ $mol^{-1}$ (4) 23.16 kJ $mol^{-1}$

**13.** Consider the change in oxidation state of Bromine corresponding to different emf values as shown in the diagram below **(2018)**



Then the species undergoing disproportionation is:

(1) $BrO_3^-$ (2) $BrO_4^-$

(3) HBrO (4) $Br_2$

**14.** In the electrochemical cell

$Zn|ZnSO_4(0.01M)||CuSO_4(1.0M)|Cu$, the emf of this Daniell cell is $E_1$. When the concentration of $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to $E_2$. From the following, which one is the relationship between $E_1$ and $E_2$?

(Given, $\frac{RT}{F} = 0.059$) **(2017-Gujarat)**

(1) $E_2 = 0 \neq E$ (2) $E_1 = E_2$

(3) $E_1 < E_2$ (4) $E_1 > E_2$

**15.** Given that $\Lambda_m^\alpha = 133.45$ $cm^2$ $mol^{-1}$ $(AgNO_3)$;

$\Lambda_m^\alpha = 149.95$ $cm^2$ $mol^{-1}$ (KCl); $\Lambda_m^\alpha = 144.9$ S $cm^2 mol^{-1}$ $(KNO_3)$, the molar conductivity at infinite dilution for AgCl is: **(2017-Gujarat)**

(1) 132 S $cm^2$ $mol^{-1}$ (2) 140 S $cm^2$ $mol^{-1}$

(3) 138 S $cm^2$ $mol^{-1}$ (4) 134 S $cm^2$ $mol^{-1}$

**16.** The zinc/silver oxide cell is used in electric watches. The reaction is as following

$Zn^{2+} + 2e^- \rightarrow Zn; E° = –0.760$ V

$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-; E° = 0.344$ V

If F is 96,500 C $mol^{-1}$, ΔG° of the cell will be: **(2017-Gujarat)**

(1) 413.21 kJ $mol^{-1}$ (2) 113.072 kJ $mol^{-1}$

(3) 213.072 kJ $mol^{-1}$ (4) 313.082 kJ $mol^{-1}$

**17.** During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is: **(2016-II)**

(1) 220 minutes (2) 330 minutes

(3) 55 minutes (4) 110 minutes

**18.** Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because: **(2016-II)**

(1) Zinc has lower negative electrode potential than iron

(2) Zinc has higher negative electrode potential than iron

(3) Zinc is lighter than iron

(4) Zinc has lower melting point than iron

**19.** The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = $1.60 \times 10^{-19}$ C): **(2016-II)**

(1) $3.75 \times 10^{20}$ (2) $7.48 \times 10^{23}$

(3) $6 \times 10^{23}$ (4) $6 \times 10^{20}$

**20.** If the E° cell for a given reaction has a negative value, which of the following gives the correct relationships for the values of $\Delta G^0$ and $K_{eq}$? **(2016-II)**

(1) $\Delta G^0 < 0 ; K_{eq} > 1$ (2) $\Delta G^0 < 0 ; K_{eq} < 1$

(3) $\Delta G^0 > 0 ; K_{eq} < 1$ (4) $\Delta G^0 > 0 ; K_{eq} > 1$

**21.** The molar conductivity of a 0.5 mol $dm^{-3}$ solution of $AgNO_3$ with electrolytic conductivity of $5.76 \times 10^{-3}$ S $cm^{-1}$ at 298 K is: **(2016-II)**

(1) 0.086 S $cm^2$ $mol^{-1}$ (2) 28.8 S $cm^2$ $mol^{-1}$

(3) 2.88 S $cm^2$ $mol^{-1}$ (4) 11.52 S $cm^2$ $mol^{-1}$

**22.** The pressure of $H_2$ required to make the potential of $H_{2}$- electrode zero in pure water at 298 K is: **(2016-I)**

(1) $10^{-4}$ atm (2) $10^{-14}$ atm

(3) $10^{-12}$ atm (4) $10^{-10}$ atm

**23.** A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as: **(2015)**

(1) Electrolytic cell (2) Dynamo

(3) Ni-Cd cell (4) Fuel cell

**24.** The pair of compounds that can exist together is: **(2014)**

(1) $HgCl_2$, $SnCl_2$ (2) $FeCl_2$, $SnCl_2$

(3) $FeCl_3$, KI (4) $FeCl_3$, $SnCl_2$

**25.** Using the Gibbs energy change, $\Delta G^0 = +63.3$ kJ, for the following reaction,

$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$ the $K_{sp}$ of $Ag_2CO_3(s)$ in water at 25°C is:

($R = 8.314$ J $K^{-1}mol^{-1}$) **(2014)**

(1) $8.0 \times 10^{-12}$ (2) $2.9 \times 10^{-3}$

(3) $7.9 \times 10^{-2}$ (4) $3.2 \times 10^{-26}$

**26.** When 0.1 mol $MnO_4^{2-}$ is oxidised, the quantity of electricity required to completely oxidise $MnO_4^{2-}$ to $MnO_4^{-}$ is: **(2014)**

(1) 96500 C (2) 2 × 96500 C

(3) 9650 C (4) 96.50 C

**27.** The weight of silver (atomic weight = 108) displaced by a quantity of electricity which displaces 5600 mL of $O_2$ at STP will be: **(2014)**

(1) 10.8 g (2) 54.0 g

(3) 108.0 g (4) 5.4 g

# Answer Key

## CONCEPT APPLICATION

**1.** 28g and 18.6g **2.** 0.00032 g/C **3.** 6.42g **4.** 120 $\Omega^{-1}$ cm$^2$ eq$^{-1}$ **5.** 3 cm$^{-1}$ **6.** $1.6 \times 10^{-5}$
**7.** $2.31 \times 10^{-10}$ **8.** (1) **9.** (1) **10.** (1) **11.** (4) **12.** (3) **13.** (3) **14.** (4) **15.** (1)
**16.** (1)

## BOARD LEVEL PROBLEMS

### Multiple Choice Questions

**1.** (4) **2.** (3) **3.** (2) **4.** (3) **5.** (3) **6.** (1) **7.** (*a*) **8.** (2)

### Assertion and Reason Questions

**1.** (1) **2.** (1)

### Match the Column Type Questions

**1.** (3) **2.** (2)

### Case Based Study Type

**1.** (1) **2.** (2) **3.** (3) **4.** (2)

## PRARAMBH EXERCISE-1 (TOPICWISE)

**1.** (1) **2.** (3) **3.** (4) **4.** (3) **5.** (2) **6.** (4) **7.** (2) **8.** (3) **9.** (1) **10.** (2)
**11.** (3) **12.** (1) **13.** (1) **14.** (3) **15.** (3) **16.** (1) **17.** (4) **18.** (2) **19.** (3) **20.** (2)
**21.** (3) **22.** (4) **23.** (2) **24.** (1) **25.** (1) **26.** (1) **27.** (3) **28.** (2) **29.** (3) **30.** (1)
**31.** (3) **32.** (1) **33.** (1) **34.** (1) **35.** (4) **36.** (3) **37.** (4) **38.** (4) **39.** (2) **40.** (1)
**41.** (4) **42.** (3) **43.** (4) **44.** (1) **45.** (2) **46.** (4) **47.** (4) **48.** (1) **49.** (4) **50.** (3)
**51.** (4) **52.** (1) **53.** (1) **54.** (2) **55.** (3) **56.** (1) **57.** (1) **58.** (3) **59.** (1) **60.** (2)
**61.** (2) **62.** (3) **63.** (1) **64.** (3) **65.** (3) **66.** (2) **67.** (3) **68.** (3) **69.** (2) **70.** (1)
**71.** (4) **72.** (4) **73.** (2) **74.** (4) **75.** (1) **76.** (4) **77.** (4) **78.** (3) **79.** (2) **80.** (2)
**81.** (4) **82.** (1) **83.** (2) **84.** (1) **85.** (4) **86.** (2) **87.** (3) **88.** (2) **89.** (2) **90.** (3)
**91.** (3) **92.** (2) **93.** (3) **94.** (4) **95.** (2) **96.** (2) **97.** (1) **98.** (2) **99.** (1) **100.** (2)
**101.** (2) **102.** (3) **103.** (1) **104.** (4) **105.** (3) **106.** (2) **107.** (2) **108.** (2) **109.** (1) **110.** (4)
**111.** (2) **112.** (1) **113.** (2) **114.** (2) **115.** (2) **116.** (4) **117.** (4) **118.** (4) **119.** (3) **120.** (1)

## PRABAL EXERCISE-2 (LEARNING PLUS)

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

## PARIKSHIT EXERCISE-3 (MULTICONCEPT)

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

## PYQ'S EXERCISE-4 (NEET PAST YEAR QUESTIONS)

**1.** (2) **2.** (4) **3.** (2) **4.** (4) **5.** (1) **6.** (2) **7.** (1) **8.** (4) **9.** (2) **10.** (1)
**11.** (3) **12.** (1) **13.** (3) **14.** (4) **15.** (3) **16.** (3) **17.** (4) **18.** (2) **19.** (1) **20.** (3)
**21.** (4) **22.** (2) **23.** (4) **24.** (2) **25.** (1) **26.** (3) **27.** (3)